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NO adsorption and reaction on single crystal rutile TiO$_2$(110) surfaces studied by UHV-FTIRS

Mingchun Xu$^{a,b}$, Yuemin Wang$^{b,c}$, Shujun Hu$^a$, Renbo Xu$^a$, Yunjun Cao$^a$ and Shishen Yan$^a$

Abstract

The adsorption and reaction of NO on both the oxidized and reduced single crystal rutile TiO$_2$(110) surfaces were studied in a UHV-FTIRS system at low temperature. The monodentate adsorption configuration of the cis-(NO)$_2$ dimer at bridge oxygen vacancy (Vo) sites was detected for the first time on reduced TiO$_2$(110) surfaces. By the aid of (NO)$_2$ dimer adsorption anisotropy, the bidentate configuration of the cis-(NO)$_2$ dimer on fivefold coordinated Ti$_{5c}^{4+}$ cation sites was clearly confirmed. The (NO)$_2$ dimer converts to N$_2$O on Ti$_{5c}^{4+}$ cation sites at higher NO dosage on both oxidized and reduced surfaces, rather than at Vo sites. The (NO)$_2$ $\rightarrow$ N$_2$O conversion is independent of the presence of Vo on TiO$_2$(110) surfaces. To explain the signs of absorption bands of the dimer monodentate configuration, the local optical constant at Vo sites was introduced.

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1. Introduction

Nitric oxide (NO) is one of the main components in the atmosphere pollution that contribute to acid rain and global warming. How to efficiently transform and remove NO is an important issue in atmospheric environmental protection.\(^1\) Titanium dioxide (TiO\(_2\)), as one of the best known photo-catalysts for its excellent physical and chemical properties, has important applications in reduction of NO and has attracted considerable attention both in theory and in experiments. Studies on NO adsorption and reaction on TiO\(_2\)(110) surfaces will be helpful in both understanding the reaction mechanism and seeking the way to (photo)catalytically transform NO in the atmospheric pollution remediation.

The unpaired \(\pi^*\) electron leads NO free radicals to be highly reactive and volatile. During NO chemical transform reactions the (NO)\(_2\) dimer usually forms as an intermediate. The adsorbed (NO)\(_2\) dimer mode had already been found on metal and metal oxide surfaces.\(^2\)\(^-\)\(^4\) Kugler et al. and Millman et al., respectively, proved that such NO-in pairs form the cis-(NO)\(_2\) dimer.\(^5\)\(^,\)\(^6\) Theoretical calculations about gas phase and adsorbed (NO)\(_2\) dimer formation have also been performed.\(^7\)\(^-\)\(^9\) In the (NO)\(_2\) dimer formation, the 2\(\pi^*\) orbitals with the unpaired electrons overlap, forming a weak \(\sigma\) bond. All these give rise to a complicated coordination chemistry of NO on surfaces.

Early in 1992, Boccuzzi et al. have shown that the powered TiO\(_2\) samples can transform NO into N\(_2\)O especially in the reduced condition using Fourier transform infrared spectroscopy (FTIRS).\(^10\) Rusu and Yates also found later that the adsorbed NO on reduced TiO\(_2\) powers forms N\(_2\)O molecule with increased NO dosage at 110 K.\(^11\) Lu et al. found the N\(_2\)O formation at NO adsorption on single crystal TiO\(_2\)(110) surfaces, and suggested that the bridge oxygen vacancy (Vo) was involved in the NO \(\rightarrow\) N\(_2\)O conversion.\(^12\) Sorescu et al. investigated NO adsorption on the defect-free TiO\(_2\)(110) surface by combining experimental and theoretical analysis. They found the intermediate (NO)\(_2\) dimer formation and identified its symmetric bidentate adsorption configuration in the singlet state.\(^13\) A recent combined experimental and computational study suggested that the monodentate adsorption configuration of cis-(NO)\(_2\) species adsorbed through an N–Ti bond is the most stable on the TiO\(_2\)(110) surface at very low coverage on the (110) facet-terminated TiO\(_2\) nanoparticles.\(^14\) However, the effects of the surface bridge Vo on NO adsorption, reaction, and the dimer adsorption state are still inconclusive so far. This is attributed to the lack of the comparison experiments for the NO adsorption and reaction on both the oxidized...
and reduced single crystal TiO$_2$(110) surfaces with irrefutable experimental evidences.

Recently, in a new-designed ultrahigh vacuum (UHV)-FTIRS system,$^{15}$ we studied in detail NO adsorption and reaction on both oxidized and reduced rutile TiO$_2$(110) surfaces by using reflection-absorption infrared spectroscopy (RAIRS) at low temperature. By combining the RAIRS measurement principle and the molecular adsorption anisotropy, the conclusive evidences of Vo effect and the (NO)$_2$-dimer adsorption structures were obtained. NO adsorbs on the Ti$_{5c}^{4+}$ sites in the cis-(NO)$_2$ dimer bidentate configuration, while at the Vo sites in a monodentate configuration. At higher NO dosage, (NO)$_2$ dimer converts to N$_2$O on the Ti$_{5c}^{4+}$ sites rather than at Vo sites. The conversion is independent of Vo’s presence on TiO$_2$(110) surfaces.

2. Experimental

The experiments were performed in a UHV-FTIRS combination system, which combines a state-of-the-art vacuum FTIR spectrometer (Bruker, VERTEX 80v) with an UHV system consisting of a load-lock, a distribution and a measurement chambers. The base pressure of the measurement chamber is about $2 \times 10^{-10}$ mbar. The oxidized single crystal rutile TiO$_2$(110) surface was cleaned by several cycles of Ar ion sputtering (2.5 kV, 10 mA) and annealing to 800K in O$_2$ atmosphere of $5 \times 10^{-7}$ mbar in the measurement chamber. The reduced surface was obtained by a controlled sputtering and then annealing to 800 K under UHV condition on the oxidized surface. The sample temperature can change from 100 K, cooled by flowing liquid nitrogen, to 1000 K, heated by electronic beam with a resistance wire located in the sample holder. The RAIRS measurements were performed with the unpolarized IR beam at a fixed incidence angle of 80°. The recorded data, the reflectivity difference, is defined as $\Delta R = R_0 - R_a$, where $R_0$ and $R_a$ denote the reflectivities of the bare TiO$_2$(110) surface and the molecule-covered surface. The spectra were obtained with 2048 scans at a resolution of 4 cm$^{-1}$. For measuring anisotropy, two crystals with the same preparation procedure were introduced with the incident infrared light plane along the [001] and [110] azimuths, respectively. During measurement, the IR detector was cooled down by liquid nitrogen. The optical path inside the IR spectrometer and the space between the UHV chamber and the spectrometer were evacuated in order to avoid any unwanted IR absorption from gas phase species. The purity of NO used in experiments was 99.8%.
3. Results and discussion

3.1 Oxidized TiO$_2$(110) surface

Fig. 1 shows the RAIR spectra of NO adsorbed on the oxidized rutile TiO$_2$(110) surface at 100 K with different NO dosage. During the measurement, the incidence plane is perpendicular to the [001] direction of the substrate. At 1.2 L dosage (1 L=1.33 × 10$^{-6}$ mbar·s), two negative bands were observed at 1876 cm$^{-1}$ and 1746 cm$^{-1}$, respectively. With increasing NO dosage, their intensities gradually decrease and completely disappear at about 20 L of NO dosage. Meanwhile, another negative band at 2243 cm$^{-1}$ appears and increases in intensity with increasing NO dosage.

The 1876 cm$^{-1}$ and 1746 cm$^{-1}$ bands are assigned to the symmetric and asymmetric N-O stretching vibrations ($\nu_s$ and $\nu_as$) of cis-(NO)$_2$ dimer. This is in contrast to some cases such as CH$_2$, CH$_3$ groups in which the asymmetric stretch has a higher frequency than the symmetric stretch. This is probably due to the weak $\sigma$ bond between the two NO free radicals within one (NO)$_2$ dimer. It was noted that the 1876 cm$^{-1}$ and 1746 cm$^{-1}$ bands always coexist even at very low NO dosage, and no obvious vibrational band of the isolated NO molecular was observed on the TiO$_2$(110) surface. One reason is that the dimers have already formed in gas phase, another reason is that the dimers formed very quickly when NO adsorbed on the surface. Such an adsorption mode of NO in pairs has already been found on many metal oxides. The 2243 cm$^{-1}$ band originates from the N-N stretching vibration of N$_2$O species. Since adsorbed NO exists on TiO$_2$(110) first in (NO)$_2$ dimers, and then N$_2$O appears at the cost of (NO)$_2$ dimers, these sufficiently demonstrate the occurrence of the (NO)$_2$ → N$_2$O conversion. In addition, the fivefold coordinated Ti$_{5c}$ cation sites are the preferred sites for adsorbed (NO)$_2$ dimers and N$_2$O molecules as Lewis acid centers with N-bound on the TiO$_2$(110) surface. Accordingly, we suggest that on the oxidized TiO$_2$(110) surface, NO adsorbs on Ti$_{5c}$ sites first in (NO)$_2$ dimer; with increasing NO dosage, the (NO)$_2$ dimer converts to N$_2$O due to one O atom removal. The 2190 cm$^{-1}$ band at low NO dosage comes from the co-adsorbed traces of CO on Ti$_{5c}$ sites from the background, which does not affect our conclusion because CO can be completely replaced at higher NO dosage.

At 20 L of NO dosage, both 1876 cm$^{-1}$ and 1746 cm$^{-1}$ bands completely disappear and the 2243 cm$^{-1}$ band reaches saturation, indicating that all the adsorbed (NO)$_2$ dimers have converted to
N\textsubscript{2}O species. Since there are very few surface defects (Vo) on the oxidized surface, we conclude that the (NO)\textsubscript{2} \rightarrow N\textsubscript{2}O conversion is independent of the presence of Vo.

As the above discussions, the reaction of NO on oxidized TiO\textsubscript{2}(110) surfaces evolves probably in the following way:

\[
\text{NO} + \text{NO} \rightarrow (\text{NO})\textsubscript{2ad},
\]

\[
(\text{NO})\textsubscript{2ad} \rightarrow \text{N}_2\text{O}_{ad} + \text{O}_{ad},
\]

\[
\text{O}_{ad} + \text{O}_{ad} \rightarrow \text{O}_2 \uparrow.
\]

Here, the subscript \textit{ad} denotes the adsorbed state.

To further identify the adsorption configuration of the adsorbates, their anisotropies on the oxidized surface were studied. The corresponding RAIR spectra are shown in Fig. 2. During the measurement, the incidence plane is along [001] direction. Interestingly, at low NO dosage (1 L), the vibrations of (NO)\textsubscript{2} dimers exhibit two absorption bands with opposite signs: negative \nu_s band at 1876 cm\textsuperscript{-1} and positive \nu_as band at 1746 cm\textsuperscript{-1}. The different signs of (NO)\textsubscript{2} dimer vibration bands compared with those shown in Fig. 1 are attributed to the anisotropy of (NO)\textsubscript{2} dimer adsorption structure on the oxidized TiO\textsubscript{2}(110) surface. With increasing NO dosage, both bands decrease and finally disappear; at the same time, the N\textsubscript{2}O vibration band at 2243 cm\textsuperscript{-1} appears and increases. This dependence of N\textsubscript{2}O vibration band upon NO dosage is similar to that shown in Fig. 1, demonstrating that N\textsubscript{2}O adsorption structure is isotropic along [001] and [1\bar{1}0] directions on the TiO\textsubscript{2}(110) surface.

Prior to elucidating the dimer configurations, the judgment principle was first introduced.\textsuperscript{22} On non-absorbing or weakly-absorbing surfaces such as semiconductor or insulator, both p-polarized and s-polarized lights interact with the transition dipole moments which arise from the vibrational modes of the adsorbed molecules. The interaction between the transition dipoles and the electric fields can give rise to absorption bands which are positive or negative, depending upon their relative alignment. When the transition dipole moment is certain, the relative alignment depends upon the angle of incidence and the polarization. At the angle higher than the Brewster angle (\theta_B, the arctangent of the ratio of the refractive indices of the substrate and vacuum), the measured absorption bands are negative, positive, and negative due to the transition dipole moment aligned along \textit{E_p}_n (vertical component of p-polarized light), \textit{E_p}_t (parallel component of s-polarized light), and \textit{E_p}_r (radial component respectively).
p-polarized light) and $E_s$ (s-polarized light) respectively.

In our measurement configuration, the incidence angle of the unpolarized infrared beam is fixed at 80° to the substrate surface normal, obviously higher than the $\theta_B$ of rutile TiO$_2$(110) (−67°).

When the incidence plane is along the [001] direction, the s-polarized light is along the [110] direction, and the p-polarized light is nearly vertical to the (110) surface with a weak parallel component along the [001] direction. According to the judgment principle introduced above, the strong positive $\nu_{as}$ band at 1746 cm$^{-1}$ indicates that the $\nu_{as}$ vibration should have a stronger parallel component to the [001] direction. Because $\nu_{as}$ is parallel to the N-N bond, as a result, the N-N bond of the (NO)$_2$ dimer should be parallel to the [001] direction on the TiO$_2$(110) surface. This means that one (NO)$_2$ dimer binds two adjacent Ti$^{4+}$ cations with two N atoms. For this bidentate adsorption structure, the cis-(NO)$_2$ dimer plane is along the [001] direction. Its schematic model is shown as State I in Fig. 4. This symmetric bidentate configuration of (NO)$_2$ dimer in the singlet state is consistent to the result of the experimental and theoretical analysis.$^{13}$ In this case, both $\nu_s$ and $\nu_{as}$ have no parallel components to the s-polarized light, and the $\nu_s$ vibration vertical to the surface exhibits a negative value. In contrast, when the incidence plane is along the [110] direction, the s-polarized light is along the [001] direction, so that the $\nu_{as}$ vibration which is along the [001] direction exhibits a negative band; On the other hand, the $\nu_s$ vibration vertical to the (110) surface is active to the vertical component of the p-polarized light ($E_p$) and exhibits also a negative value. These are all consistent with spectroscopic results as shown in Fig. 1.

In addition, the isotropic adsorption structure of N$_2$O along [001] and [110] directions on the TiO$_2$(110) surface indicates that the linear N$_2$O molecule adsorbs vertically on the Ti$^{4+}$ site with N-bound. The schematic model is shown as State II in Fig. 4. The vertical adsorption of N$_2$O also explains the fact that N$_2$O is stable for high NO dosage. Such adsorption geometry of N$_2$O on Ti$^{4+}$ sites is consistent with the theoretical calculations.$^{14,23}$

3.2 Reduced TiO$_2$(110) surface

To further elucidate the possible effect of Vo on the NO adsorption and reaction, NO adsorption on the reduced TiO$_2$(110) surface at 100 K was also studied. The corresponding RAIR spectra with
different NO dosage are shown in Fig. 3. The measurement configuration is the same as that in Fig. 1, i.e., the incidence plane is perpendicular to the [001] direction. Strangely, for all the NO dosages, both the 1878 cm$^{-1}$ and 1745 cm$^{-1}$ bands exhibit positive values. Furthermore, with increasing NO dosage, both band intensities increase. Meanwhile, the 2243 cm$^{-1}$ band exhibits the same dependence upon the NO dosage as that on the oxidized surface. At saturation, the 2243 cm$^{-1}$ band intensity is also the same as that on the oxidized surface. This means that on the reduced surface, the amount of N$_2$O molecules at saturation should be the same as that on the oxidized surface. Since N$_2$O on the oxidized TiO$_2$(110) surface are converted from all the (NO)$_2$ dimers adsorbed on Ti$_{5c}$ cation sites, it is reasonable to suggest that N$_2$O on the reduced TiO$_2$(110) surface are also converted from all the (NO)$_2$ dimers adsorbed on the Ti$_{5c}$ cation sites. In addition, it is noticed that at saturation the N$_2$O stretch shows a lineshape, i.e., besides the negative band at 2243 cm$^{-1}$, a weak positive band with a small redshift was observed. This means that the N$_2$O is a little tilted due to interactions with nearby monodentate species. As described above, the positive weak band means that there’s a small component along $E_p$ direction, i.e., the [001] direction. This is similar to that of CO or CO$_2$ adsorbed on TiO$_2$(110) at higher coverage.$^{24, 25}$

The remained positive 1878 cm$^{-1}$ and 1745 cm$^{-1}$ bands for high NO dosage on the reduced surface are reasonably assigned also to the symmetric and asymmetric stretching modes of the (NO)$_2$ dimer according to their vibrational frequencies. According to the different RAIR spectra for (NO)$_2$ dimers on two differently treated surfaces, we ascribe these extra positive absorption bands to (NO)$_2$ dimers adsorbed at Vo sites on reduced TiO$_2$(110) surfaces. Since all the N$_2$O are converted from the dimers on Ti$_{5c}$ cation sites, we conclude that the (NO)$_2$ dimers adsorbed at Vo sites won’t convert to N$_2$O even for higher NO dosage.

Considering that the parallel component of p-polarized light ($E_p$) is along the [1 $\bar{1}$ 0] direction, both $\nu_s$ and $\nu_{as}$ bands exhibit positive values simultaneously, indicating that both vibrations must have strong parallel components along the [1 $\bar{1}$ 0] direction. This means that the (NO)$_2$ dimer adsorbs at the Vo site in a monodentate structure rather than in the bidentate adsorption structure.$^{14}$ In this case, one N within (NO)$_2$ dimer is bound with two adjacent Ti$^{3+}$ cations, and the dimer plane is perpendicular to the [001] direction. The schematic mode is shown as State III in Fig. 4. This monodentate structure seems consistent with that on Ti$_{5c}$ sites at very low NO coverage by
Actually, only the monodentate configuration cannot sufficiently give rise to both strong positive bands, for which the local optical constant at Vo site should be taken into account. According to the formula described by Buchholz et al., we performed the simulation calculation of reflectivity difference ($\Delta R$) for (NO)$_2$ dimers adsorbed on Ti$_{5c}^{4+}$ sites and at Vo sites, respectively. The IR light is not polarized and the ratio between s- to p- amplitude is 1:1. The calculated $\Delta R$, as a function of the incidence angle for the p-polarized (including $E_{pn}$ and $E_{pt}$ components) and s-polarized light are respectively shown in Figs. 5a and 5b. The insets show their adsorption configurations. The calculated $\Delta R$ at incidence angle 80° just corresponds to the measured absorption bands, i.e., the positive $\Delta R$ corresponds to the positive absorption band of corresponding intensity, and vice versa. For the dimer bidentately adsorbed on Ti$_{5c}^{4+}$ sites, when the incidence light is aligned perpendicular to [001] direction, $\nu_s$ couples $E_{pn}$, and $\nu_{as}$ couples $E_s$. As shown in Fig. 5a, both $\nu_s$ and $\nu_{as}$ bands are negative. This corresponds to the case shown in Fig. 1. When the incidence light is perpendicular to [110] direction, $\nu_s$ couples $E_{pn}$, and $\nu_{as}$ couples $E_p$, therefore, the former is negative and the latter positive. This corresponds to the case in Fig. 2. For the dimer monodentately adsorbed at Vo sites, the N-N bond is tilted by about 45° away from the surface normal and the dimer plane is perpendicular to [001] direction. When the incidence light is perpendicular to [001] direction, both $\nu_s$ and $\nu_{as}$ couple both $E_{pn}$ and $E_p$, i.e., both $\nu_s$ and $\nu_{as}$ couple $E_p$. As shown in Fig. 5a, though both of $\nu_s$ and $\nu_{as}$ bands are positive, they are very weak. Therefore, at Vo sites, the optical constant of substrate is decreased to 1.9, compared with 2.4 on Ti$_{5c}^{4+}$ sites. In this case, as shown in Fig. 5b, the negative $\Delta R_{pn}$ along $E_{pn}$ component is completely canceled by the strong positive $\Delta R_{pt}$ along the parallel $E_{pt}$, and $\Delta R_p$ of both bands show stronger positive values. This is consistent with the result shown in Fig. 3.

As mentioned above, the (NO)$_2$ → N$_2$O conversion takes place on the Ti$_{5c}^{4+}$ cation sites for higher NO dosage. Because the dimer plane on Ti$_{5c}^{4+}$ cation sites are along the Ti$_{5c}^{4+}$ row direction, as shown in Fig. 4, that is, the dimers are distributed end-to-end. For densely distributed (NO)$_2$ dimers, the distance between adjacent dimers is so small that their strong interaction gives rise to one N-O bond broken within one dimer, resulting in N$_2$O formation. As for the dimers adsorbed at Vo sites, on the one hand, most of the bridge Vo are point defects because of the repulsive
interaction between them in the same row. On the other hand, the dimer plane is perpendicular to the bridge oxygen row. Both factors lead to the adjacent dimer distance not small enough for the \((\text{NO})_2 \rightarrow \text{N}_2\text{O}\) conversion to occur at Vo sites. Another possible reason is that the monodentate \((\text{NO})_2\) dimers are more stable because of the extra electron charges around the \(\text{Ti}^{3+}\) cations adjacent to Vo. On \(\text{Ti}_{5c}^{4+}\) cation sites, however, we cannot rule out the possibility that the dimer bidentate adsorption transforms to the monodentate adsorption as an intermediate during the conversion.

It is noted in experiments that the Vo density on TiO\(_2\)(110) is not decreased after the \((\text{NO})_2 \rightarrow \text{N}_2\text{O}\) conversion, which indicates that the removed O atoms during the conversion do not fill Vo, but form \(\text{O}_2\) molecules and desorb from the substrate surface. This is consistent with the reaction evolution as we suggested above.

4. Conclusions

In summary, the adsorption and reaction of NO on rutile TiO\(_2\)(110) surfaces were studied in detail by UHV-FTIRS at low temperature. NO adsorbs on TiO\(_2\)(110) in cis-(NO)\(_2\) dimer state. The dimer monodentate configuration adsorbed at bridge Vo sites was detected in experiments for the first time. On both oxidized and reduced surfaces, \((\text{NO})_2\) dimer adsorbs on the fivefold coordinated \(\text{Ti}_{5c}^{4+}\) cation sites in the bidentate configuration, in which the dimer plane is along the [001] direction. At higher NO dosage, \((\text{NO})_2\) dimer converts to \(\text{N}_2\text{O}\) on \(\text{Ti}_{5c}^{4+}\) sites rather than at Vo sites. The \((\text{NO})_2 \rightarrow \text{N}_2\text{O}\) conversion is independent of Vo’s presence, and Vo is not filled by the O atom removing from the \((\text{NO})_2\) dimer. The local optical constant at Vo sites was introduced to explain the positive absorption bands of the dimer monodentate configuration.

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References

Figure captions:

Fig. 1. RAIR spectra of NO adsorbed on the oxidized TiO$_2$(110) surface at 100 K with different NO exposure. The incidence plane is perpendicular to [001] direction.

Fig. 2. RAIR spectra of NO adsorbed on the oxidized TiO$_2$(110) surface at 100 K with different NO exposure. The incidence plane is along [001] direction.

Fig. 3. RAIR spectra of NO adsorbed on the reduced TiO$_2$(110) surface at 100 K with different NO exposure. The incidence plane is perpendicular to [001] direction.

Fig. 4. Schematic models of (NO)$_2$ dimer and N$_2$O molecule adsorbed on the reduced TiO$_2$(110) surface. Red or pink ball denotes O, grey ball Ti and green ball N.

Fig. 5. Calculated $\Delta R$ for (NO)$_2$ dimer adsorbed on Ti$_{5c}^{4+}$ sites (a) and at Vo sites (b) as a function of incidence angle for p-polarized and s-polarized light at 1746 or 1876 cm$^{-1}$. The following optical constants were used for two adsorption sites: (a) Ti$_{5c}^{4+}$ sites: refractive index $n_3 = 2.4$, extinction coefficient $k_3 = 0$, (b) Vo sites: $n_3 = 1.9$, $k_3 = 0$. For the adsorbate layer on both sites, the following parameters were used: thickness $d_2 = 1.14$ Å, $n_2 = 1.5$, $k_2 = 0.3$. $\theta_B$ denotes the Brewster angle of TiO$_2$(110) substrates.
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