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Temperature-programmed desorption study of NO reactions on rutile $TiO_2(110)$-1 × 1

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ABSTRACT

Systematic temperature-programmed desorption (TPD) studies of NO adsorption and reactions on rutile $TiO_2(110)$-1 × 1 surface reveal several distinct reaction channels in a temperature range of 50–500 K. NO readily reacts on $TiO_2(110)$ to form N_2O, which desorbs between 50 and 200 K (LT N_2O channels), which leaves the TiO_2 surface populated with adsorbed oxygen atoms (O_a) as a by-product of N_2O formation. In addition, we observe simultaneous desorption peaks of NO and N_2O at 270 K (HT1 N_2O) and 400 K (HT2 N_2O), respectively, both of which are attributed to reaction-limited processes. No N-derived reaction product desorbs from $TiO_2(110)$ surface above 500 K or higher, while the surface may be populated with O_a's and oxidized products such as NO_2 and NO_3. The adsorbate-free TiO_2 surface with oxygen vacancies can be regenerated by prolonged annealing at 850 K or higher. Detailed analysis of the three N_2O desorption yields reveals that the surface species for the HT channels are likely to be various forms of NO dimers.

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1. Introduction

As a part of the effort to reduce the NO_x emissions in combustion engines and power plants, a great deal of research has been invested in the design of efficient catalysts for the conversion of NO_x into nontoxic N_2 [1,2]. In this study, we aim to provide a fundamental level understanding of the underlying mechanism of catalytic reduction of NO [3–5] over TiO_2 catalysts. Such studies should provide a foundation for our understanding of the NO reduction over the TiO_2-based de-NO_x catalysts such as V_2O_5/TiO_2 [6,7], WO_3/TiO_2 [8], V_2O_5-WO_3/TiO_2 [9,10], and V_2O_5-MoO_3/TiO_2 [11].

A great deal of insight has been obtained from studies performed on model rutile $TiO_2(110)$ surfaces [12–16]. It has been shown that NO adsorbs molecularly below ~100 K and desorbs at 120 K [17]. Theoretical calculations revealed that NO binds to titanium sites with N atom with a binding energy of 8.4 kcal/mol [12]. A stronger binding energy of 35 kcal/mol on oxygen vacancy sites has been also predicted by theory. Further, other bonding configurations such as $(NO)_2$ dimers have been theoretically [12,15] predicted and recently observed experimentally [15,16].

In addition to molecular adsorption, the reactions of NO molecules adsorbed on $TiO_2(110)$ lead to the formation of N_2O, which desorbs in multiple peaks having temperatures of 170, 270, and 400 K [12,14,17]. Irradiation with photons can facilitate the reduction of molecularly adsorbed NO at low temperatures to initiate facile desorption of N_2O [13]. The oxygen atoms left behind, fill bridging oxygen vacancy (V_O's) defect sites effectively oxidizing the surface at the early stage of reaction [17]. According to our recent study [14], the surface charge associated with the V_O's strongly enhances the conversion of NO to N_2O at substrate temperatures as low as 50 K. A fraction of N_2O molecules desorb rapidly at 50 K while the rest can be liberated upon heating to ~180 K.

Although N_2O formation from NO has been observed on $TiO_2(110)$ in previous studies [12–14], the reaction mechanism appears complex and is far from being well-understood. This is clearly illustrated by complex N_2O desorption which exhibits several desorption channels peaking at 170, 270, and 400 K. Further, while the studies [17] performed on reduced $TiO_2(110)$ have shown that surface defects such as V_O's play an important role in NO reduction, the N_2O formation has been also observed on a fully oxidized [12] $TiO_2(110)$ with two desorption peaks at 170 and 250 K.

In this study, we focus on the coverage-dependent reactions of NO on pristine (*p*-TiO_2), reduced (*r*-TiO_2), hydroxylated (*h*-TiO_2), and oxidized TiO_2 (*o*-TiO_2). Our quantitative analysis of the N_2O desorption yields shows interesting details about the nature of the surface species responsible for the HT N_2O desorption channels.

2. Experimental details

The measurements were performed in an ultrahigh vacuum (UHV) molecular beam surface scattering apparatus with a base pressure of

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1×10^{-10} torr equipped with quadrupole mass spectrometer (UTI-100C) that was described previously [18].

The rutile $TiO_2(110)$ substrate ($10 \times 10 \times 1$ mm^3, Princeton Scientific) was mounted on a Ta plate using a ceramic glue and a front retaining ring and its temperature was controlled between 50 and 1000 K [14]. The sample was cleaned by repeated Ne^+-ion sputtering and annealing to 870 K to prepare a well-ordered rutile $TiO_2(110)$-1×1 surface as determined from a sharp 1×1 pattern in low-energy electron diffraction (LEED). The concentration of bridging oxygen vacancies (V_O's) was monitored by measuring the area of the recombinative H_2O desorption peak at 500 K in temperature-programmed desorption (TPD) spectra [19–21]. At the early stages of this study (a small number of sputter–anneal cycles), the $TiO_2(110)$ crystal was transparent, exhibited a sharp 1×1 pattern in LEED, and the V_O concentration was negligible based on H_2O TPD. We refer to this *pristine* sample as *p*-TiO_2. With an increasing number (>10) of sputter–anneal cycles, the $TiO_2(110)$ crystal turned dark blue, and the V_O concentration increased to ~5% (~2.6×10^{13} cm^{-2}) (this sample is referred to as *r*-TiO_2). We have also prepared hydroxylated [22–24] and oxidized [25,26] $TiO_2(110)$ (referred to as *h*-TiO_2 and *o*-TiO_2, respectively). On *h*-TiO_2, the V_O defect sites have been reacted away by dosing 2 monolayers (ML) of H_2O on *r*-TiO_2 at 50 K followed by annealing to 400 K [19,25]. *o*-TiO_2 was prepared by oxidizing *r*-TiO_2 with molecular O_2 either by dosing ~2×10^{15} O_2/cm^2 at 300 K or by an O_2 dose of 1–5 $\times 10^{14}$ O_2/cm^2 at 50 K followed by annealing to 300 K [25,26].

Molecular NO was dosed using a neat NO beam (Matheson, CP Grade) at substrate temperatures between 50 and 100 K while recording mass fragments of possible reaction products such as N_2, N_2O, NO, and NO_2 using a quadrupole mass spectrometer (UTI 100C). The TPD spectra of NO and N_2 were determined by subtracting the contribution of the fragments of N_2O (m/z = 44 amu) from m/z = 30 (0.38 amu) and m/z = 28 (0.15 amu), respectively. The absolute N_2O coverage (in N_2O/cm^2) was obtained by comparing the integrated TPD area of the N_2O produced with the TPD spectra from a known amount of N_2O preadsorbed on TiO_2 [27]. The absolute NO dose (in NO/cm^2) was estimated from the plot of integrated area of NO TPD spectra obtained from multilayers of NO dosed on oxidized TiO_2 against the calibrated dose of NO by assuming that the sticking coefficient is unity at the dose temperature.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a hemispherical analyzer (Omicron SPHERA 2000) and x-ray (Mg Kα) to confirm that no N species remained on the TiO_2 surface after a few cycles of TPD within detection limit of XPS.

3. Results and Discussion

Fig. 1 shows the TPD spectra of NO, N_2O, and N_2 desorbing after the NO adsorption on *p*-TiO_2 and *r*-TiO_2. We find that more NO (N_2O) desorbs from *p*-TiO_2 (*r*-TiO_2); that is, more N_2O is formed from NO on *r*-TiO_2, most likely due to the presence of V_O's [14]. Unreacted NO desorbs from both surfaces with TPD peaks at ~120 and 270 K and measurable desorption signal extending all the way to 400 K. N_2O, as a major reaction product, desorbs at a number of distinct desorption temperatures. The N_2O desorption at < 200 K is assigned to low-temperature (LT) N_2O. As shown in our previous study, N_2O forms readily even at temperatures as low as 50 K, and its formation is facilitated by the subsurface charge associated with V_O's [14]. On *r*-TiO_2, N_2O formed at the dose temperature may desorb from the surface or may remain physisorbed on the surface and contribute to the observed desorption peaks below 200 K [14].

In addition to the LT N_2O reaction channel, we also observe distinct N_2O desorption peaks at 270 and 400 K, labeled as high-temperature (HT) N_2O (HT N_2O). These HT N_2O TPD peaks are also accompanied by NO desorption. Since these desorption temperatures are much higher than the desorption temperatures of physisorbed NO and N_2O, the HT desorption peaks must result from reaction-limited desorption processes.

Fig. 1 also shows a clearly resolved desorption of N_2 at 250 K [14] in addition to N_2O desorption. The N_2 yield increases proportionally with NO dose up to ~1 ML whereupon it saturates at 0.7×10^{13} N_2/cm^2, corresponding to 3% of the NO dosed. The detailed mechanism of N_2 formation is not understood at this point, but the fact that the N_2 desorption temperature coincides with HT1 N_2O desorption suggests that the same surface species for HT1 N_2O formation is responsible for the reaction-limited N_2 formation.

NO TPD spectra following NO adsorption on *p*- and *r*-TiO_2 as a function of NO dose are shown in Fig. 2. The integrated amounts of desorbing NO are further plotted as a function of NO dose in the inset. At small NO

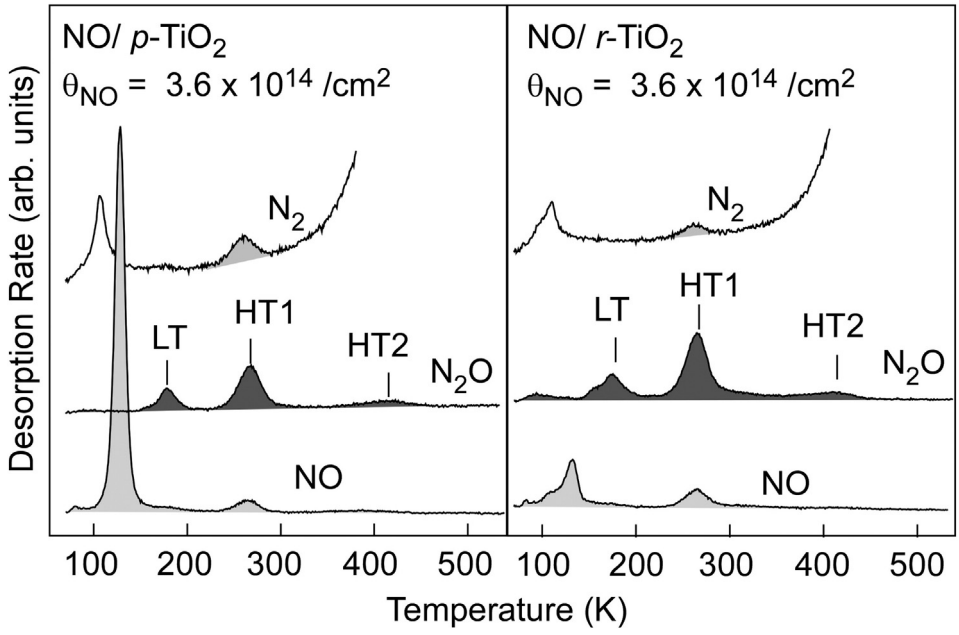

Fig. 1. NO, N_2O, and N_2 TPD spectra following NO adsorption ($\theta_{NO} = 3.6 \times 10^{14}$ NO/cm^2) on (a) *p*-TiO_2 (concentration of V_O's is <0.01 ML) and (b) *r*-TiO_2 (concentration of V_O's is 0.05 ML) at 50 K. The TPD spectra were acquired using a constant ramp rate of 1 K/s.

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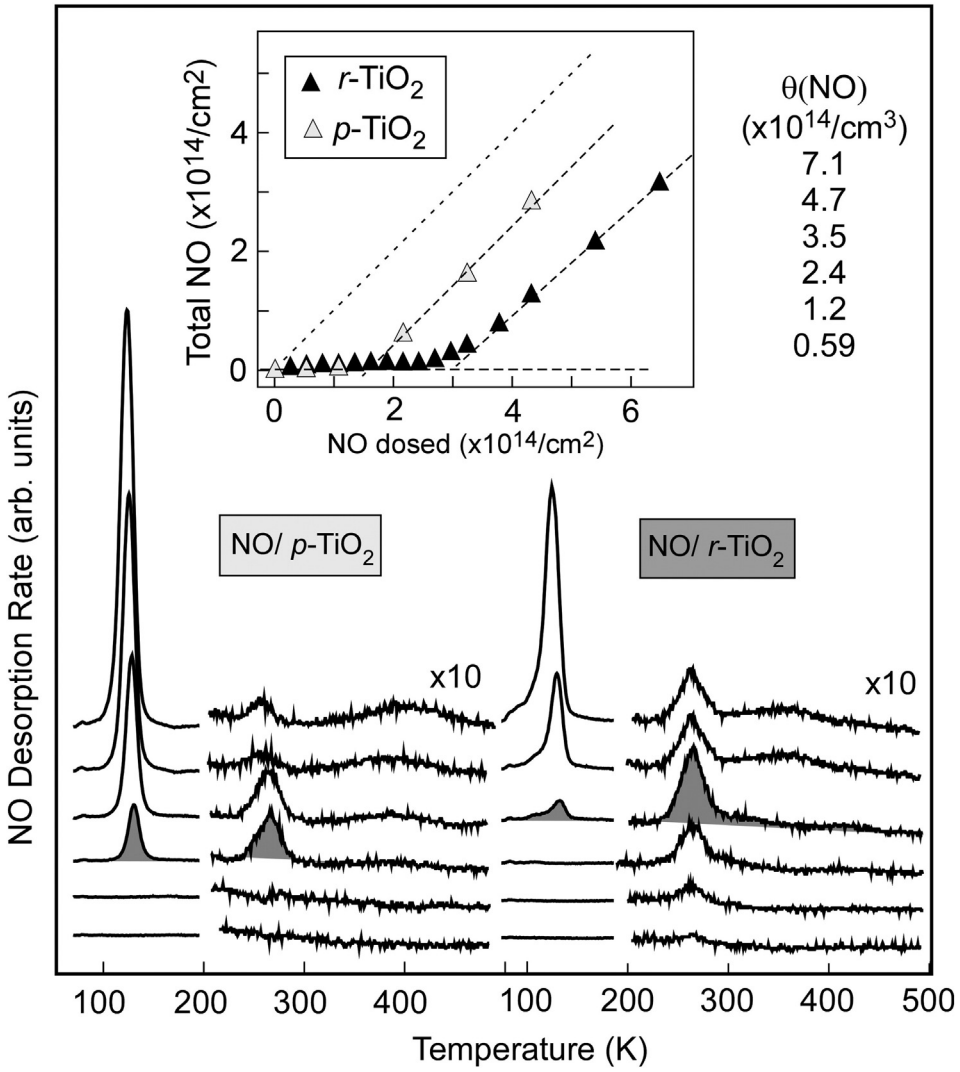

Fig. 2. NO TPD spectra from NO dosed on *p*- and *r*-TiO_2 as a function of NO dose. The inset shows the integrated amount of desorbing NO vs. NO dose. The number of Ti^{4+} sites on the surface is $5.2 \times 10^{14}/cm^2$ (≡1 ML).

doses (~1×10^{14} NO/cm^2), nearly all NO reacts to form products such as N_2O and NO_2. NO desorption is observed only above a certain threshold dose, which is 2.5×10^{14} NO/cm^2 for *r*-TiO_2 and 1×10^{14} NO/cm^2 for *p*-TiO_2. This result clearly shows that more NO reacts on *r*-TiO_2 than on *p*-TiO_2. Since the key difference between these two surfaces is the high concentration of V_O's (~5%) on *r*-TiO_2, the V_O's are attributed to the higher reactivity of *r*-TiO_2 than that of *p*-TiO_2 as has been observed from the role of V_O's in the enhanced LT N_2O formation yield [14].

Fig. 3 shows N_2O TPD spectra for different NO doses on *p*- and *r*-TiO_2. On both surfaces, the HT1 N_2O peak initially increases, maximizes at NO dose of ~3.5×10^{14} NO/cm^2 and subsequently decreases at higher NO doses. The HT2 N_2O peak is relatively small but shows a similar NO dose-dependent trend as the HT1 N_2O desorption peak. By contrast, the LT N_2O peak increases proportionally with the NO dose. A comparison of the N_2O spectra from *r*- and *p*-TiO_2 reveals that the trends are very similar except that the overall N_2O desorption yield is higher on *r*-TiO_2 at higher NO doses.

At low NO doses, the intensity of N_2O desorption peaks from *p*-TiO_2 is slightly higher than that from *r*-TiO_2. Since more N_2O desorption occurs during the NO dose on *r*-TiO_2, it is likely that more oxygen adatoms are left on the *r*-TiO_2 at the low NO dose regime. It may facilitate the formation of further oxidized forms of NO such as NO_2 and NO_3 better on *r*-TiO_2 than on *p*-TiO_2. This may act as a factor of suppressing the yield of the reductive channel (N_2O desorption) on *r*-TiO_2 than on *p*-TiO_2 at the low NO dose regime.

The integrated N_2O amounts observed in three observed N_2O TPD peaks (LT, HT1, and HT2) as well as the total N_2O from both *r*-TiO_2 and *p*-TiO_2 are plotted against the NO dose in Fig. 4. Several interesting features can be observed in the NO coverage-dependent trends of N_2O desorption yield. First, the total N_2O yield increases up to the NO dose of 2.5×10^{14} and 4×10^{14} NO/cm^2 on *p*- and *r*-TiO_2, respectively, then saturates at higher doses. The total N_2O yield from *r*-TiO_2 is higher than that from *p*-TiO_2 by ~$3.5 \times 10^{13}/cm^2$. This can be attributed to the presence of V_O's on *r*-TiO_2. The V_O's also lead to the N_2O desorption below 100 K from NO dosed on *r*-TiO_2(110) [14]. Some of N_2O formed at the dose temperature is physisorbed and desorbs below 200 K during the TPD ramp. N_2O may be also formed during the ramp as the molecularly bound NO species diffuse on the surface and react with each other forming $N_2O + O_a$ at low temperatures (up to 120 K). These possible channels contribute to LT N_2O desorption below 200 K.

Second, the HT1 N_2O yield does not saturate, but decreases at higher NO doses. The maximum yield of HT1 N_2O is reached at the NO dose of 2.5×10^{14} and 3.5×10^{14} NO/cm^2 on *p*- and *r*-TiO_2, respectively, which decreases as the NO dose increases further. The loss in HT1 N_2O yield is largely compensated by an increase in the LT N_2O yield; this results in a saturation in the total N_2O yield for both *r*- and *p*-TiO_2. As the NO dose

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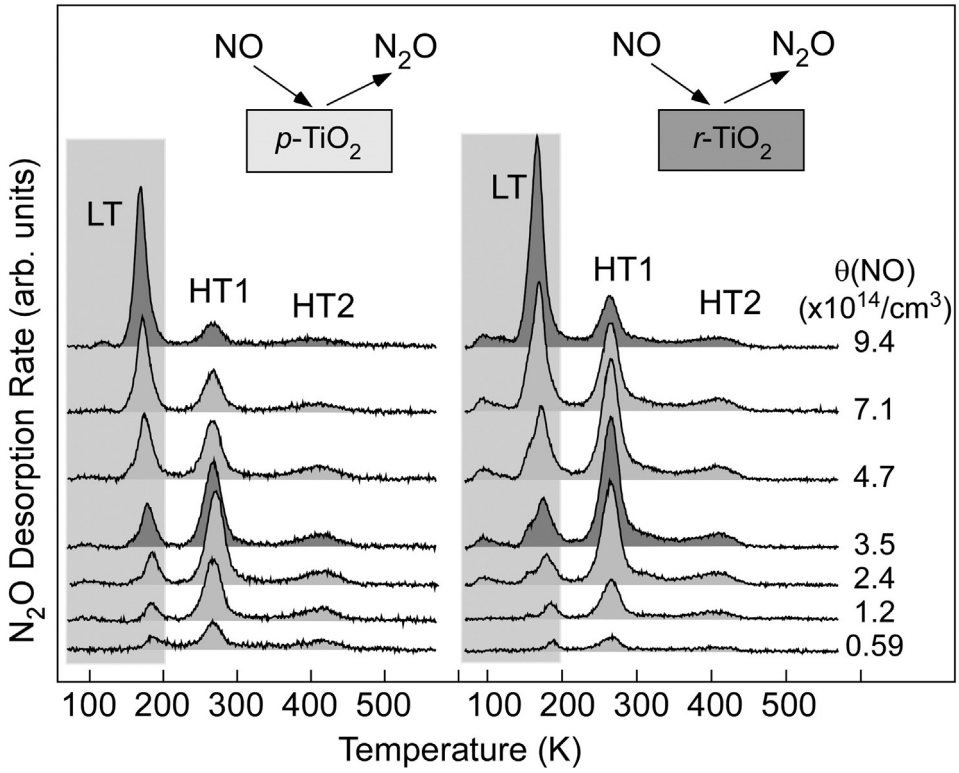

Fig. 3. TPD spectra of N_2O desorption from NO dosed on two different TiO_2 surfaces (p-TiO_2 and r-TiO_2) with increasing NO dose.

increases to a saturation of monolayer, the increased NO–NO interaction may facilitate the formation of N_2O at lower temperatures (<200 K); it may limit the formation of the surface NO-derived species responsible for the HT N_2O such as stable forms of NO dimers. The absolute yield for the HT2 N_2O is low, but the NO dose-dependent trend follows a similar trend as HT1.

Third, there is a deficiency between the NO dose and the sum of NO and N_2O desorption yields. For example, for the NO dose of 3.5×10^{14} NO/cm^2 on r-TiO_2, the total N_2O yield is ~8×10^{13} N_2O/cm^2, and the amount of unreacted NO desorption is about 5×10^{13} NO/cm^2. After adding the N_2O desorption during the NO dose (~1×10^{13} N_2O/cm^2), the total N_2O yield equals to ~9×10^{13} N_2O/cm^2 accounting for the NO dose of 1.8×10^{14} NO/cm^2. The desorbing amounts of NO and N_2O account for 2.3×10^{14} NO/cm^2. Thus, a significant fraction of NO (~1.2×10^{14} NO/cm^2) remains unaccounted. This discrepancy is larger than that expected from a possible calibration error (~10–20%), which leads us to conclude that there are N species that are not desorbed from the surface during TPD up to about 650 K. It is likely that oxidized species such as NO_2 and NO_3 are left on the surface. We cannot detect further desorption of any N-related species above 500 K up to 850 K. In addition, XPS measurements carried out after the NO TPD up to 200–500 K sometimes show noisy signals at 400–406 eV only at the first scan, which quickly disappear at the subsequent scans, resulting in no meaning features of N 1s spectra. We believe that this is because

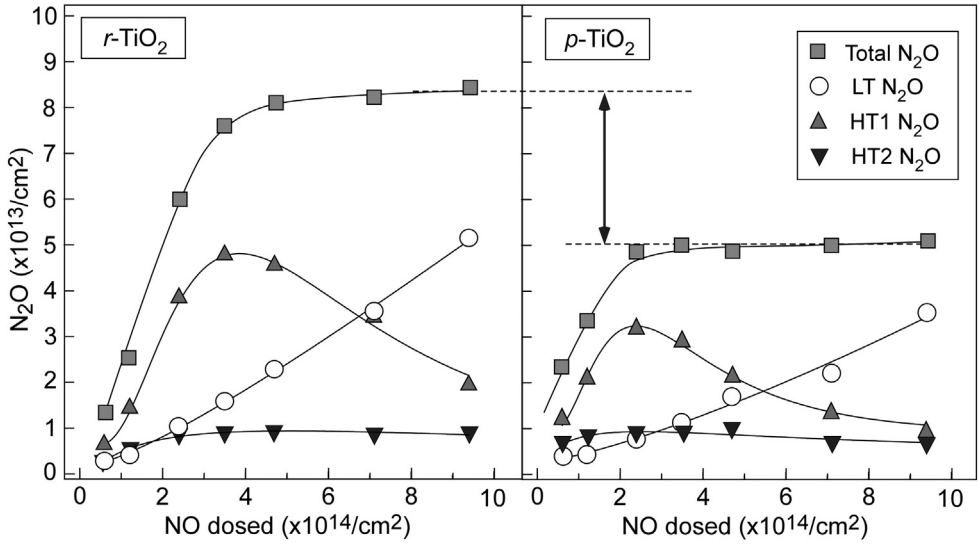

Fig. 4. The integrated amounts of N_2O for the three different channels, LT, HT1, and HT2 as well as that of total N_2O obtained from TPD peaks in Fig. 3 as a function of NO dose on p- and r-TiO_2.

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such NO_2 and NO_3 species are very unstable under x-ray irradiation in a UHV condition. Thus, we speculate that they are oxidized forms of NO such as NO_2 and NO_3, which can be produced by reactions of NO with oxygen adatoms.

However, a small measurable amount of stable N species is found from XPS after several cycles of NO TPD (>10 cycles). This fact also supports the idea that there are surface N species left from NO reactions on TiO_2, in oxidized forms such as NO_2 and NO_3; several cycles of TPD may induce the formation of stable NO_3 aggregates instead of the isolated NO_3.

A strong correlation between V_O's on *r*-TiO_2 and the NO reactivity is further corroborated from Fig. 5. It shows H_2O TPD obtained after NO TPD up to 400 K at various NO doses. After the NO TPD, H_2O is dosed to probe the V_O sites that remain following the NO adsorption and reactions. The same method has been used to determine the concentration of V_O's on bare *r*-TiO_2 surfaces as described in the experimental section [19,21,25]. The H_2O TPD spectra in Fig. 5 show that the recombinative H_2O desorption peak at 500 K ($2OH_b \rightarrow H_2O(g) + O_b + V_O$) decreases significantly already at very low NO doses ($<5 \times 10^{13}$ NO/cm^2). The dependence of the integral of the recombinative H_2O TPD peak on the NO dose is shown in the upper inset of Fig. 5. The observed dependence shows that the V_O concentration decreases quite in proportion to the NO dose and that it is reduced to one third of the initial value (2.6×10^{13} V_O/cm^2) at ~5×10^{13} NO/cm^2. We speculate that this is the result of V_O's being preferentially filled with oxygen atoms left behind from the N_2O formation from NO [14].

Considering that the formation of N_2O from NO leaves O_a on TiO_2(110), the effect of predosed oxygen on the reactivity of NO is investigated in Fig. 6. The figure shows the TPD spectra of NO and N_2O from NO dosed on O_2-predosed *r*-TiO_2 at fixed NO dose ($\theta_{NO} = 3.5 \times 10^{14}$ NO/cm^2), while the O_2 dose is increased up to 3.5×10^{14}/cm^2. NO TPD (left) shows that the LT NO desorption increases with increasing O_2, suggesting that the reactivity of NO over TiO_2 decreases due to the effect of predosed O_2. As a result, unreacted NO contributes to the increase of NO desorption yield with increasing O_2 dose as quantified in the left inset of Fig. 6. The TPD spectra of N_2O (right) show that the total N_2O desorption yield decreases with increasing O_2 doses.

The N_2O desorption yield from different channels is shown in the upper right inset of Fig. 6. Note that the decrease of HT1 N_2O yield is more pronounced than that of LT N_2O. As the predosed O_2 increases, the HT1 N_2O yield vanishes at an O_2 dose of ~2×10^{14} O_2/cm^2, while

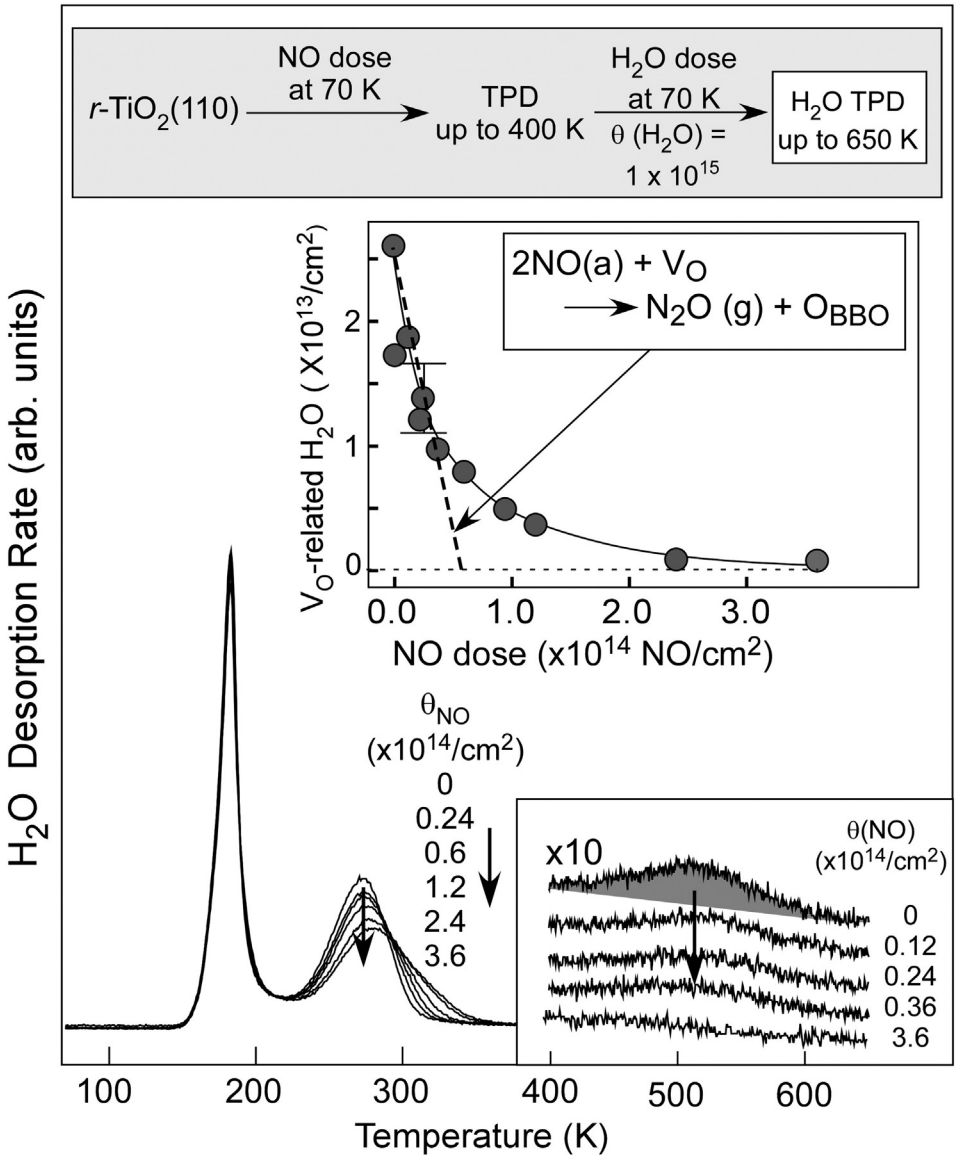

Fig. 5. H_2O TPD (dose = 1×10^{15} H_2O/cm^2) from *r*-TiO_2 after dosing different amounts of NO at 70 K and TPD to 400 K. The recombinative H_2O desorption at 500 K (bottom inset) from available V_O sites shows that V_O's are readily depleted as a result of NO adsorption and reaction.

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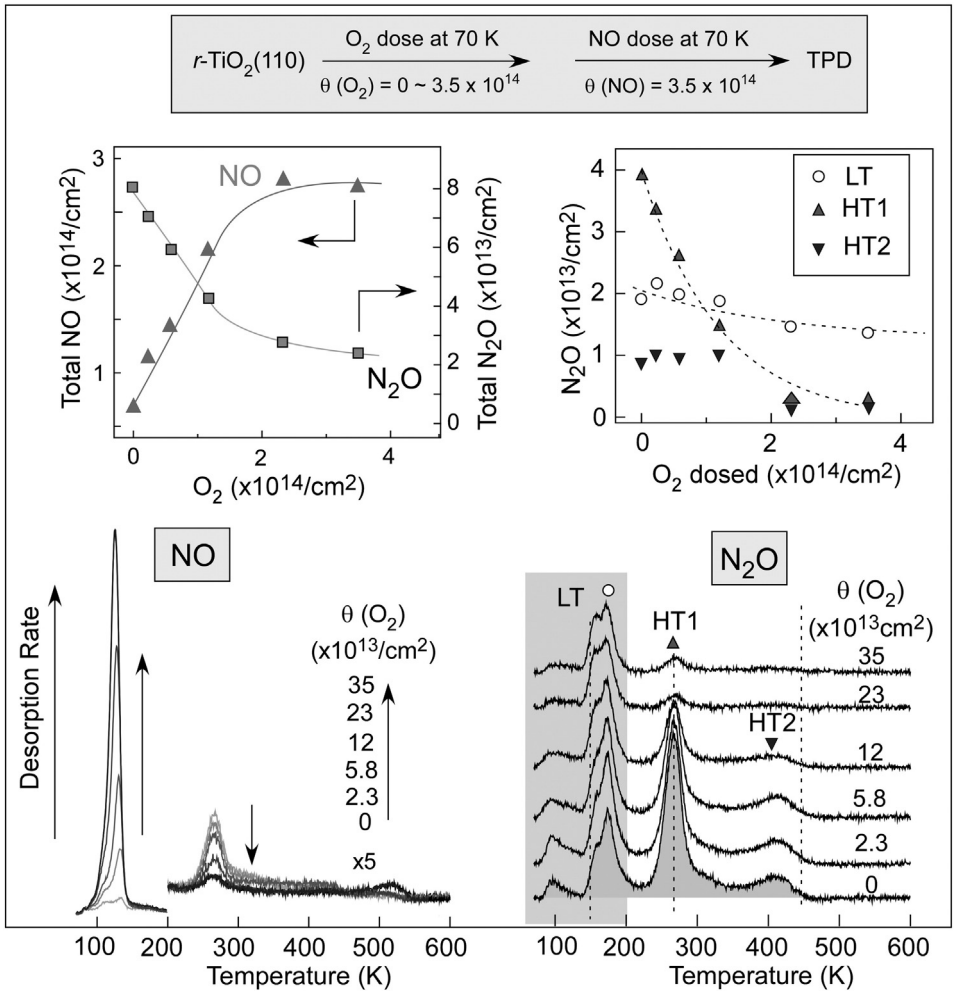

Fig 6. TPD spectra showing NO (left) and N_2O (right) desorption from NO dosed on O_2-predosed *r*-TiO_2. The insets show the total NO (top left) and N_2O (top right) yields for various N_2O desorption channels plotted as a function of the O_2 dose.

the LT N_2O yield persists. Thus, the formation of surface NO-derived species responsible for the HT N_2O is more likely to be suppressed by the presence of predosed O_2 probably via the depletion of surface charge associated with oxygen vacancies. The predosed O_2 may fill the oxygen vacancies which can otherwise act as a binding site for NO dimers, e.g., $(NO)_2^-$. The NO dimer ($(NO)_2^-$) can be a likely candidate for HT1 N_2O peak since the decomposition of the dimer into N_2O and O_a at ~270 K can readily induce desorption of N_2O (reaction-limited desorption).

The LT N_2O yield is also suppressed slightly but still shows a significant desorption yield of ~1.5×10^{13} N_2O/cm^2 even at 3.5×10^{14} O_2/cm^2. Despite the persistent nature of the LT N_2O yield, we have also seen that during the NO dose on *r*-TiO_2, the LT N_2O desorption at the dose temperature (~50 K) is also strongly influenced by the depletion of surface charges by predosed O_2 [14]. In Fig. 6, NO is subsequently dosed following the O_2 dose at the low temperature and the TiO_2 is not fully oxidized under the condition. It is attributed to the origin of the persistent LT N_2O yield.

The effect of oxygen on the N_2O desorption channels is further studied by comparing N_2O TPD spectra taken from NO dosed on two different TiO_2 surfaces of *o*-TiO_2 and *r*-TiO_2, respectively. On *o*-TiO_2 (Fig. 7(a)), LT N_2O desorption is observed only above 4×10^{14} NO/cm^2; no HT N_2O desorption is observed throughout the whole NO doses up to 1×10^{15} NO/cm^2. This is consistent with earlier observations of Sorescu *et al.* on N_2O desorption from oxidized TiO_2(110) [12]. We can speculate that the formation of possible surface precursors (e.g., NO dimers) for the HT N_2O desorption channels is inhibited as a result of the depletion of V_O's (as well as surface charges associated with them).

Fig. 8 shows the behavior of the HT N_2O desorption channels when the surface is hydroxylated (*h*-TiO_2). Fig. 8(a) compares N_2O TPD spectra taken from three different TiO_2 surfaces: *r*-TiO_2, *h*-TiO_2, and H_2O predosed *h*-TiO_2. Note that the HT1 N_2O desorption peak is significantly reduced on *h*-TiO_2 compared to *r*-TiO_2, while the LT and HT2 N_2O desorption peaks are greatly enhanced. The HT1 N_2O is nearly depleted when a small amount of H_2O (~2×10^{13} H_2O/cm^2) is predosed on the *h*-TiO_2. The quantitative evaluation on the three N_2O yields is displayed in Fig. 8(b). The sum of N_2O on *h*-TiO_2 is slightly lower than that on *r*-TiO_2 by ~0.5×10^{13} N_2O/cm^2 due to the formation of NH_3 from the reaction between HO_b's and NO [28].

The data presented above imply that the presence of hydroxyls (and water) can deplete the surface species (probably $(NO)_2^-$) that lead to the HT1 N_2O desorption channel. Despite the quenching of the HT1 N_2O channel, the total N_2O yield does not vary much over the three TiO_2 surfaces. Recent STM studies performed at RT [29] show that the adsorbed NO is stabilized next to the hydroxyl species. We speculate that the low-temperature NO adsorption can possibly also yield more stable $(NO)_2^-$ dimers on *h*-TiO_2 than on *r*-TiO_2. Such species can be a source of the HT2 N_2O desorption that is observed on *h*-TiO_2.

Oxidized NO species such as NO_2 may be further oxidized by H_2O to make nitrate (NO_3) as has been reported earlier on oxide surfaces [30], including TiO_2 [31]. HO_b's on *h*-TiO_2 may react with O_a's to form OH_t's on the Ti^{4+} rows on the TiO_2(110) surface [32], subsequently forming H_2O

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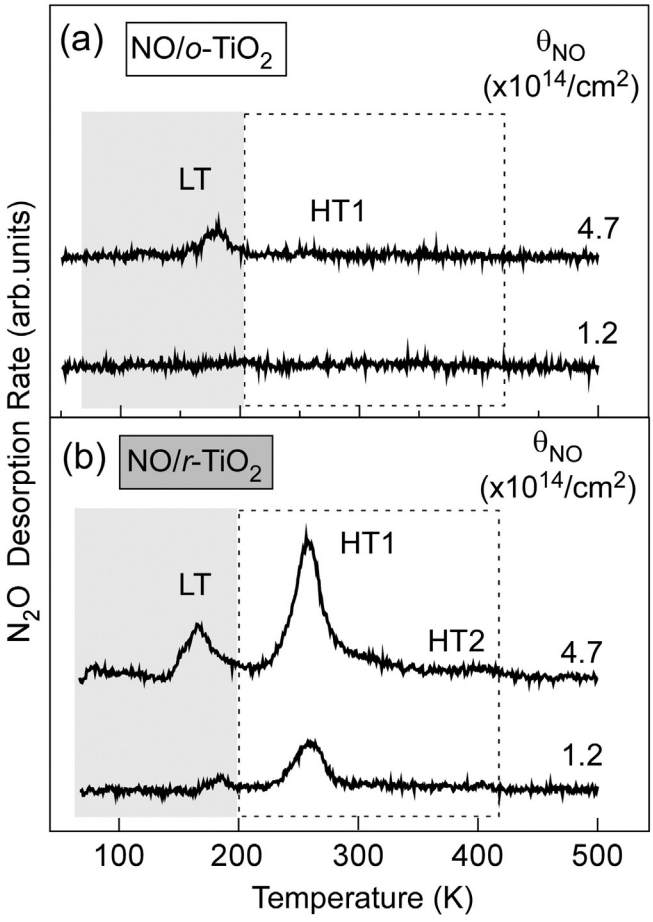

Fig. 7. Comparison of TPD spectra of N_2O desorbing from NO dosed on (a) *o*-TiO_2 and (b) *r*-TiO_2, respectively.

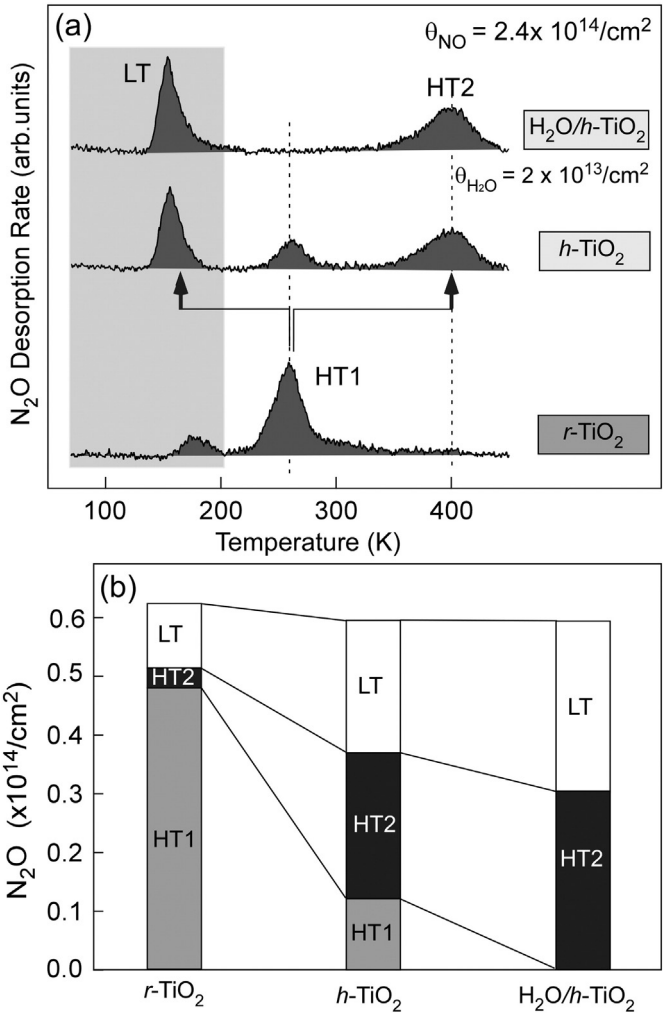

Fig. 8. (a) Comparison of TPD spectra of N_2O desorbing from NO (NO dose = 2.4×10^{14} NO/cm^2) dosed on *r*-TiO_2, *h*-TiO_2, and H_2O/*h*-TiO_2, respectively. It shows an intensity variation of each N_2O desorption channel on three different TiO_2 surfaces. (b) The N_2O desorption yields of LT, HT1, and HT2 channels compared for three different substrates of *r*-TiO_2, *h*-TiO_2, and H_2O predosed *h*-TiO_2. NO dose is fixed to 2.4×10^{14} NO/cm^2.

which desorbs at 300–400 K. Coadsorbed H_2O also interacts with O_a to form OH_t's [33]. Such OH_t species may react with NO_2 to form HNO_3, which can dissociate into H^+ and NO_3^- on TiO_2. However, this process is not likely to change the total N_2O yield as long as NO_2 and NO_3 do not contribute to the N_2O desorption channels.

The presence of hydroxyls also enhances the formation of LT N_2O (Fig. 8). The detailed mechanism for the enhanced LT N_2O desorption on *h*-TiO_2 is unclear, but we speculate that the presence of hydroxyls (and water) may also stabilize the adsorbed NO toward LT N_2O formation channel, probably via NO dimers.

We postulate that possible candidates for surface species responsible for the HT N_2O desorption channels can be NO dimers (e.g., $(NO)_2^-$) and hydroxyl-stabilized NO dimers for HT1 and HT2 N_2O, respectively. NO reduction on metal surfaces such as Ag [34,35], Au [36], Cu [37], and Pd [38] is proposed to involve $(NO)_2$ dimers as intermediates. In addition, such coupled NO species in the form of hyponitrite $(N_2O_2)^{2-}$ are also proposed as the intermediates of NO reduction cycles in biological systems employing NO reductase (NOR) [39] and flavodiiron NO reductase (FDP) [40].

NO dimers of various forms (e.g., cis and trans) have been proposed to have binding energies of 10–15 kcal/mol theoretically [12,41], which vary depending on the bonding configuration; they are suggested to decompose into $N_2O(a)$ and O_a below 200 K according to a recent FTIR study [41]. However, charged $(NO)_2^{2-}$ species may survive above 200 K and possibly contribute to HT1 N_2O desorption as previously observed for NO reactions on MnO_x/CeO_2 at 295 K [42]. In addition, bonding configuration of the NO dimers such as cis or trans can determine the energy barrier toward N_2O formation [43], which may give rise to N_2O desorption at different temperatures. Then, the observed variation in N_2O desorption channels above the threshold NO dose in Fig. 4 may be the result of varying ratio between different bonding configurations (e.g., cis and trans) with increasing NO doses. At low NO coverages the formation of trans-hyponitrites are favored and N_2O desorption is observed in the HT1 state primarily. As the surface becomes more crowded at higher NO exposures, the formation of cis-hyponitrites is prevalent. Since the decomposition of cis-hyponitrites is energetically less demanding than that of the trans conformer, N_2O desorption is observed in the LT state as the NO exposure increases.

NO_2 has been suggested to be formed from NO dosed on $TiO_2(110)$ both experimentally and theoretically [15,16]. Theoretical studies [15,44] on NO_2/TiO_2 indicate that NO_2 is more strongly bound to TiO_2 than NO when NO_2 is bound to the Ti sites with its two oxygen atoms (η^2-bonding configuration). NO_2 may be further oxidized to NO_3 species, which are likely to survive above 400 K [31,44], too. The formation of oxidized species such as NO_2 and NO_3 on the surface is suggested to be the origin of the discrepancy in the total amount of NO dosed and that desorbed in Fig. 4.

4. Conclusions

A systematic temperature-programmed desorption (TPD) study of NO reactions with rutile $TiO_2(110)$ surface has been performed. Low-

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temperature (<200 K, LT N_2O), desorption-limited, and high-temperature (>200 K, HT N_2O) reaction-limited N_2O formation channels are observed in the TPD spectra. The insight obtained from these results is summarized below.

(i) The LT N_2O desorption channel increases approximately linearly on reduced TiO_2(110) (*r*-TiO_2) with increasing NO coverages. The branching into this channel is strongly reduced in the absence of surface charge associated with bridging oxygen vacancies (V_O's) as evident from the comparison of NO reactivity on *r*-TiO_2 and *o*-TiO_2 (TiO_2(110) surface oxidized by O_2).

(ii) The HT N_2O yield exhibits a maximum at intermediate NO doses but decreases as the NO dose is increased further. The maximum yield is obtained at a NO dose of 3.5×10^{14} and 2.5×10^{14} NO/cm^2 for *r*-TiO_2 and *p*-TiO_2 (TiO_2(110) with negligible V_O coverage). The observed HT N_2O decrease is correlated with increased LT N_2O formation; this results in a saturation in the overall N_2O yield above the intermediate NO dose.

(iii) The higher HT N_2O yield on *r*-TiO_2 as compared to *p*-TiO_2 indicates the importance of V_O's (and surface charges associated with them) in the formation of surface species responsible for the HT channel. The importance of surface charge is further supported by suppression of the HT N_2O desorption channel in the presence of the predosed oxygen.

(iv) There are also reaction-limited N_2 and NO desorption peaks at the same temperature as the HT1 N_2O desorption, which may be attributed to the competition between the three competing reaction channels originating from the same surface species.

(v) The HT2 N_2O desorption channel (along with the LT N_2O channel) is enhanced in the presence of hydroxyls (*h*-TiO_2), while the HT1 N_2O desorption channel is reduced. The suppression of the HT1 N_2O channel and the appearance of a new HT2 N_2O channel on *h*-TiO_2 is likely the result of stabilization of NO (dimers) in the presence of hydroxyls.

(vi) The discrepancy between the amount of NO dosed and that desorbed exists; it is likely the result of formation of oxidized species such as NO_2 and NO_3.

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