Temperature-programmed Desorption Study of NO

Reactions on Rutile $\text{TiO}_2(110)\text{-}1\times 1$

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ABSTRACT

Systematic temperature-programmed desorption (TPD) studies of NO adsorption and reactions on rutile $\text{TiO}_2(110)\text{-}1\times 1$ surface reveal several distinct reaction channels in a temperature range of 50 – 500 K. NO readily reacts on $\text{TiO}_2(110)$ 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 byproduct 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 $\text{TiO}_2(110)$ 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.

KEYWORDS $\text{TiO}_2(110)$, temperature programmed desorption, nitric oxide, nitrogen dioxide, nitrous oxide, NO dimers

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 $\text{V}_2\text{O}_5/\text{TiO}_2$ [6, 7], WO_3/TiO_2 [8], $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ [9, 10], and $\text{V}_2\text{O}_5\text{-MoO}_3/\text{TiO}_2$ [11].

A great deal of insight has been obtained from studies performed on model rutile $\text{TiO}_2(110)$ 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 $(\text{NO})_2$ 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 $\text{TiO}_2(110)$ 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 N₂O molecules desorb rapidly at 50 K while the rest can be liberated upon heating to ~ 180 K.

Although N₂O formation from NO has been observed on TiO₂(110) in previous studies [12-14], the reaction mechanism appears complex and is far from being well-understood. This is clearly illustrated by complex N₂O desorption which exhibits several desorption channels peaking at 170, 270, and 400 K. Further, while the studies [17] performed on reduced TiO₂(110) have shown that surface defects such as V_O's play an important role in NO reduction, the N₂O formation has been also observed on a fully oxidized [12] TiO₂(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*-TiO₂), reduced (*r*-TiO₂), hydroxylated (*h*-TiO₂) and oxidized TiO₂ (*o*-TiO₂). Our quantitative analysis of the N₂O desorption yields shows interesting details about the nature of the surface species responsible for the HT N₂O desorption channels.

2. Experimental Details

The measurements were performed in an ultrahigh vacuum (UHV) molecular beam surface scattering apparatus with a base pressure of 1×10^{-10} torr equipped with quadrupole mass spectrometer (UTI-100C) that was described previously [18].

The rutile TiO₂(110) substrate (10×10×1 mm³, 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 TiO₂(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 H₂O 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 TiO₂(110) crystal was transparent, exhibited a sharp 1×1 pattern in LEED and the V_O concentration was negligible based on H₂O TPD. We refer to this *pristine* sample as *p*-TiO₂. With an increasing number (> 10) of sputter-anneal cycles, the TiO₂(110) crystal turned dark blue and the V_O concentration increased to ~5% ($\sim 2.6 \times 10^{13} \text{ cm}^{-2}$) (this sample is referred to as *r*-TiO₂). We have also prepared hydroxylated [22-24] and oxidized [25, 26] TiO₂(110) (referred to as *h*-TiO₂ and *o*-TiO₂, respectively). On *h*-TiO₂, the V_O defect sites have been reacted away by dosing 2 monolayers (ML) of H₂O on *r*-TiO₂ at 50 K followed by annealing to 400 K [19, 25]. *o*-TiO₂ was prepared by oxidizing *r*-TiO₂ with molecular O₂ either by dosing $\sim 2 \times 10^{15} \text{ O}_2/\text{cm}^2$ at 300 K or by an O₂ dose of $1 - 5 \times 10^{14} \text{ O}_2/\text{cm}^2$ 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 – 100 K while recording mass fragments of possible reaction products such as N₂, N₂O, NO and NO₂ using a quadrupole mass spectrometer (UTI 100C). The TPD spectra of NO and N₂ were determined by subtracting the contribution of the fragments of N₂O (m/z = 44 amu) from m/z = 30 (0.38 amu) and m/z = 28 (0.15 amu), respectively. The absolute N₂O coverage (in N₂O/cm²) was obtained by comparing the integrated TPD area of the N₂O produced with the TPD spectra from a known amount of N₂O preadsorbed on TiO₂ [27]. The absolute NO dose (in NO/cm²) was estimated from the plot of integrated area of NO TPD spectra obtained from multilayers of NO dosed on oxidized TiO₂ 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 K α) to confirm that no N species remained on the TiO₂ surface after a few cycles of TPD within detection limit of XPS.

3. Results and Discussion

Figure 1. NO, N₂O, and N₂ TPD spectra following NO adsorption ($\theta_{\text{NO}} = 3.6 \times 10^{14}$ NO/cm²) on (a) *p*-TiO₂ (concentration of V_O's is < 0.01 ML) and (b) *r*-TiO₂ (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.

Figure 1 shows the TPD spectra of NO, N₂O, and N₂ desorbing after the NO adsorption on *p*-TiO₂ and *r*-TiO₂. We find that more NO (N₂O) desorbs from *p*-TiO₂ (*r*-TiO₂); that is, more N₂O is formed from NO on *r*-TiO₂, 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. N₂O, as a major reaction product, desorbs at a number of distinct desorption temperatures. The N₂O desorption at < 200 K is assigned to low-temperature (LT) N₂O. As shown in our previous study, N₂O 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 -TiO₂, N₂O 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 N₂O reaction channel, we also observe distinct N₂O desorption peaks at 270 and 400 K; labelled as high-temperature (HT) N₂O (HT N₂O). These HT N₂O TPD peaks are also accompanied by NO desorption. Since these desorption temperatures are much higher than the desorption temperatures of physisorbed NO and N₂O, the HT desorption peaks must result from reaction-limited desorption processes.

Figure 1 also shows a clearly resolved desorption of N₂ at 250 K [14] in addition to N₂O desorption. The N₂ yield increases proportionally with NO dose up to ~1 ML whereupon it saturates at 0.7×10^{13} N₂/cm² ; corresponding to 3 % of the NO dosed. The detailed mechanism of N₂ formation is not understood at this point, but the fact that the N₂ desorption temperature coincides with HT1 N₂O desorption suggests that *the same surface species for HT1 N₂O formation is responsible for the reaction-limited N₂ formation.*

Figure 2. NO TPD spectra from NO dosed on *p*- and *r*-TiO₂ as a function of NO dose. The inset shows the integrated amount of desorbing NO vs. NO dose. The number of Ti⁴⁺ sites on the surface is $5.2 \times 10^{14}/\text{cm}^2$ ($\equiv 1$ ML).

NO TPD spectra following NO adsorption on *p*- and *r*-TiO₂ as a function of NO dose are shown in Figure 2. The integrated amounts of desorbing NO are further plotted as a function of NO dose in the inset. At small NO doses ($\sim 1 \times 10^{14}$ NO/cm²), nearly all NO reacts to form products such as N₂O and NO₂. NO desorption is observed only above a certain threshold dose, which is 2.5×10^{14} NO/cm² for *r*-TiO₂ and 1×10^{14} NO/cm² for *p*-TiO₂. This result clearly shows that *more NO reacts on r-TiO₂ than on p-TiO₂*. Since the key difference between these two surfaces is the high concentration of V_O's ($\sim 5\%$) on *r*-TiO₂, the V_O's are attributed to the higher

reactivity of $r\text{-TiO}_2$ than that of $p\text{-TiO}_2$ as has been observed from the role of V_O 's in the *enhanced* LT N_2O formation yield [14].

Figure 3. TPD spectra of N_2O desorption from NO dosed on two different TiO_2 surfaces ($p\text{-TiO}_2$ and $r\text{-TiO}_2$) with increasing NO dose.

Figure 3 shows N_2O TPD spectra for different NO doses on $p\text{-}$ and $r\text{-TiO}_2$. On both surfaces, the HT1 N_2O peak initially increases, maximizes at NO dose of $\sim 3.5 \times 10^{14} \text{ NO/cm}^2$ 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. In contrast, the LT N_2O peak increases proportionally with the NO dose. A comparison of the N_2O spectra from $r\text{-}$ and $p\text{-TiO}_2$ reveals that the trends are very similar except that *the overall N_2O desorption yield is higher on $r\text{-TiO}_2$ at higher NO doses.*

At low NO doses, the intensity of N₂O desorption peaks from *p*-TiO₂ is slightly higher than that from *r*-TiO₂. Since more N₂O desorption occurs during the NO dose on *r*-TiO₂, it is likely that more oxygen adatoms are left on the *r*-TiO₂ at the low NO dose regime. It may facilitate the formation of further oxidized forms of NO such as NO₂ and NO₃ better on *r*-TiO₂ than on *p*-TiO₂. This may act as a factor of suppressing the yield of the reductive channel (N₂O desorption) on *r*-TiO₂ than on *p*-TiO₂ at the low NO dose regime.

Figure 4. The integrated amounts of N₂O for the three different channels, LT, HT1 and HT2 as well as that of total N₂O obtained from TPD peaks in Figure 3 as a function of NO dose on *p*- and *r*-TiO₂.

The integrated N₂O amounts observed in three observed N₂O TPD peaks (LT, HT1 and HT2) as well as the total N₂O from both *r*-TiO₂ and *p*-TiO₂ are plotted against the NO dose in Figure 4. Several interesting features can be observed in the NO coverage-dependent trends of N₂O desorption yield. First, the total N₂O yield increases up to the NO dose of 2.5×10^{14} and 4×10^{14} NO/cm² on *p*- and *r*-TiO₂, respectively, then saturates at higher doses. The total N₂O yield from

r -TiO₂ is higher than that from p -TiO₂ by $\sim 3.5 \times 10^{13} / \text{cm}^2$. This can be attributed to the presence of V_O's on r -TiO₂. The V_O's also lead to the N₂O desorption below 100 K from NO dosed on r -TiO₂(110) [14]. Some of N₂O formed at the dose temperature is physisorbed and desorbs below 200 K during the TPD ramp. N₂O may be also formed during the ramp as the molecularly bound NO species diffuse on the surface and react with each other forming N₂O + O_a at low temperatures (up to 120 K). These possible channels contribute to LT N₂O desorption below 200 K.

Second, *the HT1 N₂O yield does not saturate, but decreases at higher NO doses*. The maximum yield of HT1 N₂O is reached at the NO dose of 2.5×10^{14} and 3.5×10^{14} NO/cm² on p - and r -TiO₂, respectively, which decreases as the NO dose increases further. *The loss in HT1 N₂O yield is largely compensated by an increase in the LT N₂O yield*; this results in a saturation in the total N₂O yield for both r - and p -TiO₂. As the NO dose increases to a saturation of monolayer, the increased NO-NO interaction may facilitate the formation of N₂O at lower temperatures (< 200 K); it may limit the formation of the surface NO-derived species responsible for the HT N₂O such as stable forms of NO dimers. The absolute yield for the HT2 N₂O 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 N₂O desorption yields*. For example, for the NO dose of 3.5×10^{14} NO/cm² on r -TiO₂, the total N₂O yield is $\sim 8 \times 10^{13}$ N₂O/cm² and the amount of unreacted NO desorption is about 5×10^{13} NO/cm². After adding the N₂O desorption during the NO dose ($\sim 1 \times 10^{13}$ N₂O/cm²), the total N₂O yield equals to $\sim 9 \times 10^{13}$ N₂O/cm² accounting for the NO dose of 1.8×10^{14} NO/cm². The desorbing amounts of NO and N₂O account for 2.3×10^{14} NO/cm². Thus, a significant fraction of NO ($\sim 1.2 \times 10^{14}$ NO/cm²) remains unaccounted. This discrepancy is larger than that expected from a possible calibration

error ($\sim 10 - 20 \%$), 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 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 .

Figure 5. H₂O TPD (dose = 1×10^{15} H₂O/cm²) from *r*-TiO₂ after dosing different amounts of NO at 70 K and TPD to 400 K. The recombinaive H₂O 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.

A strong correlation between V_O's on *r*-TiO₂ and the NO reactivity is further corroborated from Figure 5. It shows H₂O TPD obtained after NO TPD up to 400 K at various NO doses. After the NO TPD, H₂O 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*-TiO₂ surfaces as described in the experimental section [19, 21, 25]. The H₂O TPD spectra in Figure 5 show that the recombinaive H₂O desorption peak at 500 K ($2\text{OH}_b \rightarrow \text{H}_2\text{O}(\text{g}) + \text{O}_b + \text{V}_\text{O}$) decreases significantly already at very low NO doses ($< 5 \times 10^{13}$ NO/cm²). The dependence of the integral of the recombinaive H₂O TPD peak on the NO dose is shown in the upper inset of Figure 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/cm²)

at $\sim 5 \times 10^{13}$ NO/cm². We speculate that this is the result of V_O's being preferentially filled with oxygen atoms left behind from the N₂O formation from NO [14].

Figure 6. TPD spectra showing NO (left) and N₂O (right) desorption from NO dosed on O₂-predosed $r\text{-TiO}_2$. The insets show the total NO (top left) and N₂O (top right) yields for various N₂O desorption channels plotted as a function of the O₂ dose.

Considering that the formation of N₂O from NO leaves O_a on TiO₂(110), the effect of predosed oxygen on the reactivity of NO is investigated in Figure 6. The figure shows the TPD spectra of NO and N₂O from NO dosed on O₂-predosed $r\text{-TiO}_2$ at fixed NO dose ($\theta_{\text{NO}} = 3.5 \times 10^{14}$ NO/cm²) while the O₂ dose is increased up to 3.5×10^{14} /cm². NO TPD (left) shows that the LT NO desorption increases with increasing O₂, suggesting that the reactivity of NO over TiO₂ decreases

due to the effect of predosed O₂. As a result, unreacted NO contributes to the increase of NO desorption yield with increasing O₂ dose as quantified in the left inset of Figure 6. The TPD spectra of N₂O (right) show that the total N₂O desorption yield decreases with increasing O₂ doses.

The N₂O desorption yield from different channels is shown in the upper right inset of Figure 6. Note that the decrease of HT1 N₂O yield is more pronounced than that of LT N₂O. As the predosed O₂ increases, the HT1 N₂O yield vanishes at an O₂ dose of $\sim 2 \times 10^{14}$ O₂/cm², while the LT N₂O yield persists. *Thus, the formation of surface NO-derived species responsible for the HT N₂O is more likely to be suppressed by the presence of predosed O₂ probably via the depletion of surface charge associated with oxygen vacancies.* The predosed O₂ 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 N₂O peak since the decomposition of the dimer into N₂O and O_a at ~ 270 K can readily induce desorption of N₂O (reaction-limited desorption).

The LT N₂O yield is also suppressed slightly, but still shows a significant desorption yield of $\sim 1.5 \times 10^{13}$ N₂O/cm² even at 3.5×10^{14} O₂/cm². Despite the persistent nature of the LT N₂O yield, we have also seen that during the NO dose on *r*-TiO₂, the LT N₂O desorption at the dose temperature (~ 50 K) is also strongly influenced by the depletion of surface charges by predosed O₂ [14]. In Figure 6, NO is subsequently dosed following the O₂ dose at the low temperature and the TiO₂ is not fully oxidized under the condition. It is attributed to the origin of the persistent LT N₂O yield.

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

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 (Figure 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 $\text{TiO}_2(110)$ [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).

Figure 8. (a) Comparison of TPD spectra of N₂O desorbing from NO (NO dose = 2.4×10^{14} NO/cm²) dosed on *r*-TiO₂, *h*-TiO₂, and H₂O/*h*-TiO₂, respectively. It shows an intensity variation of each N₂O desorption channel on three different TiO₂ surfaces. (b) The N₂O desorption yields of LT, HT1 and HT2 channels compared for three different substrates of *r*-TiO₂, *h*-TiO₂ and H₂O pre-dosed *h*-TiO₂. NO dose is fixed to 2.4×10^{14} NO/cm².

Figure 8 shows the behavior of the HT N₂O desorption channels when the surface is hydroxylated (*h*-TiO₂). Figure 8(a) compares N₂O TPD spectra taken from three different TiO₂ surfaces; *r*-TiO₂, *h*-TiO₂ and H₂O pre-dosed *h*-TiO₂. Note that the *HT1* N₂O desorption peak is significantly reduced on *h*-TiO₂ compared to *r*-TiO₂ while the LT and HT2 N₂O desorption peaks are greatly enhanced. The HT1 N₂O is nearly depleted when a small amount of H₂O ($\sim 2 \times 10^{13}$ H₂O/cm²) is predosed on the *h*-TiO₂. The quantitative evaluation on the three N₂O yields is

displayed in Figure 8(b). The sum of N₂O on *h*-TiO₂ is slightly lower than that on *r*-TiO₂ by $\sim 0.5 \times 10^{13}$ N₂O/cm² due to the formation of NH₃ 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 N₂O desorption channel. Despite the quenching of the HT1 N₂O channel, the total N₂O yield does not vary much over the three TiO₂ 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-TiO₂ than on r-TiO₂*. Such species can be a source of the HT2 N₂O desorption that is observed on *h*-TiO₂.

Oxidized NO species such as NO₂ may be further oxidized by H₂O to make nitrate (NO₃) as has been reported earlier on oxide surfaces [30] including TiO₂ [31]. HO_b's on *h*-TiO₂ may react with O_a's to form OH_t's on the Ti⁴⁺ rows on the TiO₂(110) surface [32]; subsequently forming H₂O which desorbs at 300 – 400 K. Coadsorbed H₂O also interacts with O_a to form OH_t's [33]. Such OH_t species may react with NO₂ to form HNO₃ which can dissociate into H⁺ and NO₃⁻ on TiO₂. However, this process is not likely to change the total N₂O yield as long as NO₂ and NO₃ do not contribute to the N₂O desorption channels.

The presence of hydroxyls also enhances the formation of LT N₂O (Figure 8). The detailed mechanism for the enhanced LT N₂O desorption on *h*-TiO₂ is unclear, but we speculate that the presence of hydroxyls (and water) may also stabilize the adsorbed NO toward LT N₂O formation channel, probably via NO dimers.

We postulate that possible candidates for surface species responsible for the HT N₂O desorption channels can be NO dimers (e.g., (NO)₂⁻) and hydroxyl-stabilized NO dimers for HT1 and HT2 N₂O, respectively. NO reduction on metal surfaces such as Ag [34, 35], Au [36], Cu [37]

and Pd [38] is proposed to involve $(\text{NO})_2$ dimers as intermediates. In addition, such coupled NO species in the form of hyponitrite $(\text{N}_2\text{O}_2)^{2-}$ 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 $\text{N}_2\text{O}(a)$ and O_a below 200 K according to a recent FTIR study [41]. However, charged $(\text{NO})_2^{2-}$ species may survive above 200 K and possibly contribute to HT1 N_2O desorption as previously observed for NO reactions on $\text{MnO}_x/\text{CeO}_2$ 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 Figure 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 are 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 $\text{TiO}_2(110)$ 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 NO₂ and NO₃ on the surface is suggested to be the origin of the discrepancy in the total amount of NO dosed and that desorbed in Figure 4.

4. Conclusions

A systematic temperature programmed desorption (TPD) study of NO reactions with rutile TiO₂(110) surface has been performed. Low temperature (< 200 K, LT N₂O), desorption-limited and high temperature (> 200 K, HT N₂O) reaction-limited N₂O formation channels are observed in the TPD spectra. The insight obtained from these results is summarized below.

- (i) The LT N₂O desorption channel increases approximately linearly on reduced TiO₂(110) (*r*-TiO₂) 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*-TiO₂ and *o*-TiO₂ (TiO₂(110) surface oxidized by O₂).
- (ii) The HT N₂O 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/cm² for *r*-TiO₂ and *p*-TiO₂ (TiO₂(110) with negligible V_O coverage). The observed HT N₂O decrease is correlated with increased LT N₂O formation; this results in a saturation in the overall N₂O yield above the intermediate NO dose.
- (iii) The higher HT N₂O yield on *r*-TiO₂ as compared to *p*-TiO₂ 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 N₂O 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 ($h\text{-TiO}_2$) 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 $h\text{-TiO}_2$ 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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References

- [1] Z. Liu, S. Ihl Woo, Catal. Rev., 48 (2006) 43-89.
- [2] P. Forzatti, Appl. Catal. A, 222 (2001) 221-236.
- [3] G. Busca, M.A. Larrubia, L. Arrighi, G. Ramis, Catal. Today, 107–108 (2005) 139-148.

- [4] V.I. Pârvulescu, P. Grange, B. Delmon, *Catal. Today*, 46 (1998) 233-316.
- [5] F. Garin, *Appl. Catal. A*, 222 (2001) 183-219.
- [6] G.T. Went, L.-J. Leu, R.R. Rosin, A.T. Bell, *J. Catal.*, 134 (1992) 492-505.
- [7] S.B. Kristensen, A.J. Kunov-Kruse, A. Riisager, S.B. Rasmussen, R. Fehrmann, *J. Catal.*, 284 (2011) 60-67.
- [8] H. Zhang, J. Han, X. Niu, X. Han, G. Wei, W. Han, *J. Mol. Catal. A*, 350 (2011) 35-39.
- [9] L. Lietti, J.L. Alemany, P. Forzatti, G. Busca, G. Ramis, E. Giamello, F. Bregani, *Catal. Today*, 29 (1996) 143-148.
- [10] P.G.W.A. Kompio, A. Brückner, F. Hipler, G. Auer, E. Löffler, W. Grünert, *J. Catal.*, 286 (2012) 237-247.
- [11] L. Lietti, I. Nova, G. Ramis, L. Dall'Acqua, G. Busca, E. Giamello, P. Forzatti, F. Bregani, *J. Catal.*, 187 (1999) 419-435.
- [12] D.C. Sorescu, C.N. Rusu, J.T. Yates, *J. Phys. Chem. B*, 104 (2000) 4408-4417.
- [13] C.N. Rusu, J.T. Yates, *J. Phys. Chem. B*, 104 (2000) 1729-1737.
- [14] B. Kim, Z. Li, B.D. Kay, Z. Dohnálek, Y.K. Kim, *J. Phys. Chem. C*, 118 (2014) 9544-9550.
- [15] D. Stodt, H. Noei, C. Hattig, Y. Wang, *Phys. Chem. Chem. Phys.*, 15 (2013) 466-472.
- [16] M. Xu, Y. Wang, S. Hu, R. Xu, Y. Cao, S. Yan, *Phys. Chem. Chem. Phys.*, 16 (2014) 14682-14687.
- [17] G. Lu, A. Linsebigler, J.T. Yates, *J. Phys. Chem.*, 98 (1994) 11733-11738.
- [18] Z. Dohnálek, J. Kim, O. Bondarchuk, J. Mike White, B.D. Kay, *J. Phys. Chem. B*, 110 (2006) 6229-6235.
- [19] M.A. Henderson, *Langmuir*, 12 (1996) 5093-5098.
- [20] Y.K. Kim, B.D. Kay, J.M. White, Z. Dohnálek, *J. Phys. Chem. C*, 111 (2007) 18236-18242.
- [21] M.A. Henderson, *Surf. Sci.*, 400 (1998) 203-219.
- [22] S. Wendt, P.T. Sprunger, E. Lira, G.K.H. Madsen, Z. Li, J.Ø. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer, F. Besenbacher, *Science*, 320 (2008) 1755-1759.
- [23] C.M. Yim, C.L. Pang, G. Thornton, *Phys. Rev. Lett.*, 104 (2010) 036806-036806.
- [24] A.C. Papageorgiou, N.S. Beglitis, C.L. Pang, G. Teobaldi, G. Cabailh, Q. Chen, A.J. Fisher, W.A. Hofer, G. Thornton, *Proc. Natl. Acad. Sci.*, 107 (2010) 2391-2396.
- [25] Z. Dohnálek, I. Lyubinetsky, R. Rousseau, *Prog. Surf. Sci.*, 85 (2010) 161-205.
- [26] M.A. Henderson, W.S. Epling, C.L. Perkins, C.H.F. Peden, U. Diebold, *J. Phys. Chem. B*, 103 (1999) 5328-5337.
- [27] B. Kim, Z. Li, B.D. Kay, Z. Dohnalek, Y.K. Kim, *J. Phys. Chem. C*, 116 (2012) 1145-1150.
- [28] B. Kim, B.D. Kay, Z. Dohnálek, Y.K. Kim, *J. Phys. Chem. C*, 119 (2015) 1130-1135.
- [29] S.-C. Li, P. Jacobson, S.-L. Zhao, X.-Q. Gong, U. Diebold, *J. Phys. Chem. C*, 116 (2012) 1887-1891.
- [30] B.J. Finlayson-Pitts, L.M. Wingen, A.L. Sumner, D. Syomin, K.A. Ramazan, *Phys. Chem. Chem. Phys.*, 5 (2003) 223-242.
- [31] J. Haubrich, R.G. Quiller, L. Benz, Z. Liu, C.M. Friend, *Langmuir*, 26 (2010) 2445-2451.
- [32] Z. Zhang, Y. Du, N.G. Petrik, G.A. Kimmel, I. Lyubinetsky, Z. Dohnálek, *J. Phys. Chem. C*, 113 (2009) 1908-1916.
- [33] Y. Du, N.A. Deskins, Z. Zhang, Z. Dohnalek, M. Dupuis, I. Lyubinetsky, *Phys. Rev. Lett.*, 102 (2009) 096102-096102.
- [34] Z.-P. Liu, S.J. Jenkins, D.A. King, *J. Am. Chem. Soc.*, 126 (2004) 7336-7340.
- [35] W.A. Brown, D.A. King, *The Journal of Physical Chemistry B*, 104 (2000) 2578-2595.

- [36] Z. Wu, L. Xu, W. Zhang, Y. Ma, Q. Yuan, Y. Jin, J. Yang, W. Huang, *J. Catal.*, 304 (2013) 112-122.
- [37] A. Shiotari, Y. Kitaguchi, H. Okuyama, S. Hatta, T. Aruga, *Phys. Rev. Lett.*, 106 (2011) 156104.
- [38] L.-y. Huai, C.-z. He, H. Wang, H. Wen, W.-c. Yi, J.-y. Liu, *J. Catal.*, 322 (2015) 73-83.
- [39] J. Wang, M.P. Schopfer, S.C. Puiu, A.A.N. Sarjeant, K.D. Karlin, *Inorganic Chemistry*, 49 (2010) 1404-1419.
- [40] T. Hayashi, J.D. Caranto, D.A. Wampler, D.M. Kurtz, P. Moënne-Loccoz, *Biochemistry*, 49 (2010) 7040-7049.
- [41] Y. Wang, R. Kováčik, B. Meyer, K. Kotsis, D. Stodt, V. Staemmler, H. Qiu, F. Traeger, D. Langenberg, M. Muhler, C. Wöll, *Ang. Chem.*, 46 (2007) 5624-5627.
- [42] J. Szanyi, J.H. Kwak, *Chem. Comm.*, 50 (2014) 14998-15001.
- [43] A.M. Wright, T.W. Hayton, *Inorganic Chemistry*, 54 (2015) 9330-9341.
- [44] J.A. Rodriguez, T. Jirsak, G. Liu, J. Hrbek, J. Dvorak, A. Maiti, *J. Am. Chem. Soc.*, 123 (2001) 9597-9605.

Graphical abstract