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The effect of H_2 and the presence of *hot*-$O_{(ads)}$ during the decomposition of N_2O on platinum

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The decomposition of N_2O was studied using a silica-supported Pt catalyst. The catalyst was found to exhibit short-lived activity at low temperatures to yield N_2 and $O_{(ads)}$, the latter remained adsorbed on the surface and poisoned the active sites. Creation of *hot*-$O_{(ads)}$ atoms during N_2O decomposition is proposed to allow O_2 desorption at intermediate temperatures. Inclusion of H_2 as a reducing agent greatly enhanced the activity and suppressed low temperature deactivation. Simultaneous and sequential pulsing of N_2O and H_2 showed that H_2 inclusion with the N_2O gas stream produced the greatest activity. A mechanism involving $H_{(ads)}$ addition to "hot" oxygen atoms for H_2O formation is proposed.

KEY WORDS: $N_2O + H_2$; platinum; catalysts.

1. Introduction

Nitrous Oxide, N_2O, is a potent greenhouse gas and also participates in stratospheric ozone depletion [1,2]. Its low temperature formation in catalytic converters, particularly for diesel engines and for gasoline engines under "cold-start" conditions, is a growing area of concern. Currently, no onboard technology is employed to eliminate N_2O.

Many catalytic systems have been employed to remove N_2O, and these have been reviewed extensively by Kapteijn and co-workers [3,4]. A general mechanism was proposed by Winter in the late 1960's [5–7].

$$N_2O + {}^* \rightarrow N_2 + O_{(ads)} \qquad (1)$$

$$2O_{(ads)} \leftrightarrow O_2 + 2^* \qquad (2)$$

$$N_2O + O_{(ads)} \rightarrow N_2 + O_2 \qquad (3)$$

Dissociative adsorption of N_2O on supported Pt was studied by Kim *et al.* [8] who claimed that, regardless of the conclusions drawn from UHV studies for N_2O on platinum, their experiments showed decomposition of N_2O on Pt at 363 K and 76 Torr yielding $N_{2(g)}$ and an $O_{(ads)}$ monolayer. Denton *et al.* [9], using N_2O pulse experiments with 0.9% Pt/SiO_2 at 220 °C, showed that N_2O decomposition does occur, producing N_2 and adsorbed oxygen (TPD experiments show that O_2 does not desorb from platinum below 600 °C [10]). As the surface concentration of oxygen increases, the activity decreases. No decomposition of N_2O is observed on a completely oxidized surface [9]. Therefore, equations (2) and (3), which involve removal of strongly adsorbed oxygen, would not be expected to occur at low temperatures.

The NO + H_2 reaction with Platinum Group Metals (PGMs) has been studied in significant detail due to its importance in de-NO*x* catalysis [11–14]. However, the $N_2O + H_2$ reaction has received considerably less study. Nieuwenhuys and co-workers [15,16] described oscillations in the rate of N_2O decomposition over Ir(110), but only within specific experimental parameters (460–464 K, N_2O pressure of 1×10^{-6} mbar, N_2O/H_2 close to 1). Oscillations in the rate of N_2O decomposition have also been reported for Rh–ZrNdOx when N_2O is fed with H_2O and O_2 [1,2].

The role of H_2 has been reported to merely scavenge $O_{(ads)}$ from the surface [15]:

$$H_2 + 2^* \rightarrow 2H_{(ads)} \qquad (4)$$

$$2H_{(ads)} + O_{(ads)} \rightarrow H_2O_{(g)} + 3^* \qquad (5)$$

On the other hand, the existence of metastable "hot" oxygen atoms on metal surfaces has been proposed several times in the literature, most notably by Roberts and co-workers [17,18]. They reported that oxygen chemisorption could lead to the activation of unreactive molecules and proposed the formation of $O^-_{(s)}$ as the surface transient responsible for such activation. The basic concept was that in the process of adsorption of an O_2 molecule, bond cleavage during the formation of a strongly chemisorbed $O_{(ads)}$ would lead to the second oxygen being released onto the surface as a thermally "hot" atom that could then migrate several atomic distances before becoming trapped as a normal adsorbed oxygen ion. In the case of dissociative adsorption of N_2O on a Mg(0001) surface they proposed the following scheme:

$$N_2O_{(g)} \rightarrow N_2O_{(ads)} \rightarrow N_{2(g)} + O^-_{(s)} \rightarrow O^{2-}_{(ads)} \qquad (6)$$

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The "hot" oxygen was defined by Roberts and co-workers as "the transient electrophilic $O^-_{(s)}$ species rather than $O^{2-}_{(ads)}$ (more thermodynamically stable)" [17]. This early research of Roberts and co-workers has been supplemented by the STM images of O_2 on Pt(111) by Ertl and co-workers [19] and Stipe *et al.* [20]. Horino *et al.* [21] have also studied N_2O dissociation and N_2 desorption on Pd(110) using TDS and proposed that the $O_{(ads)}$ produced in equation (1) may have a higher energy than those produced by simply adsorbing molecular oxygen on the Pd surface. They also report that about 2 eV [22] is released by N_2O dissociation and subsequent formation of the O–metal bond [21,22].

In this letter we report the effects of inclusion of H_2 during N_2O decomposition with *real* supported Pt catalysts. The recombination of $2O_{(ads)}$ is considered in the context of the "hot" oxygen model of Roberts and co-workers referred to above to explain the desorption of molecular oxygen at relatively low temperatures in the absence of H_2. In the presence of H_2 a mechanism involving $H_{(ads)}$ addition to *hot*-$O_{(ads)}$ is proposed.

2. Experimental

A sample of 5% Pt/SiO_2 was prepared by incipient wetness impregnation using Pt-DNDA (Johnson Matthey) precursor and acid washed silica (Grace 432) with mesh range 250–850 μm. After impregnation, the catalyst was dried at 120 °C overnight prior to calcination at 500 °C for 2 h. 100 mg test samples were positioned in a Pyrex tube and held in place between two quartz wool plugs. A thermocouple was positioned in the catalyst bed to monitor temperature and the reactor furnace was controlled using a Eurotherm 818 controller. The reactant gases, He (100%, BOC Gases), N_2O (0.2% in He, BOC Gases), H_2 (3% in He, BOC Gases) were fed from independent Aera mass flow controllers. Reaction products were monitored using a computer interfaced Fisons Gaslab 300 Mass Spectrometer, operated using the corresponding Thermosoft software. Prior to testing, all samples were pre-treated in 1% H_2/He, total flow rate = 50 cm^3 min^{-1}, for 30 min at 500 °C. The size of the sample loop was designed to titrate 10% of the surface per pulse, assuming 1 : 1 N_2O : Pt.

Steady-state experiments were monitored using a PC interfaced Perkin Elmer Autosystem XL GC fitted with a 13X molecular sieve column. 100 mg samples were held between two quartz wool plugs in a quartz reactor. The sample was pre-treated with 1%H_2/He, total flow rate = 200 cm^3 min^{-1}, for 30 min at 500 °C.

3. Results

3.1. N_2O decomposition in the absence of H_2

The results of N_2O pulse experiments over a reduced 5% Pt/SiO_2 catalyst are presented in figure 1. Each pulse was calculated to titrate 10% of the surface platinum atoms, assuming 1 : 1 N_2O : Pt. It is clear that at 25 °C, approximately 90% conversion of N_2O was observed for the first three pulses before conversion began to decrease. This suggests that there are a limited number of surface sites active for N_2O decomposition at room temperature. When the temperature was increased to 150 °C, the activity was extended to four pulses before a decrease in the N_2O conversion was observed. Repetition of the pulsing over a reduced catalyst at 250 °C also showed approximately 100% N_2O conversion, but extended to five pulses (approximately 50% of the surface) before deactivation starts to occur. It is clear from the figure that a reduced catalyst at 450 °C decomposed approximately 100% of the first nine pulses, before the activity decreased. However, at this temperature, the decrease in activity was not total and a "steady-state" conversion of about 60% was observed

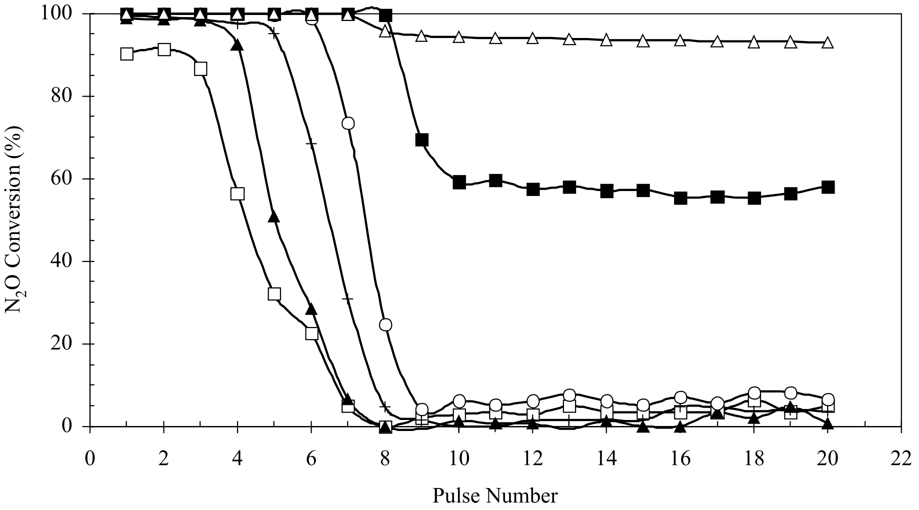

Figure 1. Conversion of N_2O as a function of pulse number for different temperatures over reduced 5% Pt/SiO_2. Total gas flow = 50 cm^3 min^{-1}, Pulses of 2000 ppm N_2O, He balance. 25 °C (□), 150 °C (▲), 250 °C (+), 350 °C (○), 450 °C (■), 500 °C (△).

for the remainder of the experiment. At 500 °C, this "steady-state" was over 90%.

At lower temperatures, no O_2 response was observed, while significant quantities of N_2 were produced. O_2 desorption was observed to occur at the higher temperatures. It should also be stressed that, above 400 °C, O_2 desorption was not observed until approximately pulse 10. This suggested that the concentration of adsorbed oxygen must be relatively high since 10 pulses of N_2O should be sufficient to fully saturate the Pt surface with an O : Pt ratio of 1 : 1. The N-balance for this reaction shows that no N-containing species remain adsorbed. N_2O appears either to decompose to form N_2 or it does not react or adsorb at all. There is no accumulation of $N_2O_{(ads)}$ on the surface [R. Burch *et al.*, submitted for publication].

3.2. The N_2O + H_2 reaction with Pt

To study the effect of a reducing agent on the decomposition of N_2O on a Pt catalyst, H_2 was pulsed either simultaneously with the N_2O or sequentially after the N_2O. The effects of simultaneous pulsing of N_2O and H_2 are shown in figure 2. Comparison of figures 1 and 2 shows that the activity of the catalyst was extended at all temperatures. With simultaneous pulsing of H_2 + N_2O (1 : 1 ratio) deactivation did not commence at 22 °C until after pulse 4, compared to deactivation after pulse 3 with no H_2 present. At 100 °C the activity was improved significantly by the addition of H_2 to the N_2O pulse. Under these conditions, 100% N_2O decomposition was extended to 11 pulses, and a steady-state conversion of approximately 50% was then observed. At both 200 and 400 °C the conversion of N_2O was 100% for the N_2O + H_2 reaction.

The effects of *sequential pulsing* (60 s between the introduction of the N_2O pulse and introduction of the H_2 pulse) of N_2O with H_2 at 400 °C are shown in figure 3 and compared with the direct N_2O decomposition reaction and the simultaneous N_2O + H_2 pulse experiments. We recall from figure 2 that during direct decomposition of N_2O, the conversion decreases after

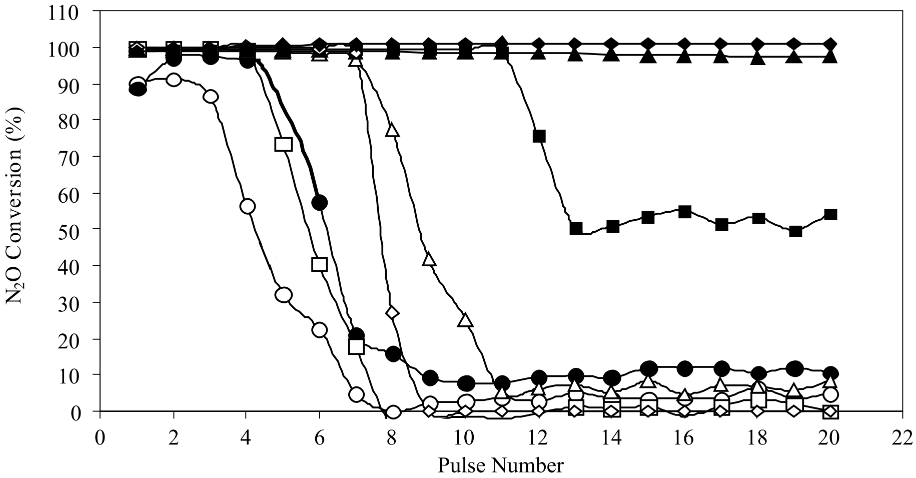

Figure 2. N_2O conversion for direct N_2O decomposition and the N_2O + H_2 reaction as a function of temperature. Open symbols are without H_2, closed symbols are with H_2 (2000 ppm N_2O : 2000 ppm H_2, 100 mg sample of 5% Pt/SiO_2 · 22 °C (○) and (●), 100 °C (□) and (■), 200 °C (△) and (▲), 400 °C (◇) and (◆).

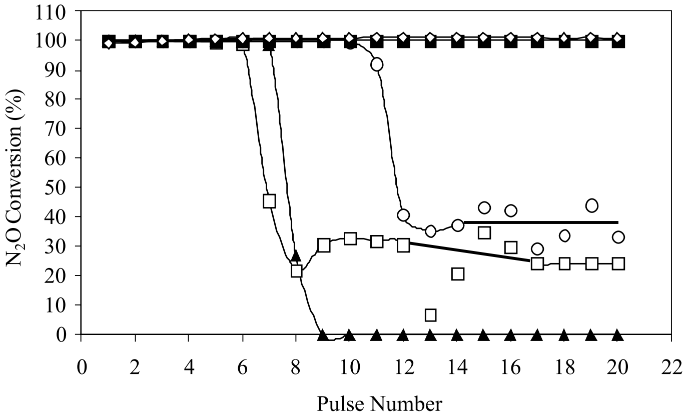

Figure 3. N_2O conversion for the sequential pulsing of N_2O and H_2 and comparison with the direct N_2O decomposition reaction and the simultaneous pulsing N_2O + H_2 reaction at 400 °C. 2000 ppm N_2O, 100 mg sample of 5% Pt/SiO_2 · N_2O only (▲), N_2O + H_2 sequential pulses (1 : 1) (□), N_2O + H_2 sequential pulses (1 : 2) (○), N_2O + H_2 sequential pulses (1 : 3) (■), N_2O + H_2 (1 : 1) simultaneous pulses (◇).

seven pulses. In the sequential pulsing experiments with a 1 : 1 ratio of $N_2O : H_2$ the decrease in conversion occurs after a similar number of pulses (6 versus 7), However, in the sequential pulsing experiments the conversion of N_2O stabilizes at about 30%.

Sequential pulsing of N_2O and then H_2 with a 1 : 2 ratio produced an increased level of N_2O conversion with 100% conversion extended to 10 pulses. However, the 100% N_2O conversion observed during the *simultaneous pulsing* of $N_2O + H_2$ (1:1) was not observed in the *sequential pulsing* until a $N_2O : H_2$ ratio of 1 : 3 was used. This indicates that the *simultaneous* presence of H_2 during the N_2O pulse significantly increased the activity of the catalyst for N_2O decomposition.

3.3. *Steady-state decomposition of N_2O and the $N_2O + H_2$ reaction*

The results of the pulsing experiments have shown that a Pt catalyst exhibited activity towards N_2O decomposition. However, at lower temperatures, this activity was quickly lost by the accumulation of $O_{(ads)}$ on the surface, which blocked the active sites and poisoned the catalyst. The addition of H_2 to the N_2O pulse significantly enhanced the activity of the catalyst by removing the adsorbed oxygen and recycling the active sites.

Figure 4 shows the results of *steady-state experiments* for direct decomposition of N_2O and for the $N_2O + H_2$ at varying concentration ratios. Clearly the direct decomposition of N_2O on the catalyst did not occur below about 350 °C. This suggests that below this temperature, the catalyst has been oxidized during the initial exposure to N_2O and had become self-poisoned. Above 350 °C, O_2 desorption was observed which could explain why the steady-state N_2O conversion increases.

The addition of H_2 improved the activity of the catalyst (figure 4). However, even at 400 °C 100% conversion of N_2O required a ratio of $H_2 : N_2O > 1$. These results are consistent with the $N_2O + H_2$ pulse experiments when the N_2O and H_2 are pulsed simultaneously. Thus figure 2 shows that above 200 °C the $N_2O + H_2$ simultaneous pulses give 100% conversion, and figure 4 shows a steady-state conversion of 100% at 250 °C.

4. Discussion

Pt-based catalysts exhibit poor steady-state activity for the low temperature decomposition of N_2O. Indeed, temperatures of greater than about 350 °C are required before any steady-state activity is measurable. However, the results of our N_2O pulsing experiments presented here and previously [R. Burch *et al.*, submitted for publication] showed that Pt is active towards N_2O decomposition, but the active sites are rapidly poisoned by adsorbed oxygen. $O_{(ads)}$–$O_{(ads)}$ recombination at higher temperatures allows regeneration of the active sites and significant steady-state activity [R. Burch *et al.*, submitted for publication].

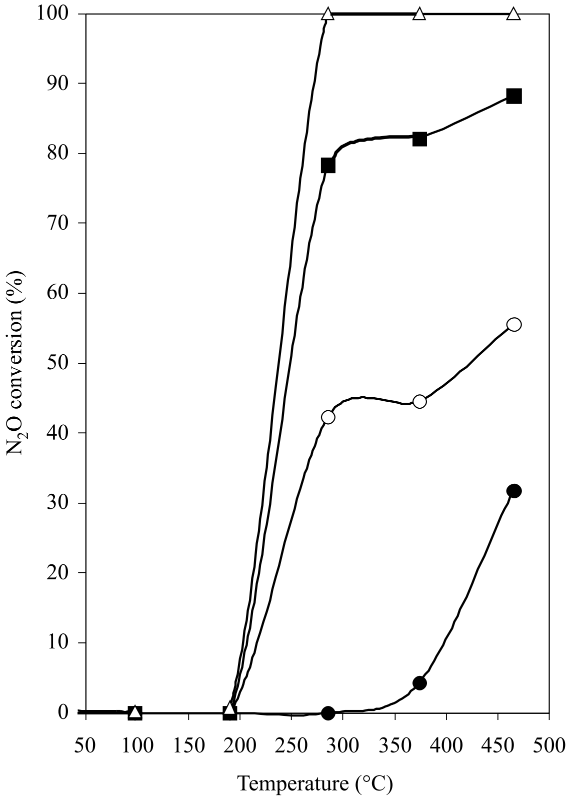

Figure 4. Steady-state N_2O conversion for continuous direct N_2O decomposition and comparison with the continuous $N_2O + H_2$ reaction as a function of temperature. 2000 ppm N_2O, 100 mg sample of 5% Pt/SiO_2 · N_2O only (●), $N_2O + H_2$ (1 : 0.5) (○), $N_2O + H_2$ (1 : 1) (■), $N_2O + H_2$ (1 : 2) (△).

It was clear from figures 2 and 3 that addition of H_2 to the N_2O pulse greatly improved the activity of the catalyst. By removing some of the $O_{(ads)}$, the active sites could be available to dissociate more N_2O.

The introduction of a H_2 pulse produced results that were dependent on the pulsing sequence as can be seen by comparing figures 3 and 4. This indicated that the hydrogen might have interacted directly with the N_2O pulse: a H-assisted N_2O dissociation mechanism may have been occurring in the simultaneous pulsing, which did not occur with the sequential pulsing.

$$N_2O + H_{(ads)} \rightarrow N_2 + OH_{(ads)} \qquad (7)$$

A similar mechanism was proposed by Hecker and Bell [23] for H-assisted NO decomposition on PGMs. This H-assisted NO decomposition mechanism has been shown to have a lower activation energy by Shustorovich and Bell [24].

In the case of N_2O, however, Miyamoto *et al.* [25], on the basis of their kinetic isotope studies with Pt/Al_2O_3, rejected the idea that an N_2O molecule attacked adsorbed hydrogen atoms on the catalyst. Indeed, they proposed that N_2O reacted with a vacant metal site to form N_2 and $O_{(ads)}$, after which H_2 attacked $O_{(ads)}$ and formed $H_2O_{(g)}$ and a vacant metal site.

Another possible explanation of the effect of H_2 on the removal of $O_{(ads)}$ is that the oxygen produced from dissociative adsorption of N_2O was easier to remove immediately after N–O bond fission, before a stable $O_{(ads)}$ species was formed. It has been reported that O_2 does not desorb from an oxidised Pt surface below 600 °C under TPD conditions [10]. This suggests that the O_2 observed in our pulse experiments [R. Burch *et al.*, submitted for publication] was either adsorbed at different sites with weaker adsorption energies, or that the nature of the pulse experiment assisted the recombination of $2O_{(ads)}$ and desorption of O_2. Tanaka *et al.* [26,27] proposed surface recombination of adsorbed oxygen atoms *via* a Langmuir-Hinshelwood mechanism on a rhodium catalyst. It was suggested that molecular oxygen is formed *via* reaction-assisted desorption. They proposed that N_2O decomposition forms a strong O–Rh bond (an exothermic process), the energy of which is transferred to adjacent surface-adsorbed oxygen atoms allowing subsequent recombination and desorption.

Following the publications of Roberts and co-workers [17,18] regarding so-called "hot" oxygen atoms, a similar proposal has been made regarding Pt(111) [19,20], and also specifically for N_2O dissociation on Pd surfaces [21,22,28]. Formation of the O–metal bond releases a significant amount of energy. Horino *et al.* [21,22] performed TDS experiments with N_2O on Pd(110) and proposed that formation of a *hot*-$O_{(ads)}$ was highly probable since the heat of adsorption of N_2O is very small and the $O_{(ads)}$ product atom has a very high heat of adsorption. Ertl and co-workers [19] proposed that *hot*-$O_{(ads)}$ created on Pt(111) move parallel to the surface over a few lattice distances.

The *hot*-$O_{(ads)}$ model is consistent with our previous report [R. Burch *et al.*, submitted for publication] in which we found that O_2 desorption at the comparatively low temperature of 450 °C only occurred as we approached surface saturation by $O_{(ads)}$. The *hot*-$O_{(ads)}$ created during N_2O decomposition may not be able to collide with a *normal* $O_{(ads)}$ on surfaces with a low surface coverage of $O_{(ads)}$, thus leading to the desorption of molecular oxygen, before the *hot*-$O_{(ads)}$ becomes trapped as a normal $O_{(ads)}$.

The participation of *hot*-$O_{(ads)}$ is also possible in the presence of H_2. Simultaneous pulsing of N_2O and H_2 resulted in significant H_2O production and enhanced activity of the Pt catalyst at temperatures from 100 °C upwards, as shown in figure 2. However, when N_2O and H_2 were pulsed sequentially with a delay of 1 min between the N_2O and H_2 pulse, the enhancement of the activity of the Pt was decreased significantly. A similar mechanism for reaction between a proposed *hot*-$O_{(ads)}$ and a hydrogen-containing species ($NH_{3(ads)}$) has been reported by Au and Roberts [17].

The proposed mechanism is illustrated in figure 5. Formation of a *hot*-$O_{(ads)}$ on the Pt surface occurs during N_2O decomposition. If surface $O_{(ads)}$ coverage is high, the short-range mobility of the *hot*-$O_{(ads)}$ allows recombination with a neighboring $O_{(ads)}$ and desorption of O_2. In the presence of $H_2/H_{(ads)}$, combination may yield H_2O at lower temperatures than O_2 formation and, therefore, H_2O is produced. However, when the pulse of hydrogen is introduced 1 min later, the extra energy gained by the $O_{(ads)}$ has decreased due to movement on the surface and the $O_{(ads)}$ would no longer be "hot". This produces a more stable $O_{(ads)}$ species, which requires either higher temperatures or increased H_2 concentration to remove as H_2O.

5. Conclusions

Inclusion of H_2 with N_2O greatly enhances the activity of a Pt catalyst at low temperatures for the conversion of N_2O to N_2. Simultaneous and sequential pulsing of N_2O and H_2 produced significantly different results, which indicated that $H_2/H_{(ads)}$ must be present with the N_2O pulse to attain the higher conversion rates. It was proposed that this was due to the formation of a *hot*-$O_{(ads)}$ atom after N_2O dissociation, which could then rapidly react with $H_{(ads)}$ and form H_2O. Delaying the pulse of H_2 enabled the extra energy of the *hot*-$O_{(ads)}$ to dissipate into the system. In the absence of H_2 it was also proposed that *hot*-$O_{(ads)}$ from N_2O dissociation

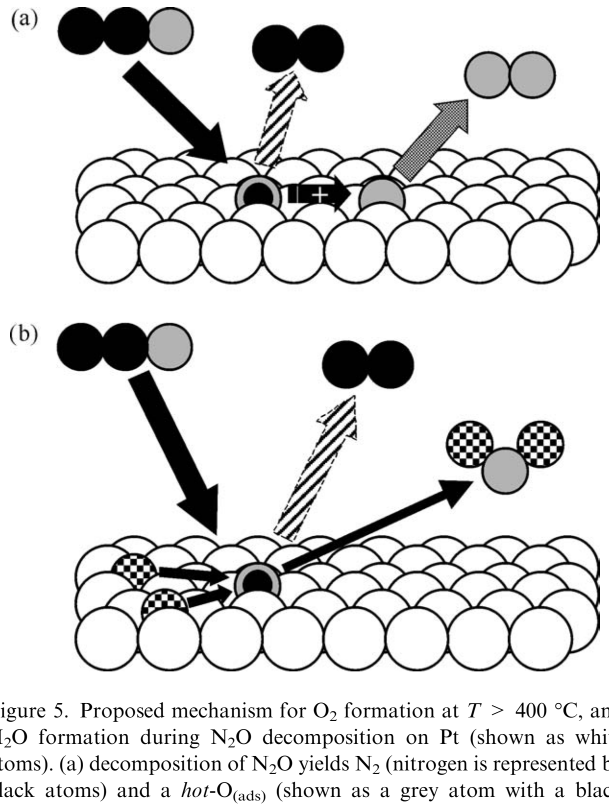

Figure 5. Proposed mechanism for O_2 formation at $T > 400$ °C, and H_2O formation during N_2O decomposition on Pt (shown as white atoms). (a) decomposition of N_2O yields N_2 (nitrogen is represented by black atoms) and a *hot*-$O_{(ads)}$ (shown as a grey atom with a black centre). This may then move parallel to the surface over a few lattice distances and reacts with an adjacent *normal*-$O_{(ads)}$ (shown as a pure grey atom) to yield O_2. (b) Production of the *hot*-$O_{(ads)}$ may react with $H_{(ads)}$ (shown as atom with a chess-board design) to produce H_2O at low temperatures ($T \geq 100$ °C).

recombined to produce O_2 at lower temperatures than during conventional oxygen TPD experiments.

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