

NO Oxidation Catalysis on Pt Clusters: Elementary Steps, Structural Requirements, and Synergistic Effects of NO₂ Adsorption Sites

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Kinetic and isotopic methods show that NO oxidation on supported Pt clusters involves kinetically relevant reaction of O₂ with vacancy sites on surfaces nearly saturated with oxygen adatoms (O*). The oxygen chemical potential at Pt surfaces that determines the O* coverage is rigorously described by an O₂ virtual pressure and determined by the thermodynamics of NO₂–NO interconversion reactions. NO oxidation and oxygen isotopic exchange processes are described by the same rate constant, consistent with similar kinetically relevant O₂ dissociation steps for both reactions. NO oxidation, NO₂ decomposition, and ¹⁶O₂–¹⁸O₂ exchange rates increased markedly with increasing Pt cluster size (1–8 nm); these clusters remain metallic at all O₂ virtual pressures prevalent during NO oxidation. These effects of cluster size reflect the higher vacancy concentrations and more facile oxygen desorption on larger Pt clusters, which bind oxygen adatoms weaker than more coordinatively unsaturated surface Pt atoms on smaller clusters. These trends are similar to those found for methane and dimethyl ether combustion on Pt and Pd catalysts, which also require vacancy sites on O*-saturated cluster surfaces in their respective kinetically relevant steps. Inhibition of NO oxidation by NO₂ persists to undetectable NO₂ concentrations; thus, NO oxidation turnover rates increase significantly when NO₂ adsorption sites present on BaCO₃/Al₂O₃ are placed within diffusion distances of Pt clusters. NO oxidation rates on intrapellet catalyst-adsorbent mixtures are described accurately by a simple reaction-adsorption model in which NO₂ adsorbs via displacement of CO₂ on BaCO₃ surfaces.

1. Introduction

NO_x storage systems consisting of noble metal catalysts and alkali or alkaline-earth adsorbents offer potential strategies to remove NO_x from fuel-lean combustion exhaust¹ but require larger amounts of costly noble metals than alternate abatement strategies, thus hindering their widespread use.^{2,3} In these systems, noble metals catalyze NO oxidation to form NO₂, which then binds onto adsorbents;¹ the detailed mechanisms for oxidation and adsorption and for the coupling of these two functions remain controversial and incompletely understood.²

NO oxidation kinetics on Pt/Al₂O₃ are consistent with kinetically relevant molecular O₂ adsorption on Pt surfaces nearly saturated with chemisorbed oxygen (O*).⁴ Density functional theory (DFT) treatments concluded that chemisorbed NO increases O₂ dissociation rates and leads to higher O* coverages than achieved by exposing catalysts to O₂ in the absence of NO_x coreactants.⁵ Rate data on catalysts with varying Pt dispersion and cluster size indicate that NO oxidation occurs more rapidly on large than small Pt clusters.⁶ These studies, however, failed to show whether cluster size effects reflect the formation of inactive Pt oxides or stronger surface Pt–O bonds for small clusters.⁶

The effects of NO₂ adsorbents on NO oxidation processes have been examined by measuring NO conversion rates on catalyst-adsorbent mixtures. These studies have claimed that atomic contact among Pt and BaO species is required for efficient NO₂ removal.^{7–9} These conclusions relied on data from materials for which the structure of Pt clusters and of BaO

adsorption sites changed concurrently with their proximity.^{7–9} Detailed kinetic interpretations have also been rendered equivocal by the complete NO conversion levels that prevailed throughout these studies.^{7–9}

Here, we provide kinetic and isotopic evidence for the identity and relevance of elementary steps involved in NO oxidation on Pt clusters under conditions of strict kinetic control. We show that oxygen isotopic exchange requires kinetically relevant steps identical to those involved in NO oxidation, confirming that these processes reflect the dynamics of O₂ reaction with surface vacancies and the thermodynamics of oxygen binding. We also show that steady-state O* coverages during NO oxidation are lower than those that would exist in equilibrium with prevailing O₂ pressures and that the observed effects of Pt cluster size on turnover rates reflect the stronger binding of chemisorbed oxygen on low-coordination surface atoms that prevail on small clusters. These effects of size on turnover rates reflect the requirement for vacancies within chemisorbed oxygen adlayers in kinetically relevant steps, as also shown for CH₄ oxidation on Pt and PdO_x clusters^{10,11} and dimethyl ether oxidation on Pt clusters.¹² Finally, we have measured NO oxidation rates on mixtures of Pt catalysts and BaCO₃ adsorbents to show that adsorbents increase NO oxidation rates by scavenging NO₂ molecules that inhibit NO oxidation. The pervasive proximity requirements in catalyst-adsorbent formulations appear, for the most part, to result from NO₂ inhibition of NO oxidation rates on Pt, which persists even at the very low NO₂ pressures (<1 Pa) prevalent in catalyst-adsorbent systems, instead of an essential requirement for atomic connectivity between Pt and BaO sites.

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2. Experimental Methods

2.1. Catalyst Synthesis and Characterization of Pt Clusters. γ -Al₂O₃ (Sasol SBa-200, 150 m² g⁻¹) support powders were heated to 1023 K at 0.07 K s⁻¹ in flowing dry air (Praxair, extra dry, 1 cm³ s⁻¹ g⁻¹) for 4 h before impregnation with precursor salts at ambient temperature. Pt(NH₃)₄(NO₃)₂ (Alfa Aesar, 99.99%) or Ba(CH₃COO)₂ (Alfa Aesar, 99.999%) was dissolved in deionized water to prepare catalysts with 1.2 wt % Pt content and adsorbents with 17 wt % BaCO₃. Solutions were added dropwise to Al₂O₃ (3–5 g) up to the point of incipient wetness (0.5 cm³ g⁻¹). Impregnated materials were treated in stagnant ambient air at 393 K for 4 h. Al₂O₃ samples impregnated with Pt were heated in flowing dry air (Praxair, extra dry, 1 cm³ s⁻¹ g⁻¹) at 0.07 K s⁻¹ to temperatures between 673 and 948 K and held at the final temperature for 4 h; these procedures led to samples with a range of Pt fractional dispersions (0.1–0.7) and cluster size (1–8 nm). Samples impregnated with Ba(CH₃COO)₂ were heated to 723 K in flowing dry air (Praxair, extra dry, 1 cm³ s⁻¹ g⁻¹) at 0.07 K s⁻¹, held at 723 K for 3 h, cooled to ambient temperature, and treated in flowing 10% CO₂/He (Praxair, 99.999%, 1 cm³ s⁻¹ g⁻¹) to form reproducible samples containing BaCO₃, which would have otherwise formed upon intervening exposure to ambient air.¹³

The fraction of Pt atoms exposed at surfaces was measured from uptakes of irreversibly chemisorbed H₂ at 313 K (Quantachrome analyzer).¹² Average cluster sizes were estimated from Pt dispersion values by assuming hemispherical clusters with the metal density of bulk Pt (21.45 g cm⁻³).¹⁴ X-ray diffraction patterns were measured using a Siemens D5000 diffractometer, Cu K α radiation and a scan rate of 0.2° min⁻¹. PtO₂ (99.9%) was obtained from Sigma-Aldrich.

2.2. NO Oxidation Rate Measurements. Reactant gases (99.999% purity) were obtained from Praxair (2% NO/2% Ar/He, 1% NO₂/He, 10% O₂/He) and metered using electronic controllers (Porter Instruments). He (Praxair, 99.999%) was used as an inert carrier. NO₂-containing mixtures were passed through 200 mg of Pt/SiO₂ (0.36 dispersion, prepared in the same manner as Pt/Al₂O₃; Davison grade 62 Silica Gel) kept at 323 K to remove impurities; such impurities have been claimed by others¹⁵ and caused significant deactivation unless removed in our case. Catalysts were pelleted and sieved to retain 0.18–0.25 mm aggregates and held within a fritted quartz reactor (10 mm) kept at constant temperature by a resistively heated furnace. Temperatures were measured by K-type thermocouples at the outer reactor wall and controlled electronically (Watlow Series 96). Concentrations in the inlet and outlet streams were measured with a MKS Multigas 2030 infrared analyzer (2 cm³ cell; 2 cm path length, 338 K). NO oxidation rates are reported here as turnover rates (per surface Pt atom, Pt_s) at NO conversions below 25%. For conversions above 10%, rates were determined by an integral reactor formalism that incorporated the measured rate equation and plug-flow hydrodynamics.

Rates were measured between 553 and 683 K for inlet streams containing NO (0.048–0.242 kPa), O₂ (0.3–8 kPa), and NO₂ (0.002–0.129 kPa). Pt catalysts were treated at 673 K in flowing 2 kPa H₂/He (Praxair, 99.999% purity, 8 cm³ s⁻¹ g⁻¹) for 1 h before rate measurements. NO oxidation rates were also measured after catalysts were exposed to flowing O₂ (Praxair, 99.999% purity, 8 cm³ s⁻¹ g⁻¹, 101 kPa) as noted in section 3.3.

Catalyst-adsorbent mixtures were prepared by mixing Pt/Al₂O₃ and BaCO₃/Al₂O₃ components (0.005–0.05 g of catalyst (g of adsorbent)⁻¹) within the same pellets (0.12–0.18 mm

diameter) or as separate pellets (0.12–0.43 mm diameter). The size of the grains within pellets was <0.04 mm. Catalyst-adsorbent mixtures were heated to 573 K at 0.08 K s⁻¹ in a flowing mixture containing 0.5 kPa O₂ and 0.5 kPa CO₂ (8 cm³ s⁻¹ g⁻¹) and held for 1 h in flowing 0.5 kPa O₂ before exposure to NO oxidation reactant mixtures. Adsorbent materials did not catalyze reactions of NO-O₂ in the absence of Pt catalysts. The cumulative NO_x adsorption on γ -Al₂O₃ (20 μ mol NO_x g⁻¹) was much less than on BaCO₃/Al₂O₃ (170 μ mol NO_x g⁻¹); thus, NO_x adsorption on Pt/Al₂O₃ did not contribute significantly to the measured rate transients at the catalyst to adsorbent ratios used here. The dilution of Pt/ γ -Al₂O₃ catalysts with additional γ -Al₂O₃ within pellets or the dilution of catalyst-adsorbent mixtures with separate quartz particles within the bed (Sigma-Aldrich, acid washed and calcined, 1.25 g, 0.18–0.25 mm) did not affect steady-state NO oxidation rates, confirming the absence of intrapellet or bed temperature gradients.¹⁶

2.3. Oxygen Isotopic Exchange Rate Measurements. ¹⁶O₂–¹⁸O₂ exchange rates were measured on Pt/Al₂O₃ in a gradientless recirculating batch reactor (498 cm³ volume, Agilent 5890 gas chromatograph, mass selective detection).¹⁷ Reactants and inert gases (99.999% chemical purity) were obtained from Praxair (He, H₂, 90% O₂/10% Ar), Ikon Isotopes (2% ¹⁸O₂/2% Ar/He, 96% isotopic purity), and Sigma-Aldrich (¹⁸O₂, 98% isotopic purity). Catalysts were heated to 723 K at 0.1 K s⁻¹, held for 1 h in 5 kPa H₂/He (30 cm³ s⁻¹ g⁻¹), and cooled to reaction temperatures (613–693 K) in flowing He (30 cm³ s⁻¹ g⁻¹). A flow of 2 kPa O₂/He (30 cm³ s⁻¹ g⁻¹) was maintained for 1 h before each experiment to ensure O₂ adsorption-desorption equilibrium. The batch reactor was filled with an equimolar mixture of ¹⁸O₂–¹⁶O₂ at either 2 or 20 kPa total O₂ pressures; Ar was used as an internal standard and He as an inert to maintain ambient pressure. Exchange rates were determined from measured isotopic contents in dioxygen as a function of contact time, using methods described in the Supporting Information (section A.1) and previously proposed.¹⁸

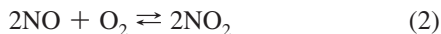
The rates of ¹⁸O₂(g) exchange with chemisorbed ¹⁶O* were measured in the flow reactor described in Section 2.2. Pt/Al₂O₃ catalysts were heated in flowing 2 kPa H₂ (4 cm³ s⁻¹ g⁻¹) to 873 K at 0.08 K s⁻¹ and held for 1 h. Samples were cooled to 698 K in He (4 cm³ s⁻¹ g⁻¹) and treated in 2 kPa ¹⁶O₂ (4 cm³ s⁻¹ g⁻¹) for 1 h, and then cooled to 373 K. These samples were then exposed to 2 kPa ¹⁸O₂ and 2 kPa Ar (0.5 cm³ s⁻¹ g⁻¹) and heated to 698 K at 0.17 K s⁻¹, while the isotopic content of the effluent was determined by mass spectrometry (Transpector 2; Inficon) during this process.

3. Results and Discussion

3.1. Kinetics and Mechanistic Interpretation of NO Oxidation Pathways on Pt Clusters. Figure 1 shows the kinetic response of NO oxidation reactions to NO, NO₂, and O₂ pressures on Pt/Al₂O₃ (0.47 dispersion) at 573 K. NO oxidation turnover rates are proportional to NO and O₂ pressures and inversely proportional to NO₂ throughout the range of reactant and product concentrations examined here. Measured NO oxidation rates are accurately described by the equation:

$$r_{\text{NO}} = k_{\text{Pt}}[\text{NO}]^1[\text{O}_2]^1[\text{NO}_2]^{-1}(1 - \eta) \quad (1)$$

consistent with previous data.⁴ Here, η is the approach-to-equilibrium factor, given by $K_{\text{R}}^{-1}[\text{NO}_2]^2[\text{NO}]^{-2}[\text{O}_2]^{-1}$, and K_{R} is the equilibrium constant for the overall reaction:



The value of K_R was determined from thermodynamic data.¹⁴

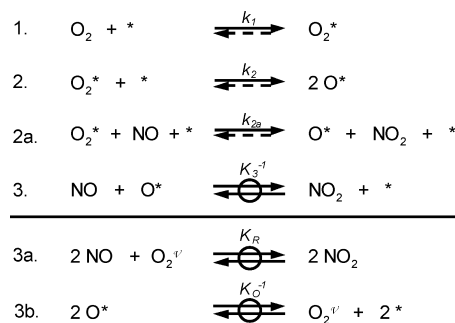
We consider the sequence of elementary steps previously proposed for NO oxidation^{4,15} and depicted in Scheme 1. O_2 adsorbs molecularly onto a vacant site ($*$; step 1) and dissociates via reaction with a vicinal site to form chemisorbed oxygen (O^* ; step 2) or via reaction with chemisorbed NO to form adsorbed NO_2 and O^* (step 2a). Vacancies form via reactions of NO with O^* to form NO_2 in quasi-equilibrated steps. Step 3 is not an elementary reaction as written, but instead reflects a sequence of quasi-equilibrated elementary steps that can be rigorously combined in the kinetic analysis. When O^* and $*$ are the most abundant surface intermediates and O_2^* species dissociate before they desorb, step 1 becomes the sole kinetically relevant step and NO oxidation rates are given by

$$r_{\text{NO}} = \frac{k_1[\text{O}_2]}{1 + K_3[\text{NO}_2][\text{NO}]^{-1}}(1 - \eta) \quad (3)$$

Here, η has the same meaning as in eq 1 and represents the ratio of the forward to the reverse rate of NO oxidation, as derived from rigorous nonequilibrium thermodynamic treatments of chemical kinetics.¹⁹ Equation 3 becomes identical to the expression that accurately describes all rate data (eq 1) when chemisorbed O^* atoms are the most abundant adsorbed intermediates ($K_3[\text{NO}_2][\text{NO}]^{-1} \gg 1$), an assumption that we use throughout the rest of this manuscript. As we discuss in section 3.3, the ability of this equation to accurately describe NO oxidation rates indicates that the number and reactivity of active sites are unchanged throughout the entire range of oxygen chemical potential prevalent during catalysis.

3.2. Oxygen Isotopic Exchange and NO Oxidation Rates on $\text{Pt}/\text{Al}_2\text{O}_3$. The NO oxidation rate expression (eqs 1 and 3) is consistent with the reaction of O_2 and an oxygen vacancy in the kinetically relevant step. Here, we probe O_2 interactions with vacancies on surfaces nearly saturated with O^* by measuring rates of NO oxidation and $^{16}\text{O}_2$ – $^{18}\text{O}_2$ exchange. These data and the preferential formation of mixed isotopomers during initial

SCHEME 1: Proposed NO Oxidation Mechanism



contact of $^{18}\text{O}_2$ with $^{16}\text{O}^*$ confirmed that O_2 dissociation occurs without assistance from NO and involves mobile O-adatoms, which react with O^* to form O_2 during exchange and with NO during its oxidation to form NO_2 .

$^{16}\text{O}_2$ – $^{18}\text{O}_2$ exchange (in the absence of NO) occurs at O^* coverages in chemical equilibrium with prevalent dioxygen pressures. The oxygen chemical potentials that determine O^* coverages during NO oxidation, however, depend on NO_2/NO ratios instead of O_2 pressures. As a result, rigorous comparisons between isotopic exchange and NO oxidation rates require that we measure both reaction rates at the same oxygen chemical potential. We relate oxygen chemical potentials in both processes by noting that the quasi-equilibrated step that determines O^* coverages during NO oxidation (step 3 of Scheme 1) can be rigorously separated into two steps: the stoichiometric NO oxidation reaction (step 3a) and a quasi-equilibrated O_2 dissociation step (step 3b). The latter reflects equilibration with a hypothetical or virtual O_2 pressure, which represents the chemical potential of oxygen at surfaces during catalysis. Its value determines the coverage of chemisorbed O^* and the tendency of metal clusters to form bulk oxides. Chemisorbed O^* coverages during NO oxidation catalysis are those that would be in equilibrium with this virtual oxygen pressure, O_2^v (instead of $\text{O}_2(\text{g})$), which is determined by the equilibration of $\text{NO}_2(\text{g})$ and $\text{NO}(\text{g})$ with chemisorbed oxygen (in step 3). This virtual O_2 pressure is given by:

$$\text{O}_2^v = [\text{NO}_2]^2[\text{NO}]^{-2}K_R^{-1} \quad (4)$$

where K_R is the equilibrium constant for eq 2 and is available from thermodynamic data for gas phase reactants and products. Therefore, oxygen coverages during NO oxidation catalysis are identical to those present during isotopic exchange only when the virtual O_2 pressures during the former equal the actual $\text{O}_2(\text{g})$ pressures used during isotopic exchange measurements. This treatment also shows that the equilibrium constant for step 3, K_3 , is related to K_R and to the equilibrium constant for dissociative oxygen chemisorption, K_{O} , by

$$K_3 = (K_{\text{O}}/K_R)^{1/2} \quad (5)$$

Insertion of eqs 4 and 5 into eq 3 leads to NO oxidation rates that can be expressed solely in terms of the actual and virtual O_2 pressures, the dynamics (k_1) of molecular O_2 reaction with vacancies, and the thermodynamics (K_{O}) for O_2 dissociation on Pt clusters

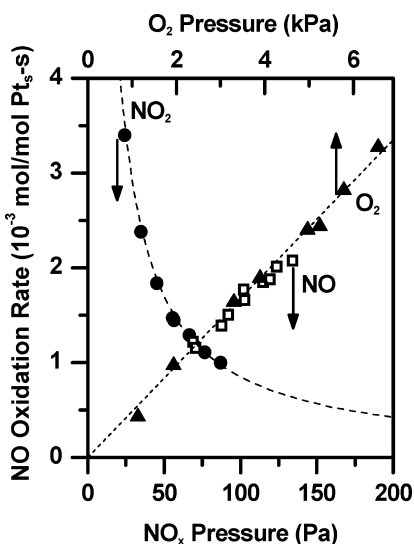


Figure 1. Effects of NO ($\square$), NO_2 ($\bullet$), and O_2 ($\blacktriangle$) pressures on forward NO oxidation rates on $\text{Pt}/\text{Al}_2\text{O}_3$ (0.47 dispersion) at 573 K. Each pressure was varied separately while others were kept at 5 kPa O_2 , 56 Pa NO_2 , or 113 Pa NO.

$$\bar{r}_{\text{NO}} = \frac{k_1[\text{O}_2]}{K_{\text{O}}^{1/2}[\text{O}_2^v]^{1/2}} \quad (6)$$

This equation shows that NO oxidation rates depend only on the dynamics and thermodynamics of oxygen adsorption and are independent of the binding properties of NO and NO₂.

We compare next isotopic exchange rates measured at particular O₂(g) pressures with NO oxidation rates measured at equivalent virtual O₂ pressures (determined by NO₂/NO ratios). Specifically, we compare reverse NO oxidation rates with isotopic oxygen exchange rates because both depend only on oxygen chemical potentials. Reverse rates of NO oxidation (NO₂ decomposition) are given by the product of the forward rate (eq 6) and the approach-to-equilibrium factor, η (eq 4)

$$\bar{r}_{\text{NO}} = \frac{k_1}{K_{\text{O}}^{1/2}}[\text{O}_2^v]^{1/2} \quad (7)$$

Reverse NO oxidation rates are also equal to NO₂ decomposition rates for reactant mixtures with equivalent values of O₂^v; both rates reflect the molecular desorption of O₂^{*} intermediates (the reverse of step 1 in Scheme 1). The mechanism for NO oxidation and its reverse includes a set of elementary steps that could occur during isotopic exchange (steps 1 and 2 of Scheme 1). If all of the kinetically relevant rate constants for NO oxidation and for isotopic exchange were equal, then reverse NO oxidation rates would be identical to isotopic exchange rates when reactant pressures are adjusted to achieve a standard oxygen chemical potential.

Figure 2a shows reverse NO oxidation rates at 2 kPa O₂^v and ¹⁶O₂–¹⁸O₂ exchange at 2 kPa O₂(g) on Pt/Al₂O₃ (0.47 dispersion). Reverse NO oxidation rates were obtained from the product of η and the forward NO oxidation rate measured at 7 kPa O₂(g), and also from direct measurements of NO₂ decomposition rates (without added O₂). Measured NO₂ decomposition rates were identical to those calculated for the reverse reaction from NO oxidation rates on Pt/Al₂O₃ (0.47 dispersion) at similar virtual O₂ pressures, consistent with the accuracy of eqs 3 and 7 and of the defining equation for O₂ virtual pressures (eq 4). These two rates were also identical to ¹⁸O₂–¹⁶O₂ exchange rates at all temperatures, and similar activation energies were found for all of these processes (108 ± 16 kJ mol^{−1} for exchange; 120 ± 10 kJ mol^{−1} for NO₂ decomposition; 116 ± 8 kJ mol^{−1} for reverse NO oxidation; 613–693 K), suggesting that both processes have similar kinetic parameters. Isotopic O₂ exchange rates on Pt films are proportional to [O₂]^{1/2},²⁰ similar to the dependence of reverse NO oxidation rates on the oxygen chemical potential (eq 7). Isotopic exchange rates on Pt/Al₂O₃ (0.47 dispersion) were 7 × 10^{−3} and 3 × 10^{−2} mol/mol Pt_s·s at 2 and 20 kPa O₂, respectively, also consistent with the [O₂]^{1/2} dependence. ¹⁶O₂–¹⁸O₂ exchange rates per surface Pt atom increased sharply as Pt dispersion increased (Figure 2b). The turnover rates for isotopic exchange reported here on small clusters (2–8 nm) are lower (by factors of 3–23 times at 673 K) than rates on Pt films (extrapolated to 673 K from 523 K).²⁰ These effects of cluster size are similar to those reported here (Figure 3) and in a previous study⁶ for NO oxidation and NO₂ decomposition on Pt clusters.

The similar rates and (virtual) [O₂]^{1/2} dependences for NO₂ decomposition and ¹⁶O₂–¹⁸O₂ exchange indicate that O₂^{*} desorption from Pt surfaces is kinetically relevant in both processes and that O^{*} coverages are in equilibrium with O₂^v

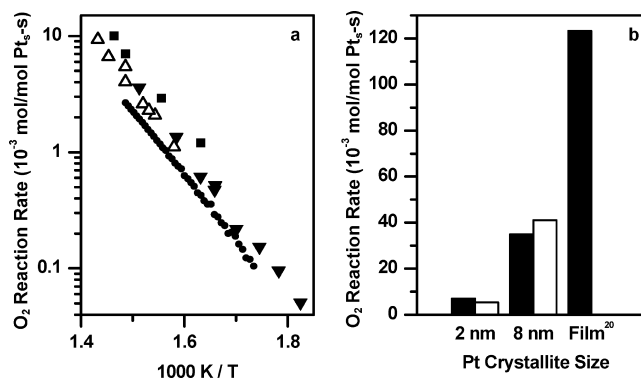


Figure 2. (a) Rates of ¹⁶O₂–¹⁸O₂ exchange at 2 kPa O₂(g) (■), ¹⁸O₂–¹⁶O^{*} exchange at 2 kPa O₂(g) (●), NO₂ decomposition at 2 kPa O₂^v (△), and reverse NO oxidation at 2 kPa O₂^v and 7 kPa O₂(g) (▼) on Pt/Al₂O₃ with 0.47 dispersion. (b) ¹⁶O₂–¹⁸O₂ exchange at 2 kPa O₂(g) (black) and reverse NO oxidation rates at 2 kPa O₂^v (white) on Pt/Al₂O₃ at 673 K. The results for Pt film are extrapolated from ref 20 and assume 10¹⁵ Pt_s cm^{−2}.

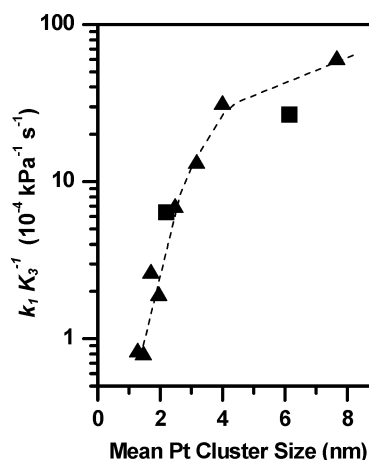


Figure 3. NO oxidation rate constants, $k_1 K_3^{-1}$, as a function of mean cluster size on Pt/Al₂O₃ at 603 K for NO oxidation measured at 0.15 kPa O₂^v, 5 kPa O₂ (▲) and from ref 6 (●).

during catalysis and with O₂(g) during exchange. The reaction of O₂ with a vacancy proceeds at the same rate as O₂^{*} desorption (its microscopic reverse) during isotopic exchange, which occurs at chemical equilibrium. These results and the pseudosteady state hypothesis (PSSH) on reaction intermediates lead to a rate expression for isotopic exchange, which we describe briefly here and in more detail in section A.1 of the Supporting Information. Application of PSSH to each O₂^{*} intermediate leads to

$$\frac{[^{16}\text{O}_2^*]}{[\text{O}_2^*]} = \left(\frac{[^{16}\text{O}^*]}{[\text{O}^*]} \right)^2 \quad (8)$$

$$\frac{[^{18}\text{O}_2^*]}{[\text{O}_2^*]} = \left(\frac{[^{18}\text{O}^*]}{[\text{O}^*]} \right)^2 \quad (9)$$

$$\frac{[^{16}\text{O}^{18}\text{O}^*]}{[\text{O}_2^*]} = 2 \frac{[^{16}\text{O}^*][^{18}\text{O}^*]}{[\text{O}^*]^2} \quad (10)$$

These equations show that the isotopic fractions of O₂^{*} species adopt a binomial distribution that depends on the fraction of ¹⁶O^{*} and ¹⁸O^{*} on the surface. Application of PSSH to O^{*}

species leads to an expression for their isotopic fraction in terms of gas phases concentrations

$$\frac{[^{16}\text{O}^*]}{[\text{O}^*]} = \frac{[^{16}\text{O}_2 + ^{16}\text{O}^{18}\text{O}/2]}{[\text{O}_2]} \quad (11)$$

$$\frac{[^{18}\text{O}^*]}{[\text{O}^*]} = \frac{[^{18}\text{O}_2 + ^{16}\text{O}^{18}\text{O}/2]}{[\text{O}_2]} \quad (12)$$

The exchange rate, r_{exch} , is obtained by combining eqs 8–12 with the rate of any elementary adsorption step, leading to

$$r_{\text{exch}} = \frac{k_1}{K_{\text{O}}^{1/2}} [\text{O}_2]^{1/2} \left(\frac{[^{16}\text{O}_2][^{18}\text{O}_2]}{[\text{O}_2]^2} - \frac{[^{16}\text{O}^{18}\text{O}]^2/4}{[\text{O}_2]^2} \right) \quad (13)$$

This equation shows that isotopic exchange involves the same rate constants as forward and reverse NO oxidation (eqs 6 and 7) and the same $[\text{O}_2]^{1/2}$ dependence as NO_2 decomposition (eq 7). The exchange rate also includes a factor (in the parentheses of eq 13) that we have already accounted in Figure 2, which is independent of the kinetically relevant exchange steps¹⁸ and corrects for the changing isotopic fractions in the gas phase.

As shown by eqs 6 and 13, the kinetically relevant steps of NO oxidation and isotopic exchange involve the reaction of molecular O_2 with *. We investigate next whether the subsequent O_2^* dissociation steps require two vacancies (according to step 2 of Scheme 1) by considering the interaction of $^{18}\text{O}_2(\text{g})$ with surfaces nearly saturated by $^{16}\text{O}^*$. This process differs from $^{16}\text{O}_2$ – $^{18}\text{O}_2$ exchange because the isotopic fractions of O^* species depend on rates of elementary steps, as opposed to gas phase concentrations (eqs 11–12, which are valid when PSSH applies). Thus, the exchange pathway that involves O_2 dissociation on two vacancies and O^* recombination (step 2 in Scheme 1) leads to the initial formation of only $^{16}\text{O}_2$ during $^{18}\text{O}_2$ – $^{16}\text{O}^*$ exchange (additional details given in section A.1 of the Supporting Information). The measured $^{18}\text{O}_2(\text{g})$ consumption rate (at 2 kPa $^{18}\text{O}_2$) during $^{18}\text{O}_2$ – $^{16}\text{O}^*$ exchange was similar to reverse NO oxidation and $^{16}\text{O}_2$ – $^{18}\text{O}_2$ exchange rates (Figure 2a), confirming that O_2 dissociation occurs by the same kinetically relevant step in all cases. The initial $^{18}\text{O}_2$ – $^{16}\text{O}^*$ exchange product was mainly $^{16}\text{O}^{18}\text{O}$, which formed more than twice as fast as $^{16}\text{O}_2$ (exchange rates versus temperature, 573–683 K, reported in section A.1 of the Supporting Information). The predominant formation of $^{16}\text{O}^{18}\text{O}$ during initial contact of $^{18}\text{O}_2$ with $^{16}\text{O}^*$ surfaces is consistent with exchange (and O_2 dissociation) that occurs via the formation of a mobile oxygen atom from O_2^* , which reacts mainly with chemisorbed O^* (to give $^{16}\text{O}^{18}\text{O}$ during $^{18}\text{O}_2$ – $^{16}\text{O}^*$ exchange) and to a lesser extent with vacancies (to give $^{16}\text{O}_2$). The involvement of fast mobile oxygen species on O^* -covered surfaces, detected here from isotopic exchange rates and selectivities, has been previously proposed to account for the effects of O_2 pressure on the rates of NO decomposition.²¹ We conclude that O_2 activation on O^* -covered surfaces is limited by the reaction of O_2 with a vacancy to form O^* and mobile oxygen adatoms that rapidly migrate among strongly bound O^* species. These data and conclusions suggest that the cleavage of $\text{O}=\text{O}$ bonds occurs rapidly even without the assistance of coadsorbed reactants (e.g., NO^* or CO^* , as proposed elsewhere^{15,22}). Neither O_2^* reactions with NO^* (step 2a) nor their microscopic reverse are required in NO/ NO_2

TABLE 1: Pre-Exponential Factors, A , and Apparent Activation Energies, $E_1 + Q_{\text{O}}/2$, for $k_1 K_{\text{O}}^{-1/2}$ on $\text{Pt}/\text{Al}_2\text{O}_3$

mean cluster size (nm)	A (10^8 s^{-1})	$E_1 + Q_{\text{O}}/2$ (kJ mol^{-1})
8	4 ± 3	121 ± 5
2	1 ± 0.9	125 ± 4
1	1 ± 0.6	129 ± 4

interconversions because direct dissociation involving mobile O species proceeds at much higher rates than these alternate pathways.

3.3. Effects of Pt Cluster Size on NO Oxidation and O_2 Exchange Rates. The effects of Pt cluster size on NO oxidation rate constants ($k_1 K_3^{-1}$) are shown in Figure 3. NO oxidation rate constants increased monotonically with increasing cluster size,⁶ concurrently with increases in isotopic oxygen exchange and NO_2 decomposition rates (Figure 2b). Surface vacancies required in kinetically relevant steps for NO oxidation become increasingly scarce as the binding energy of chemisorbed oxygen atoms increases. NO_2 decomposition and exchange rates also decrease with increasing O^* binding energy, because these reactions involve desorption of O_2^* (via the microscopic reverse of the O_2 dissociation pathways discussed previously), which becomes slower with increasing oxygen binding energy. Coverage-averaged heats of dissociative O_2 adsorption (Q_{O}) decrease from 270 kJ mol O_2^{-1} on Pt clusters (2.5 nm) to 220 kJ mol O_2^{-1} on larger crystallites prevalent on Pt powders (1600 nm),²³ suggesting that the cluster size effects are related to the oxygen binding energy through the K_{O} term in the rate constant (eq 6). Density functional theory calculations²⁴ have shown that O^* binding energies decrease with cluster size because surface atoms in small clusters have higher degrees of coordinative unsaturation than surface Pt atoms in larger clusters; these trends are consistent with the observed effects of Pt cluster size on NO oxidation turnover rates.

Oxygen binding energies influence apparent NO oxidation rate constants through the effects of the K_{O} term in the denominator of the rate equation (eq 6), which depends, in turn, on the heat of adsorption of O^* ($Q_{\text{O}}/2$) (defined as the negative of the adsorption enthalpy)

$$\frac{k_1}{K_{\text{O}}^{1/2}} = A \exp\left(-\frac{E_1 + Q_{\text{O}}/2}{k_{\text{B}}T}\right) \quad (14)$$

Here, E_1 is the activation barrier for O_2 reaction with * and A is the pre-exponential factor given by

$$A = \frac{k_{\text{B}}T}{h} \exp\left(\frac{\Delta S_1^\ddagger - \Delta S_{\text{O}}/2}{k_{\text{B}}}\right) \quad (15)$$

The activation entropy reflects the difference between the activation entropy for step 1 of Scheme 1 ($\Delta S_1^\ddagger$) and the entropy for the dissociative O_2 chemisorption reaction to form O^* ($\Delta S_{\text{O}}/2$; step 3b of Scheme 1). Measured pre-exponential factors and apparent activation energies are shown in Table 1 on $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts with 0.12, 0.47, and 0.72 Pt dispersions. These pre-exponential factors give apparent activation entropies of $-90 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$, consistent with immobile transition states and immobile chemisorbed O^* species (based on a standard entropy of $205 \text{ J mol}^{-1} \text{ K}^{-1}$ for $\text{O}_2(\text{g})$ ¹⁴). For small values of E_1 , the measured NO oxidation activation energies correspond to dissociative heats of adsorption (at near saturation coverages)

and increase from 240 to 260 kJ (mol O₂)⁻¹ as Pt cluster diameters increase from 1 to 8 nm. These values are similar to heats of dissociative O₂ adsorption on Pt clusters (270 kJ (mol O₂)⁻¹ on 2.5 nm Pt clusters²³). Heats of O* adsorption on Pt single crystals decrease from 300 kJ (mol O₂)⁻¹ at low coverages on Pt(111) and Pt(110) facets to 140 kJ (mol O₂)⁻¹ and 220 kJ (mol O₂)⁻¹, respectively, at 0.30 coverages.^{25,26} Average heats of adsorption tend to overestimate the binding energy of the most weakly adsorbed oxygen adatoms, which desorb to form vacancies on saturated surfaces. Yet, these average values (270 kJ (mol O₂)⁻¹ on 2.5 nm Pt clusters²³) are only slightly larger than those inferred here ($Q_0 = 240\text{--}260$ kJ (mol O₂)⁻¹) from NO oxidation activation energies and the assumption of non-activated O₂ adsorption ($E_1 = 0$). O₂ activation barriers estimated from DFT on Pt(111) nearly saturated by CO have been reported to be as high as 35 kJ mol⁻¹, as a result of Coulombic repulsion among coadsorbed species.²⁷ Such effects are likely to be even stronger on O*-saturated surfaces and to lead to significant activation barriers for O₂ activation. Non-negligible activation barriers for O₂ reaction with *, E_1 , would decrease the heat of adsorption, Q_0 , required to describe measured NO oxidation activation energies. An increase in E_1 as O* binding decreases with cluster size would be expected from ubiquitous linear free energy relations and may explain why the variation in measured NO oxidation activation energies with cluster size (10 kJ mol⁻¹ for 1–8 nm clusters) is smaller than expected from the concomitant change in the heat of dissociative O₂ chemisorption (50 kJ (mol O₂)⁻¹ for 3–1000 nm crystallites²³).

Cluster size effects similar to those reported here for NO oxidation are also evident for the combustion of CH₄^{10,11} and dimethyl ether¹² on PdO_x and Pt clusters. These reactions also require vacancies on O*-saturated surfaces in their respective kinetically relevant steps, the activation of C–H bonds on *-O* site pairs, in which C-atoms interact with a vacancy and H-atoms with O*. We conclude that these strong effects of cluster size are general features of reactions requiring vacancies on O*-saturated surfaces. In contrast, CO oxidation turnover rates, also limited by molecular adsorption of O₂, but on CO*-covered surfaces, are independent of Pt or Pd cluster size (1.5–10 nm).^{28,29} Apparently, the size effects on binding energy are less pronounced for CO, which prefers atop sites,³⁰ than for O*, which prefers multicoordinate sites²⁴ whose binding properties more strongly depend on surface structure.

We also consider that cluster size effects on NO oxidation turnover rates may arise from preferential formation of less reactive bulk oxides for smaller Pt clusters. Metal–oxygen bonds on metal cluster surfaces weaken as oxygen coverages increase^{25,26} because of Coulombic repulsion between adsorbates.⁵ Such effects persist and become stronger as oxygen atoms start to bind with Pt atoms within clusters at higher oxygen chemical potentials. Thus, the formation of bulk oxides, per se, seems unlikely to make surfaces unreactive by decreasing vacancy concentrations during NO oxidation. Indeed, CH₄ combustion turnover rates are much lower on Pd than on PdO clusters of similar size, because of the weaker surface Pd–O bonds on the latter, which leads to higher concentrations of the vacancies required for C–H bond activation.¹¹

The remarkable accuracy with which the rate equations reported here and in a previous study^{4,6} (eqs 3, 6) describe all NO oxidation rate data on large and small clusters over a 10³-fold range in O₂ virtual pressures and a ~100 K range in temperatures indicates that either the phase of Pt clusters did not change within this range of oxygen chemical potentials or that such changes were catalytically inconsequential (Figure 4).

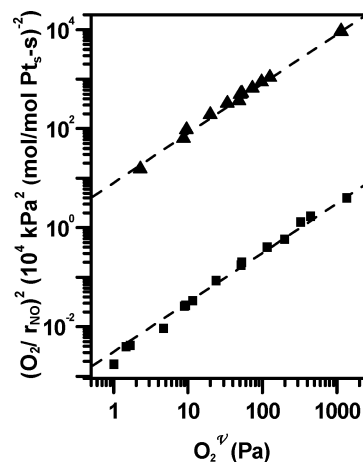


Figure 4. NO oxidation kinetic response to O₂^v on Pt/Al₂O₃ with 0.13 (■) and 0.54 (▲) dispersion at 573 K with 0.3–8 kPa O₂, 0.01–0.13 kPa NO₂, 0.05–0.24 kPa NO. The dashed lines model the data with eq 6 and have slopes equal to $K_O k_1^{-2}$.

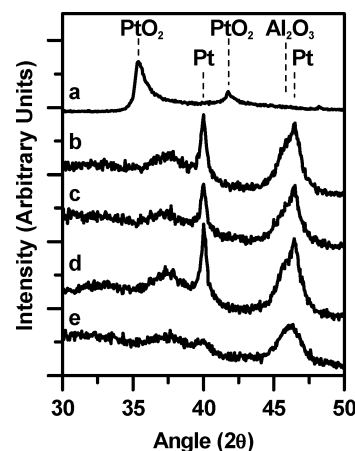


Figure 5. X-ray diffractograms of (a) PtO₂ (standard), (b) Pt/Al₂O₃ (0.13 dispersion) treated with 101 kPa O₂ (698 K, 12 h), (c) Pt/Al₂O₃ (0.13 dispersion) after 101 kPa O₂ (633 K, 12 h), (d) Pt/Al₂O₃ (0.13 dispersion) after 2 kPa H₂ (673 K, 1 h), and (e) Pt/Al₂O₃ (0.5 dispersion) after 2 kPa H₂ (673 K, 1 h). Diffractograms collected in ambient conditions.

Specifically, eq 6 requires that $(O_2/r_{NO})^2$ be strictly proportional to O₂^v with a slope equal to $K_O k_1^{-2}$. The data in Figure 4 show that this is indeed true throughout a 10³-fold range in oxygen virtual pressures (O₂^v = 0.001–1 kPa) on both large and small clusters. Thus, neither small nor large clusters undergo any phase change consequential to surface reactivity for any subset of clusters within the respective size distributions in these catalysts; large clusters show higher turnover rates for all values of the prevalent oxygen chemical potential. Every cluster within the size distribution of these samples must therefore remain in either metal or oxide form throughout a 10³-fold change in prevalent oxygen chemical potentials.

We use thermodynamic data to assess the Pt phase that is present during NO oxidation. The enthalpy of PtO_x formation (-66 ± 20 kJ (mol O)⁻¹)^{31,32} and the reported Pt–PtO_x phase diagrams (for bulk Pt; 2–400 MPa O₂, 873–1173 K)³³ extrapolated to NO oxidation conditions suggest that large Pt clusters should remain as the metal phase for all O₂^v pressures below 1 kPa at 573 K. X-ray diffraction (Figure 5) confirmed that 8 nm Pt clusters are indeed metallic after treatment in H₂ (2 kPa, 473 K, 1 h) or O₂ (101 kPa, 603 or 698 K, 12 h); the latter O₂(g) pressures are much larger than the O₂^v values

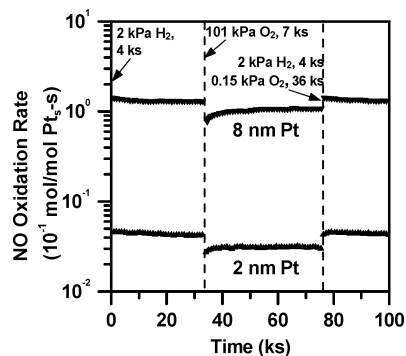


Figure 6. NO oxidation rates on Pt/Al₂O₃ with 0.13 and 0.54 dispersion as a function of time-on-stream at 603 K, 0.15 kPa O₂^v, 5 kPa O₂. Vertical dashed lines represent treatments at the listed conditions.

prevalent during NO oxidation catalysis (0.001–2 kPa; 553–673 K). Small Pt clusters (2 nm) did not show detectable diffraction lines before or after catalytic reactions, but their rates were also accurately described by eq 6 at all O₂^v pressures. Thus, these Pt clusters are also metallic at all conditions; otherwise, higher O₂^v pressures would progressively oxidize an increasing fraction of the smaller clusters present within their size distribution and preferentially retain larger clusters as metals. These trends would cause significant deviations from the linear dependence of (O₂/T_{NO})² on oxygen virtual pressure (Figure 4) if the Pt phase changed with cluster size for a given oxygen chemical potential and the oxidation state of Pt atoms within clusters were consequential for oxygen binding and catalytic reactivity. The conclusion that 2 nm clusters in Pt/Al₂O₃ (0.5 dispersion) are metallic during NO oxidation (<2 kPa O₂^v; 553–673 K) is consistent with oxygen uptake measurements showing that only surface oxidation of Pt/Al₂O₃ (0.56 dispersion) occurs at these conditions (101 kPa O₂; 300–900 K).³⁴

The electronic and binding differences between small and large clusters are predominantly associated with the properties of their surfaces and cause smaller clusters to interact more strongly with adsorbed species. Adsorbed species decrease surface energies more effectively for small clusters because of their stronger binding, which reduces any incentive for small clusters to form bulk oxides at lower oxygen chemical potentials than larger clusters. We also expect that any effects of size on bulk oxidation tendency, inferred from surface energy and M–O binding energy considerations, would be modest, because of the similar coordination of bulk atoms within large and small clusters and because of the weak effects (<1 kJ mol⁻¹)⁵ of atoms beyond nearest and next-nearest neighbor positions on binding properties. The effects of coordination environment on surface energies appear to be much stronger than any effects of curvature enforced by size alone,^{24,35} suggesting that the effects of size on bulk oxidation are much more modest than previously claimed.³⁶

The conclusion that the strong effects of cluster size on NO oxidation turnovers do not reflect preferential bulk oxidation of small clusters is consistent with NO oxidation turnover rates measured after thermal treatments intended to reduce or oxidize Pt clusters (Figure 6). NO oxidation rates on Pt/Al₂O₃ catalysts with 0.13 and 0.54 dispersion treated in H₂ before reaction (2 kPa; 673 K, 1 h) decreased only slightly (<5%) during subsequent NO oxidation for 30 ks. Initial NO oxidation rates were smaller (by a factor of ~2; 0.13 dispersion) when treated in O₂ (101 kPa O₂, 603 K, 2 h) instead of H₂ before reaction, but rates increased gradually with time and reached values only ~20% smaller than on samples pretreated in H₂. These slight

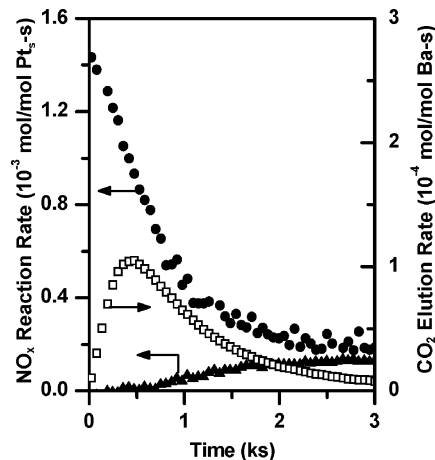


Figure 7. NO oxidation (●) and NO₂ (▲) and CO₂ (□) elution rates after exposure of 0.5 kPa O₂, 0.178 kPa NO to Pt/Al₂O₃ (1.4 mg, 0.2 dispersion) mixed within pellets of BaCO₃/Al₂O₃ (125 mg) at 573 K.

effects of thermal treatment and reaction time were even weaker on smaller Pt clusters (0.54 dispersion). NO oxidation rates have similar values after H₂ treatments (2 kPa H₂, 673 K, 1 h) and after O₂ treatments at pressures corresponding to the O₂^v values prevalent during NO oxidation (0.15 kPa O₂; 603 K, 12 h), suggesting that Pt surface structures are unaffected at lower oxygen chemical potentials. Large clusters gave higher turnover rates than small clusters after all treatments and at all reaction times. These data show that clusters less active for NO oxidation bind oxygen more strongly, thus disfavoring the formation of vacancies, but do not form bulk oxides; such oxides would, in any case, lead to weaker metal–oxygen bonds than in chemisorbed layers and to more reactive cluster surfaces. The weaker binding of oxygen on bulk oxides (relative to oxygen chemisorbed on metals) may also account for the high reactivity reported for Co₃O₄ catalysts in NO oxidation³⁷ and oxygen isotopic exchange²⁰ reactions.

3.4. NO Oxidation Turnover Rates on Mixtures of Pt/Al₂O₃ and NO₂ Adsorbents. The mechanism in Scheme 1 and its associated rate equation (eq 3) indicate that NO₂ inhibits NO oxidation at any NO₂/NO ratio that causes Pt surfaces to remain nearly saturated with O* via NO–NO₂ equilibration; such conditions persist throughout the accessible range of experimental O₂^v pressures (0.001–2 kPa) and detectable NO₂ pressures (>1 Pa). In this section, we explore the catalytic consequences of depleting NO₂ around NO oxidation sites on Pt clusters via NO₂ adsorption onto nearby binding sites.

Figure 7 shows NO oxidation and NO₂ evolution rates (per surface Pt atom) as a function of time on Pt/Al₂O₃ catalysts (0.2 dispersion; 1.4 mg) present as intrapellet mixtures with BaCO₃/Al₂O₃ adsorbents (125 mg). NO oxidation rates decreased with time from 1.5 to 0.15 mol NO/mol Pt_s at steady-state (>2 ks). The NO₂ concentration in the effluent increased with time as the number of adsorption sites decreased due to the displacement of CO₂ with NO₂; CO₂ evolution rates (per Ba atom) concurrently decreased (Figure 7). NO₂ evolution and NO consumption rates became similar only after NO₂ binding sites reached saturation. The NO₂ evolution rate reflects the difference between NO oxidation, r_{NO} , and NO₂ adsorption, r_{Ba} , rates per surface site

$$\nu \frac{d[\text{NO}_2]}{dz} = \hat{L}_{\text{Pt}} \langle r_{\text{NO}} \rangle - \hat{L}_{\text{Ba}} \langle r_{\text{Ba}} \rangle \quad (16)$$

Here, z is the axial distance along the reactor, ν is the superficial gas velocity, and $\hat{L}_{\text{Pt}}$ and $\hat{L}_{\text{Ba}}$ represent the number of Pt surface atoms and of NO_2 binding sites per unit volume, and $\hat{L}_{\text{Ba}}$ decreases with time as adsorption sites saturate. Rates are defined at their local averages (bracket notation) because their actual values may differ from those expected at the concentration of various species in the extrapellet fluids because of intrapellet concentration gradients. Mean distances between NO oxidation and NO_2 adsorption sites, NO_2 diffusivities within the connecting pore structure, and NO_2 adsorption rates determine local NO_2 concentrations in catalyst and adsorbent mixtures (present within the same pellet or as separate pellets). Separate pellets of catalysts and adsorbents led to initial NO oxidation rates that increased by only a factor of ~ 1.5 as mean pellet diameters decreased from 0.34 mm to 0.15 mm (Table 2). Mixing the two components within the same pellet increased NO oxidation rates by only ~ 1.3 times compared with separate pellets of similar size (0.12–0.18 mm). Intrapellet mixtures contained grains < 0.04 mm in diameter; the > 10 -fold decrease in the distance between sites relative to separate pellets had a weak effect on NO oxidation rates. These weak effects of site proximity and their interpretation as evidence of kinetic control are consistent with estimates of the Mears parameter:³⁸

$$\Omega = \frac{\hat{r}_{\text{NO}}}{D_{\text{NO}_2} [\text{NO}_2] L^{-2}} \quad (17)$$

Small Ω values (< 1) would indicate negligible intrapellet gradients. These values are near unity (1–2) for separate pellets (0.13–0.42 mm diameter), but much smaller for intrapellet mixtures (0.1, for 0.04 mm grains; Table 2) (details in Supporting Information; section A.2). These data are consistent with the absence of NO_2 concentration gradients within intrapellet mixtures; thus, we remove the brackets in eq 16 and use kinetic rate equations for NO oxidation and NO_2 adsorption steps

$$\nu \frac{d[\text{NO}_2]}{dz} = \hat{L}_{\text{Pt}} r_{\text{NO}} - \hat{L}_{\text{Ba}} r_{\text{Ba}} \quad (18)$$

The rate of NO_2 elution from the reactor, r_{NO_2} , is given by integration of eq 18 throughout the reactor length. NO_2 evolution rates were much smaller than NO oxidation rates ($r_{\text{NO}}/r_{\text{NO}_2} > 10$) during initial contact of these mixtures with NO/O_2 reactants (< 0.8 ks). Thus, NO oxidation and NO_2 adsorption rates are much larger than their difference, and NO_2 can be treated as a reactive intermediate present at its pseudosteady-state concentration ($d[\text{NO}_2]/dt \sim 0$):

$$\chi k_{\text{Pt}} \frac{[\text{NO}][\text{O}_2]}{[\text{NO}_2]} = r_{\text{Ba}} \quad (19)$$

where χ is the ratio of the number of Pt surface atoms to NO_2 adsorption sites

$$\chi = L_{\text{Pt}}/L_{\text{Ba}} \quad (20)$$

TABLE 2: Effect of Physical Proximity on NO Oxidation Rates in Catalyst-Adsorbent Mixtures

catalyst pellet diameter (mm)	initial NO oxidation rate (mol/mol Pt_s -s) ^a	initial NO_2 pressure (Pa)	$\hat{r}_{\text{NO}}/D[\text{NO}_2]L^{-2}$
mixed within adsorbent pellets	1.3	0.8	0.1 ^b
0.13–0.18	1.0	1.0	1.1
0.18–0.25	0.8	1.2	1.4
0.25–0.42	0.7	1.5	2.3

^a Rates measured at 0.5 kPa O_2 , 0.17 kPa NO, 573 K over mixtures containing 6 mg $\text{Pt}/\text{Al}_2\text{O}_3$ (0.2 dispersion) and 125 mg $\text{BaCO}_3/\text{Al}_2\text{O}_3$. ^b L estimated from the size of the largest grains, 0.04 mm.

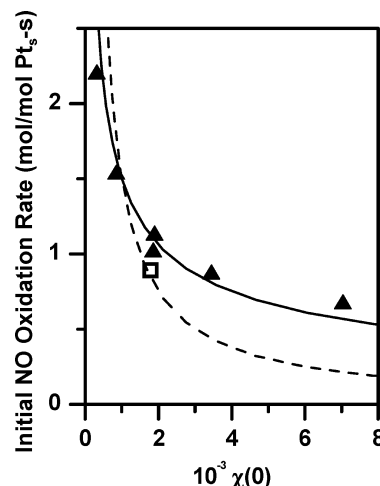


Figure 8. NO oxidation rates at 573 K, 0.5 kPa O_2 , 0.178 kPa NO without CO_2 in the inlet stream ($\blacktriangle$) and with 0.5 kPa CO_2 ($\square$) over $\text{Pt}/\text{Al}_2\text{O}_3$ (0.2 dispersion) mixed within pellets of $\text{BaCO}_3/\text{Al}_2\text{O}_3$ as a function of catalyst to adsorbent ratio, $\chi(0)$. The solid and dashed lines show the χ dependence of eqs 26 and 27, respectively.

and increases with time as adsorption sites saturate. L_{Ba} is given by the cumulative NO_2 uptakes up to saturation coverages (0.24 ± 0.02 per Ba atom for the sample and conditions here). Equation 19 indicates that the intrinsic adsorption rate, r_{Ba} , and its dependence on reactant (NO , O_2) or product (NO_2 , CO_2) concentrations and on the surface coverages of NO_2 and CO_2 determine prevalent NO_2 concentrations and thus NO oxidation rates in these catalyst-adsorbent systems.

Next, we explore the effects of initial χ values, $\chi(0)$, on NO oxidation rates to probe the kinetics and mechanism of NO_2 adsorption. Figure 8 shows NO oxidation rates as a function of $\chi(0)$, varied by the ratio of catalyst to adsorbent within intrapellet mixtures. Initial NO oxidation rates decreased with increasing $\chi(0)$, consistent with the higher local NO_2 concentrations that prevail as the number of NO_2 adsorption sites decreases relative to the number of Pt sites that form NO_2 . CO_2 pressures and elution rates varied with time (Figure 7), but the addition of CO_2 (0.5 kPa) to $\text{NO}-\text{O}_2$ reactants even at pressures (0.5 kPa) higher than those present for CO_2 -free reactants (< 0.01 kPa) decreased NO oxidation rates by less than 20% (Figure 8). These data indicate that the replacement of the adsorbed CO_2 initially present on adsorption sites by NO_2 occurs via irreversible steps.

We consider these effects of $\chi(0)$ and of CO_2 on NO oxidation rates in the context of a rate equation and mechanism for NO_2 adsorption and of the known rate equation for NO oxidation on Pt sites (eq 3). The replacement of chemisorbed CO_2 by NO_2 can occur via either concerted reactions (Scheme 2, step 1) or

sequential CO₂ desorption and NO₂ adsorption onto the vacant site (Scheme 2, steps 1a and 1b). The respective adsorption rates for these two pathways are given by

$$r_{\text{Ba}} = k_1^{\text{Ba}}[\text{NO}_2] \quad (\text{step 1}) \quad (21)$$

$$r_{\text{Ba}} = \frac{k_{1\text{b}}^{\text{Ba}} k_{1\text{a}}^{\text{Ba}} [\text{NO}_2]}{k_{-1\text{a}}^{\text{Ba}} [\text{CO}_2] + k_{1\text{b}}^{\text{Ba}} [\text{NO}_2]} \quad (\text{steps 1a and 1b}) \quad (22)$$

The weak effects of high CO₂ pressures (0.5 kPa) on rates indicate that CO₂ desorption is irreversible ($k_{-1\text{a}}^{\text{Ba}} [\text{CO}_2] \ll k_{1\text{b}}^{\text{Ba}} [\text{NO}_2]$), because CO₂ would otherwise inhibit NO₂ adsorption (eq 22), leading to higher local NO₂ concentrations (eq 19) and lower NO oxidation rates. Thus, eq 22 becomes

$$r_{\text{Ba}} = k_{1\text{a}}^{\text{Ba}} \quad (23)$$

Concerted (eq 23) and sequential (eq 21) CO₂ displacement routes lead to different NO₂ adsorption rate equations, which when inserted into the NO₂ mole balance (eq 19) give local NO₂ concentrations

$$[\text{NO}_2] = \left(\chi \frac{k_{\text{Pt}}}{k_1^{\text{Ba}}} [\text{NO}][\text{O}_2] \right)^{1/2} \quad (24)$$

$$[\text{NO}_2] = \chi \frac{k_{\text{Pt}}}{k_{1\text{a}}^{\text{Ba}}} [\text{NO}][\text{O}_2] \quad (25)$$

for concerted and sequential NO₂ adsorption routes, respectively. The use of these expressions for NO₂ in eq 1 gives NO oxidation turnover rates in terms of $\chi(0)$

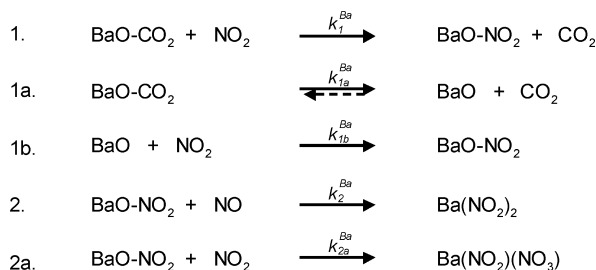
$$r_{\text{NO}} = \left(\frac{k_{\text{Pt}} k_1^{\text{Ba}} [\text{NO}][\text{O}_2]}{\chi(0)} \right)^{1/2} \quad (26)$$

$$r_{\text{NO}} = \frac{k_{1\text{a}}^{\text{Ba}}}{\chi(0)} \quad (27)$$

for concerted and sequential routes, respectively.

These rate equations were integrated assuming 20% NO conversion and plug-flow hydrodynamics, and their respective forms are shown in Figure 8 (solid and dashed lines for eqs 26 and 27, respectively) together with NO oxidation rate data. Concerted routes (eq 26; Scheme 2, step 1) provide a more

SCHEME 2: Elementary Steps of NO₂ Adsorption



accurate description of the measured effects of $\chi(0)$ on NO oxidation rates than sequential pathways (eq 27 and steps 1a and 1b of Scheme 2). These conclusions are consistent with DFT estimates of NO₂ binding energies on model BaCO₃ slabs, which suggest that the formation of vacancies by CO₂ desorption is unfavorable.³⁹ Our results indicate that such pathways are also kinetically inaccessible and that NO₂ chemisorption occurs via concerted displacement of chemisorbed CO₂ with NO₂.

The displacement of chemisorbed CO₂ by NO₂ (Scheme 2, step 1) may be followed, however, by other adsorption events. For example, we have observed that the cumulative amount of NO and NO₂ retained by the adsorbent is about two times larger (2.0 ± 0.4) than the cumulative amount of CO₂ eluted over the same time period. These data suggest that a second NO or NO₂ molecule immediately adsorbs after the first adsorption event to form a nitrite, Ba(NO₂)₂ (step 2, Scheme 2) or a nitrite-nitrate pair, Ba(NO₂)(NO₃) (step 2a, Scheme 2). If NO₂ is the second molecule adsorbed, our treatment above remains unchanged, except our estimate of the number of NO₂ binding sites would decrease by half since each binding sites adsorbs two NO_x species. Thus, we consider only the implications of a second adsorption event that involves NO, because such events would lead to NO oxidation rates no longer given solely by the depletion on NO from the effluent stream, because NO would also be consumed via adsorption onto sites already containing chemisorbed NO₂.

DFT studies showed that the adsorption of a second NO or NO₂ species onto a BaO site stabilizes isolated chemisorbed NO_x species.^{40–42} Low exposures of NO₂ (<10⁻⁴ Pa-s) to BaO surfaces formed nitrite and nitrate species at 100 K, but only nitrites at 300 K, consistent with molecular adsorption of two NO₂ species onto a single BaO site at the lower temperatures (step 2a of Scheme 2).^{43,44} We have observed that NO and NO₂ were consumed in equimolar amounts upon exposure of BaCO₃/Al₂O₃ to NO/NO₂ mixtures (170 Pa NO, 30 Pa NO₂, 573 K),⁴⁵ consistent with the exclusive formation of nitrites via concurrent adsorption of NO and NO₂ (Scheme 2, step 2), instead of the adsorption of two NO₂ molecules, even at the NO/NO₂ ratios (~6) and high temperatures in these experiments. The additional NO adsorption step (Scheme 2, step 2) occurs at the same rate as the first adsorption step (step 1 of Scheme 2) so that BaO-NO₂ species remain at pseudosteady state and NO₂/NO consumption ratios at their measured equimolar values. The NO conversion rate, r_{NO} , in the catalyst-adsorbent mixtures is then given by:

$$r_{\text{NO}} = k_{\text{Pt}} \frac{[\text{NO}][\text{O}_2]}{[\text{NO}_2]} + \frac{k_1^{\text{Ba}} [\text{NO}_2]}{\chi(0)} \quad (28)$$

where the first term describes NO oxidation on Pt sites and the second term describes NO adsorption on BaO-NO₂. The expression for the NO₂ concentration (eq 24) remains unchanged and its insertion into eq 28 yields NO oxidation rates given by

$$r_{\text{NO}} = 2 \left(\frac{k_{\text{Pt}} k_1^{\text{Ba}} [\text{NO}][\text{O}_2]}{\chi(0)} \right)^{1/2} \quad (29)$$

We conclude that NO conversion rates on catalyst-adsorbent mixtures depend similarly on the catalyst/adsorbent ratio, $\chi(0)$, for NO₂ and NO adsorption events that occur concurrently (eq 29) and for the direct adsorption of a single NO₂ (eq 26).

Synergistic effects of NO₂ adsorption and NO oxidation sites present within typical diffusion distances for NO₂(g) reflect the local depletion of NO₂ molecules, which inhibit NO oxidation even at undetectable pressures (<1 Pa). NO₂ inhibits rates at the low O₂ virtual pressures and chemical potentials (10⁻⁶–10⁻⁵ kPa) prevalent in intrapellet mixtures, because O* remains present at near-saturation coverages, as a result of its strong binding energy ($Q_0 \sim 270$ kJ (mol O₂)⁻¹).²³ Proximity among adsorption and catalytic sites influences these synergistic effects because intimacy (in the ~ 1 μ m length scale) prevents intrapellet NO₂ concentration gradients, but atomic connectivity between BaO and Pt sites does not appear to be required for the depletion of NO₂ near Pt surfaces.

4. Conclusions

The kinetics of NO oxidation on Pt clusters are consistent with a mechanism involving kinetically relevant O₂ reaction with vacancies in chemisorbed oxygen monolayers. Chemisorbed O* coverages during NO oxidation are characterized by an oxygen virtual pressure, which is determined by the thermodynamics of NO-NO₂ interconversion reactions. The virtual pressure concept shows that NO oxidation rates depend on the dynamics of O₂ interactions with vacancies and on the thermodynamics of O* binding, and also allows NO oxidation to be rigorously compared with oxygen isotopic exchange. Both processes have similar rate constant parameters, consistent with the kinetic-relevance of O₂ reaction with a vacancy to form O* and a mobile oxygen intermediate. Apparent activation energies for both forward and reverse NO oxidation rates and isotopic exchange reflect primarily heats of O* adsorption; rates of all of these reactions are much higher on large clusters, which bind oxygen more weakly than small clusters. These trends with cluster size, which are observed for CH₄ and dimethyl ether oxidation, but not for CO oxidation, are general for reactions occurring on O* covered surfaces. Bulk oxidation did not contribute to the cluster size effects measured here because the NO oxidation rate constant for small clusters was constant and uniformly lower than that for large, metallic clusters over a wide range of oxygen virtual pressures, suggesting that every cluster had identical phase throughout the measurement.

NO₂ adsorption sites present within diffusion distances of catalyst sites increase NO oxidation rates by scavenging NO₂ molecules that inhibit NO oxidation even at the low pressures (<1 Pa) in catalyst-adsorbent systems. A simple reaction-adsorption model in which NO₂ adsorbs via displacement of CO₂ on BaCO₃ surfaces accurately describes NO oxidation rates on intrapellet catalyst-adsorbent mixtures. The persistent NO₂ inhibition of NO oxidation catalysis implies that the dynamics of NO₂ adsorption control NO oxidation rates and noble metal efficiency in NO_x storage systems.

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Supporting Information Available: A.1 Rates of ¹⁶O₂–¹⁸O₂ and ¹⁸O₂–¹⁶O* exchange on Pt/Al₂O₃; A.2 Calculation of the Mears parameter in catalyst-adsorbent mixtures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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