Mechanism and site requirements for NO oxidation on Pd catalysts

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ABSTRACT

Kinetic and isotopic methods were used to establish the identity and kinetic relevance of elementary steps and the effects of cluster size for NO oxidation on supported Pd catalysts. O\(_2\) activation on vacancies within nearly saturated oxygen adlayers is the sole kinetically relevant step. Water, present in combustion effluents, inhibits NO oxidation via reversible adsorption on vacancies to form unreactive OH species. The coverage and chemical potential of oxygen are determined by the NO\(_2\)/NO ratios prevalent during catalysis; they are rigorously described by O\(_2\) virtual pressures accessible to measurement. At a given oxygen chemical potential, O\(_2\) activation during \(^{16}\text{O}_2-{^{18}}\text{O}_2\) exchange and NO oxidation occur at similar rates, indicating that NO-assisted O\(_2\) activation is not required for NO oxidation turnovers. These findings confirm the rigor and relevance of O\(_2\) virtual pressure as a measurable surrogate for the oxygen chemical potential during catalysis, as well as the role of mobile oxygen species, which allow O\(_2\) dissociation to occur on isolated vacancies. Oxygen chemical potentials prevalent during NO oxidation cause active clusters to exist as PdO at all relevant conditions, consistent with steady-state turnover rates that are insensitive to reductive or oxidative treatments. NO oxidation turnover rates decrease as PdO clusters become smaller because of stronger oxygen binding and lower vacancy concentrations in small clusters. Such requirements lead to strong NO\(_2\) inhibition effects and to a marked increase in NO oxidation rates when NO\(_2\) adsorbents, present as physical mixtures, decrease NO\(_2\) concentrations near active sites.

1. Introduction

Combustion engines become more efficient at high air-to-fuel ratios, but these conditions lead to higher NO\(_x\) levels and low reductant (CO, hydrocarbons) concentrations in effluent streams [1]. Conventional exhaust catalysts are ineffective for these systems; an alternate abatement strategy first oxidizes NO to NO\(_2\), which then adsorbs on metal oxides [2]. NO oxidation is also critical in soot combustion, in which NO\(_2\) acts as an oxygen carrier between carbon particles and non-vicinal metal clusters that dissociate O\(_2\) [3]. Pt is often used to catalyze NO oxidation, but Pd [4–7] and other transition metals [8–11] also show significant reactivity. The mechanism and site requirements for NO oxidation on Pd catalysts have not been addressed in previous studies [12], and rigorous mechanistic and reactivity comparisons between Pd and Pt catalysts have not been reported to date.

O\(_2\) interacts with sparse vacancies on surfaces nearly saturated with chemisorbed oxygen (O\(^+\)) in the kinetically relevant step for NO oxidation on supported Pt clusters [13,14]. O\(^+\) coverages reflect the equilibration of NO and NO\(_2\) with surface vacancies [13,14]. A comparison between the rates of isotopic oxygen exchange and NO oxidation confirmed the kinetic significance of O\(_2\) activation steps and suggested that O\(_2\) dissociation involves mobile oxygen-derived intermediates [14]. NO oxidation and oxygen exchange rates decreased sharply with decreasing Pt cluster size [14,15] because O\(^+\) binds more strongly on the coordinatively unsaturated Pt atoms that prevail on small cluster surfaces [14]. NO oxidation catalysis on Pt is inhibited by NO\(_2\) because of its role in establishing O\(^+\) coverages during steady-state NO oxidation catalysis; as a result, NO oxidation rates are much higher when Pt catalysts are mixed with NO\(_2\) adsorbents, because they decrease local NO\(_2\) concentrations at active sites [14].

Here, we provide evidence for the elementary steps and cluster size effects in NO oxidation catalyzed by PdO. Kinetic and isotopic methods show that rate-determining steps are similar on Pd and Pt catalysts, but that Pd clusters are present as oxides during NO oxidation, in contrast to Pt clusters, which retain their metallic bulk character. Water, a ubiquitous component in automotive exhaust, inhibits NO oxidation by forming hydroxyls on vacant sites (\(^{1}\)) required in kinetically relevant steps. NO oxidation rates are significantly higher on larger PdO clusters, a trend also observed on Pt clusters [14,15]; these trends reflect the stronger oxygen bonds on the surfaces of smaller clusters, which lead to lower vacancy...
concentrations. We show that NO oxidation rates are significantly higher in intimate mixtures of Pd catalysts and BaCO₃ adsorbents, which scavenge NO₂ and decrease NO₂ local concentrations and its inhibiting effect on NO oxidation, thus confirming the critical synergy between the metal and adsorbent functions in lean NO traps.

2. Experimental methods

2.1. Material synthesis and catalyst characterization

γ-Al₂O₃ (Sasol, SBA-200) supports were heated at 0.07 K s⁻¹ to 1023 K in flowing dry air (Praxair, Extra Dry, 1 cm³ s⁻¹ g⁻¹) and held for 4 h. A 10 wt.% Pd(NO₃)₂/γ-Al₂O₃ aqueous solution (Sigma–Aldrich, 99.99% metal purity) diluted with de-ionized distilled water (Barnstead, Nanopure) was added dropwise to γ-Al₂O₃ to the incipient wetness point (0.45 g solution (g Al₂O₃)⁻¹) to prepare catalyst samples with 1.0 and 1.5 wt.% Pd contents. Impregnated supports were treated in ambient air to 393 K for 4 h and then in 9% H₂/He (Praxair, 99.999% purity, 1 cm³ s⁻¹ g⁻¹) for 4 h by heating at 0.07 K s⁻¹ to a temperature between 773 and 1023 K. Samples were subsequently treated in He (Praxair, 99.999% purity, 1 cm³ s⁻¹ g⁻¹) at 773 K for 1 h and then in 0.5% O₂/He (Praxair, 99.999% purity, 1 cm³ s⁻¹ g⁻¹) at ambient temperature for 1 h to passivate their surfaces. Adsorbents (15 wt.% BaCO₃/Al₂O₃) were prepared from Ba(O₂C₂H₃)₂ (Sigma–Aldrich, 99.995%) precursors by incipient wetness methods described previously [14].

The fraction of surface Pd atoms (Pd₄) was measured by O₂ chemisorption using an Autosorb-1 titration apparatus (Quanta-chrome). Catalysts (1 g) were treated at 673 K (0.07 K s⁻¹ heating rate) in flowing H₂ (Praxair, 99.999%, 0.2 cm³ s⁻¹ g⁻¹) for 1 h and then under vacuum for 1 h. Pd dispersions were determined from irreversible O₂ (Praxair, 99.999%) uptakes at 313 K assuming a stoichiometry of one O-atom per surface Pd atom [16]. Average cluster diameters were estimated from dispersion values, by assuming spherical clusters with atomic densities for bulk Pd metal (12 g cm⁻³; 68 Pd nm⁻³) [17]. These procedures gave samples with 0.08–0.74 Pd dispersions and 10–110 nm average cluster diameters.

2.2. NO oxidation rate measurements

NO oxidation rates were measured on pre-formed pellets (0.12–0.18 mm) of Pd/Al₂O₃ catalysts and on mixtures of Pd/Al₂O₃ and BaCO₃/Al₂O₃, that were combined within pellets (0.12–0.18 mm) or as intrapellet mixtures (0.12–0.18 mm to 0.18–0.25 mm). Samples were held on a porous quartz (10 mm) frit within a tubular flow reactor (10 mm). Reactant (15% O₂/He, 2% NO/He, 1% NO₂/He, and 5% CO₂/He) and He carrier gases (Praxair, 99.999% purity) were obtained from Praxair (90% O₂/Ar, He) and Ikon Isotopes (18O₂, 96% isotopic 18O purity). Catalysts were heated to reaction temperature (643–698 K) at 0.07 K s⁻¹ and held for 1 h in flowing 2 kPa 18O₂/He (30 cm³ s⁻¹ g⁻¹) before the reactor was evacuated and filled with an equimolar 16O₂–18O₂ mixture and He as balance. Isotopomer concentrations during 16O₂–18O₂ exchange were measured by periodic injections into a mass spectrometer (Spectra Mini-Lab).

The exchange rates of 18O₂(g) with pre-adsorbed 16O² were measured in the tubular flow reactor described in Section 2.2 with isotopic analysis by a mass spectrometer (Spectra Mini-Lab). Pre-reduced catalysts were heated from ambient temperature to 698 K at 0.08 K s⁻¹ in flowing 2 kPa 16O₂ (1 cm³ s⁻¹ g⁻¹) and held for 1 h to form PdO [19,20]. 18O₂–16O₂ exchange rates were measured in flowing 2 kPa 18O₂/He (Ikon Isotopes, 96% atom purity; 1 cm³ s⁻¹ g⁻¹) isothermally (698 K) or during a temperature ramp from 373 to 773 K (0.17 K s⁻¹).

3. Results and discussion

3.1. NO oxidation kinetics and elementary steps on Pd catalysts

The effects of NO, NO₂, and O₂ pressure on NO oxidation rates are shown in Fig. 1 for one of the Pd/Al₂O₃ catalysts used in this study (0.33 Pd dispersion). Forward NO oxidation rates (rₙₒₓ) were derived from measured rates (rₓₒ) by accounting for the approach-to-equilibrium [21] of NO oxidation reactions:

\[ 2\text{NO} + \text{O}_2 \rightleftharpoons \text{2NO}_2 \quad (1) \]

\[ r_{\text{NO}} = r_{\text{xO}}(1 - \eta) \quad (2) \]

\[ \eta = \left[ \frac{[\text{NO}]_1^2}{[\text{NO}]_0^2 + [\text{O}_2]_0} \right] K_r^{-1} \quad (3) \]

where \( K_r \) is the known equilibrium constant [17] for the overall reaction defined by Eq. (1).

![Fig. 1](image_url)
Steady-state forward NO oxidation rates were accurately described by the equation:

$$r_{NO} = k_{app}[O_2][NO][NO_2]^{-1}$$  \hspace{1cm} (4)

as shown by the dashed lines in Fig. 1. This rate equation is the same as that found for NO oxidation on Pt metal clusters [13,14], suggesting that kinetically relevant steps are the same on both catalysts. We conclude that NO oxidation on Pd also involves kinetically relevant O$_2$ reactions on isolated vacancies (*) within a nearly saturated O$^*$ adlayer (Step 1, Scheme 1) [13,14]. Vacancy concentrations are determined by the equilibration of NO, NO$_2$, and O$^*$ (Step 2, Scheme 1). The subsequent O$_2$ dissociation steps are not accessible to measurement during steady-state catalysis and are represented by the ellipsis shown in Scheme 1. The elementary steps in Scheme 1 are consistent with the approach-to-equilibrium factor in Eq. (3) and with the rate expression of:

$$r_{NO} = \frac{2k_1[O_2]}{1 + K_2[NO_2][NO]}$$  \hspace{1cm} (5)

when * and O$^*$ are the most abundant surface intermediates. This expression simplifies to Eq. (4), which describes all measured rate data on Pd, when (*) $\ll$ (O$^*$).

The * and O$^*$ surface coverages and the tendency of Pd clusters to form bulk oxides depend on the oxygen chemical potential at catalyst surfaces. This oxygen chemical potential can be expressed as a virtual oxygen pressure, O$_2^*$ [14,21], defined as the O$_2$ pressure that would give at conditions of adsorption–desorption equilibrium the same O$^*$ coverage present during steady-state catalysis in the presence of a given NO–NO$_2$ mixture. The equilibrium reaction that determines O$^*$ during steady-state NO oxidation (Step 2, Scheme 1) is equivalent to the combined Steps 2a and 2b (Scheme 1), which give the value of O$_2^*$ as:

$$[O_2^*] = [NO_2^*]^2[NO]^2k_1^{-1}$$  \hspace{1cm} (6)

where $K_2$ is the known equilibrium constant [17] for the overall NO oxidation reaction (Eq. (1)). This treatment shows that $K_2$, the equilibrium constant for the interaction of NO and O$^*$, is related to the equilibrium constant for O$_2$ adsorption, $K_0$:

$$K_2 = K_0^{1/2}/k_1^{1/2}$$  \hspace{1cm} (7)

The forward NO oxidation rate expression depends only on the prevalent O$_2$(g) pressure and the virtual oxygen pressure (O$_2^*$) as shown by combining Eqs. (5)–(7):

$$r_{NO} = \frac{2k_1[O_2]}{1 + (K_0[O_2]^2)^{1/2}}$$  \hspace{1cm} (8)

This expression shows that the effective NO oxidation rate constant depends only on the rate constant for O$_2$ activation on isolated vacancies ($k_1$) and on the standard thermodynamic properties of atomic O$^*$ species ($K_0$) on nearly saturated surfaces.

NO oxidation occurs sufficiently near thermodynamic equilibrium ($\eta$ values of 0.01–0.30) for its reverse reaction (NO$_2$ decomposition) to occur at detectable rates. The rate of this reverse reaction is obtained from the forward rate (Eq. (8)) and the approach-to-equilibrium factor, $\eta$ (Eq. (3)):

$$r_{NO} = \frac{2k_1[O_2]}{1 + (K_0[O_2]^2)^{1/2}}$$  \hspace{1cm} (9)

Eq. (9) is consistent with the thermodynamics for the overall reaction, for which forward and reverse NO oxidation rates become identical at chemical equilibrium when the oxygen chemical potential at the surface, O$_2^*$, and in the gas phase, O$_2$(g) are equal.

### 3.2. Isotopic oxygen exchange and NO oxidation rates

We probe next the kinetic relevance and reversibility of the proposed O$_2$ activation step by considering the mechanism and rates of oxygen isotopic exchange, a reaction that reflects the dynamics and thermodynamics of the interaction between O$_2$ and catalyst surfaces. A rigorous comparison of exchange and NO oxidation rates first requires an interpretation of isotopic exchange measurements in terms of O$_2$ activation rates, which we derive briefly by following previous methods [14,22].

$^{16}$O$_2$–$^{18}$O$_2$ exchange in the absence of co-reactants occurs at chemical equilibrium, while reaction intermediates are present at their pseudo-steady-state concentrations. Thus, the overall desorption rate of O$_2$ from the surface equals the O$_2$ adsorption rate ($r_{O_2}$), and the net reaction rate of each O$_2$ isotopomer is equal to the observed exchange rate ($r_{ex}$):

$$r_{O_2} = \sum \tilde{r}_i = \sum \tilde{r}_k$$  \hspace{1cm} (10)

$$r_{ex} = (\tilde{r}_k - \tilde{r}_i)/\tilde{v}_k$$  \hspace{1cm} (11)

where $i$ and $k$ denote each oxygen isotope ($^{16}$O or $^{18}$O) and the stoichiometric factors ($\tilde{v}_k$) are for the overall exchange reaction:

$$^{18}$O$_2$ + $^{16}$O$_2$ $\leftrightarrow$ $^{216}$O$_2$O$^*$  \hspace{1cm} (12)

Eqs. (10) and (11) give solutions for the reaction rates of each O$_2$ isotopomer:

$$\tilde{r}_i = r_{O_2}\tilde{v}_i$$  \hspace{1cm} (13)

$$\tilde{r}_k = \frac{\tilde{v}_k}{\tilde{v}_i}\frac{r_{O_2}\tilde{v}_i}{X_k}$$  \hspace{1cm} (14)

where $X_k$ and $X_i$ are the fractions of each isotope in the reaction mixture and $\tilde{v}_i$ is the fraction of each [O$^*$$O$] isotopomer among O$_2$ molecules. The exchange rate ($r_{ex}$) then is related to $r_{O_2}$ by:

$$\frac{r_{ex}}{y_{^{16}O^{18}O}} = r_{O_2}(1 - \eta_{ex})$$  \hspace{1cm} (15)

$$\eta_{ex} = \frac{y_{^{18}O^{16}O}^2}{4y_{^{16}O^{18}O}y_{^{18}O^{18}O}}$$  \hspace{1cm} (16)

The denominator term in Eq. (15) reflects the probability that a reaction event increases the $^{16}$O$^{18}$O content, and $\eta_{ex}$ accounts for the approach of the system to isotopic equilibrium.

The relationship between exchange rates ($r_{ex}$) and O$_2$ activation rates ($r_{O_2}$) in Eq. (15) allows $^{16}$O$_2$–$^{18}$O$_2$ exchange rates to be compared rigorously with NO oxidation rates. Specifically, we compare O$_2$ activation rates during exchange ($r_{O_2}$) and NO oxidation ($r_{NO}$) at a particular value of the surface and gas phase oxygen chemical potentials (2 kPa O$_2^*$; Fig. 2). NO oxidation rates were measured near chemical equilibrium at 2 kPa O$_2^*$ and either 0 or 7 kPa O$_2$(g), and corrected to their equilibrium values (at 2 kPa O$_2^*$, 2 kPa O$_2$(g)) by Eqs. (8) and (9). The $^{16}$O$_2$–$^{18}$O$_2$ exchange rates are
We probe the mobility of these surface intermediates involved in O\textsubscript{2} dissociation by considering isotopomer selectivities during transient exchange of \textsuperscript{18}O\textsubscript{2} with pre-adsorbed \textsuperscript{16}O\textsubscript{2} on Pd/Al\textsubscript{2}O\textsubscript{3}. Initial \textsuperscript{18}O\textsubscript{2}--\textsuperscript{16}O\textsubscript{2} exchange rates were identical to both \textsuperscript{18}O\textsubscript{2}--\textsuperscript{16}O\textsubscript{2} exchange and NO oxidation rates on Pd/Al\textsubscript{2}O\textsubscript{3} samples with both high and low dispersion (Fig. 2). \textsuperscript{16}O\textsubscript{2} conversion rates during \textsuperscript{18}O\textsubscript{2}--\textsuperscript{16}O\textsubscript{2} exchange reflect the same kinetically relevant step during \textsuperscript{18}O\textsubscript{2}--\textsuperscript{16}O\textsubscript{2} exchange and NO oxidation (Step 1 in Scheme 1; Eq. (17)). Both \textsuperscript{16}O\textsubscript{18}O\textsubscript{2} and \textsuperscript{18}O\textsubscript{2} formed as initial products of isothermal \textsuperscript{18}O\textsubscript{2}--\textsuperscript{16}O\textsubscript{2} exchange with their selectivities given in Table 1 for large and small Pd clusters. Similar non-zero initial selectivities to \textsuperscript{16}O\textsubscript{18}O\textsubscript{2} were observed during previous measurements of isothermal \textsuperscript{18}O\textsubscript{2}--\textsuperscript{16}O\textsubscript{2} exchange on PdO[29] and during temperature program \textsuperscript{18}O\textsubscript{2}--\textsuperscript{16}O\textsubscript{2} exchange on Pt catalysts [14]. The initial formation of \textsuperscript{16}O\textsubscript{18}O\textsubscript{2} and the kinetic relevance of O\textsubscript{2} dissociation on isolated vacancies for exchange events are consistent with dissociation steps occurring on \textsuperscript{18}O site pairs to give mobile superoxo-intermediates (Scheme 2, Step 1), with the same rate constant as Step 1 in Scheme 1 (k\textsubscript{1}). This intermediate then reacts with a vacant O* during migration and desorbs with another O* (to form \textsuperscript{18}O\textsubscript{16}O\textsubscript{2} in the early stages of exchange when \textsuperscript{18}O is the most abundant surface isotopomer) or combines with a distant vacant site to form a strongly chemisorbed O* species (Scheme 2, Step 1a). The initial selectivity to \textsuperscript{16}O\textsubscript{18}O\textsubscript{2} during \textsuperscript{18}O\textsubscript{2}--\textsuperscript{16}O\textsubscript{2} exchange arises from \textsuperscript{18}O\textsubscript{2} that has been mobilized to a superoxo-position, rather than by the direct recombination of vicinal O* species. The elementary steps in Scheme 2 give an expression for the initial isotopomer selectivity during \textsuperscript{18}O\textsubscript{2}--\textsuperscript{16}O\textsubscript{2} exchange in terms of the ratio of the rates of each step in Scheme 2:

$$\frac{r_{\text{18}O\textsubscript{2}O\textsubscript{16}O}}{r_{\text{18}O\textsubscript{2}O\textsubscript{18}O} + r_{\text{18}O\textsubscript{2}O\textsubscript{16}O}} = \frac{r_{\text{O}^+}}{k_{-1a}}$$

(19)

Our results indicate that mobile oxygen species form at similar rates by O\textsubscript{2} adsorption and O* mobilization, apparently because both steps depend directly on the strength of surface oxygen bonds. Small clusters give much smaller exchange rates and higher initial selectivities to \textsuperscript{16}O\textsubscript{18}O\textsubscript{2}. These trends reflect in both cases stronger O* bonds on smaller clusters (as we discuss in Section 3.4), which lead in turn to smaller vacancy concentrations and to less frequent
dissociation of superoxo-species on vacant sites. Mobile oxygen species have been previously proposed to account for O₂ formation on O⁻-covered surfaces during NO decomposition on Pt at temperatures (573–698 K) similar to those required for the reverse of NO oxidation [24]. As expected, microscopic reversibility would implicate similar steps and the involvement of mobile oxygen species as intermediates in O₂ adsorption on metal surfaces nearly saturated with O⁻.

3.3. Effect of H₂O and CO₂ pressures on NO oxidation rates

Combustion effluent streams contain significant levels of H₂O and CO₂. As a result, NO oxidation catalysts must function without strong inhibition by these combustion products. NO oxidation rates on Pd/Al₂O₃ (0.12 dispersion) were essentially unaffected by CO₂, but inhibited by H₂O (Fig. 3a). NO oxidation rates decreased with increasing NO₂/NO ratios at high H₂O pressures (Fig. 3b). These kinetic effects are accurately described by the equation:

\[
\tilde{r}_\text{NO} = \frac{2k_1[O_2]}{K_{NO_2}[NO]^{-1} + K_{app}[H_2O]^{1/2}[NO_2]^{1/2}[NO]^{-1/2}} \tag{20}
\]

as shown by the dashed curves in Fig. 3a and b. The first term in denominator can be extracted to give:

\[
\tilde{r}_\text{NO} = \frac{r_0}{1 + K_{app}[H_2O]^{1/2}[NO]^{-1/2}[NO_2]^{1/2}} \tag{21}
\]

where \( r_0 \) is the NO oxidation rate in the absence of H₂O (Eq. (4)). These H₂O inhibition effects reflect competitive reactions of H₂O and O₂ with O⁻⁻ site pairs, in which H₂O forms unreactive OH species (Scheme 1, Step 4) that occupy vacant sites required for O₂ activation. Eq. (21) is equivalent to:

\[
\tilde{r}_\text{NO} = \frac{r_0}{1 + K_{H_2O}^{1/2}K_{O}^{1/4}[H_2O]^{1/2}[O_2]^{1/4}} \tag{22}
\]

This equation applies for surfaces predominantly covered by O⁻ and OH⁻⁻; the second denominator term in Eqs. (21) and (22) represents the \((\text{OH}⁻⁻)/(O⁻⁻)\) ratio during steady-state NO oxidation catalysis. Similar inhibition and elementary steps involving H₂O have been reported for CH₄ and dimethylether oxidation on Pd catalysts [30,31], but inhibition effects were not detected for NO oxidation on Pt above 573 K [32], apparently because hydroxyls on Pt surfaces are less stable relative to chemisorbed oxygen than on PdO.

3.4. Site requirements and cluster size effects for NO oxidation on Pd catalysts

Next, we consider the catalyst oxidation state and cluster size and their consequences for NO oxidation turnover rates. The rigorous definition of an oxygen virtual pressure (Eq. (6)) allows the oxidation state of Pd clusters during steady-state catalysis to be determined purely from thermodynamic data.

We first confirmed that steady-state was achieved after both O₂ and H₂ treatments intended to form Pd oxide or metal clusters, respectively, on catalyst samples containing large clusters (0.12 dispersion; Fig. 4). NO conversion rates (at 0.17 kPa O₂, 5 kPa O₂, 603 K) were independent of initial treatment in H₂ (101 kPa, 2 h) or O₂ (101 kPa, 24 h) and reached constant values in both cases after ~3 h in contact with reactants. The formation of nitrates on Al₂O₃ from NO₂ in the inlet stream influenced initial NO conversion rates after both H₂ and O₂ treatments. The similar NO oxidation rates after H₂ or O₂ treatments indicate that Pd clusters formed identical structures during catalysis, irrespective of their initial state after pre-treatment. The thermodynamics of Pd/PdO transition for bulk systems \((\Delta H^0 = -119 \text{ kJ mol}^{-1}, \Delta S^0 = -109 \text{ J mol}^{-1} \text{ K}^{-1}) [33,34]\) shows that PdO is the stable bulk phase at 603 K for
any oxygen chemical potentials corresponding to (virtual) O₂ pressures above 10⁻⁷ kPa. Pd(1 1 1) samples exposed to O₂ (6.5 kPa, 600 K) “adsorbed” ~20 O-atoms per surface Pd atom within 600 s, consistent with the formation of ~20 layers of a stable Pd oxide [35]. Thus, oxygen diffusion within the Pd bulk occurs sufficiently fast at typical NO oxidation temperatures to rapidly and completely oxide Pd clusters smaller than ~10 nm.

NO oxidation rate constants (from rate data, Eq. (8), and η, Eq. (3)) were unaffected by O₂ pressures between 0.003 and 33 kPa at 623 K (Fig. 5); O₂ rigorously represents the kinetic and thermodynamic driving force for the oxidation of Pd clusters. Fig. 5 shows that Eq. (8) is valid and that \( k_1 K_0^{1/2} \) values remain constant throughout this range of oxygen chemical potentials, implying that no changes in phase or structure consequential for reactivity occur throughout the range of NO oxidation conditions. Thus, catalytic clusters are either Pd metal or Pd oxide and remain so at all reaction conditions. Pd/PdO thermodynamic data [33,34] show PdO is the stable bulk phase above 10⁻⁶ kPa O₂ at 623 K and at all conditions used in this study (573–673 K, 10⁻¹⁻¹⁰⁻¹ kPa O₂; PdO favored above 10⁻⁵ kPa O₂ at 673 K). These thermodynamic data are applicable to bulk structures, in which Pd atoms are predominantly present in the coordinatively saturated environment of a bulk solid. Pd atoms at coordinatively unsaturated corner and edge sites in small clusters tend to oxidize more readily than Pd atoms in larger clusters. Thus, we conclude that the small Pd clusters used here for NO oxidation would also be present as oxides during catalysis.

The similar rate expression for metal (Pt [13,14]) and oxide (PdO) catalysts suggests that the oxidation state of the catalyst is inconsequential to the identity of the kinetically relevant elementary steps, although the rate constants for these steps clearly differ among the various catalytic elements.

NO oxidation and oxygen exchange rate constants on Pt catalysts increased markedly with cluster size [14,15]. Similar effects are observed for NO oxidation (Fig. 6a) and oxygen exchange (Fig. 2) rate constants (\( k_1 K_0^{1/2} \)) on Pd-based catalysts. NO oxidation turnover rate constants increased sharply with increasing PdO cluster size (1–5 nm) and more modestly for clusters above 6 nm. Similar size effects have been reported for CH₄ and dimethylether oxidation on Pd [Fig. 6b] and Pt [30,31,36–38] reactions that also require vacancies on surfaces nearly saturated with O’ or OH’. These trends reflect larger values of \( K_0 \) (in Eq. (8)) and smaller concentrations of vacant sites, as a result of the stronger binding of oxygen and hydroxyl species on smaller clusters. O₂ activation rate constants (\( k_1 \)) may also be affected by cluster size, but they contribute less to the apparent rate constant than \( K_0 \) because heats of O’ adsorption are much larger than O₂ dissociation barriers on vacant sites [26,39]. Larger metal clusters expose more low-index surface planes, which bind O’ more weakly than the corner and edge sites prevalent on smaller clusters [40,41]. In contrast to Pt, Pd clusters are present as oxides during NO oxidation catalysis. Such PdO clusters are semiconductors [42] for which electron delocalization and small HOMO–LUMO or band gaps are critical for the stability of reduced centers [43,44]. Band gaps vary sensitively with cluster size and increase as domains become smaller and valence electrons become more confined [45]. As a result, vacancies in small oxide clusters are less stable than vacancies in larger clusters because the electrons remaining after oxygen removal must be delocalized into higher energy states [43,44]. Thus, small oxide clusters bind oxygen more strongly than larger clusters [43,44], and oxidation rates that depend on the generation of vacant surface sites are lower on these small clusters [30,31,36–38].

3.5. Effects of NO₂ scavenging on NO oxidation rates

NO₂ inhibits NO oxidation (Eq. (4)) because of its role in determining the concentration of the vacancies required for O₂ activation (Scheme 1, Step 2). Adsorbents can scavenge NO₂ molecules [46] with significant consequences for NO oxidation turnover rates that are inversely proportional to local NO₂ pressure [14]. We examine next NO oxidation rates in catalyst–adsorbent mixtures to determine the inhibiting effects of NO₂ at the low pressures.
present in NO₂ trapping systems and also the effect of catalyst-adsorbent proximity on local NO₂ concentrations.

NO oxidation rates were measured on catalyst pellets with mean radii of 77 and 125 μm that were mixed with adsorbent pellets of the same size, which showed no reactivity toward NO/O₂ mixtures. The resulting NO oxidation and NO₂ elution rates at initial contact times are shown in Table 2. NO consumption rates (0.038–0.046 mol NO (mol PdO)⁻¹ s⁻¹) were much higher than NO₂ elution rates from the reactor (<0.001 mol NO₂ (mol PdO)⁻¹ s⁻¹) at these early contact times confirming that adsorbents effectively retained NO₂, which was not detected in the outlet stream. The low NO₂ concentrations were coincident with initial NO oxidation rates that were ~10 times higher than their steady-state value (0.005 mol NO (mol PdO)⁻¹ s⁻¹), which was reached after ~3 ks when NO₂ pressures were 4 Pa. Initial NO oxidation rates were slightly higher when the pellet size in the reactor decreased from 125 to 77 μm. A substantial decrease in the distance between NO oxidation and NO₂ adsorption sites from mixtures of pellets (77 μm) to mixtures within pellets (<22 μm) led to a relatively modest increase in NO consumption rates (from 0.046 to 0.079 mol NO (mol PdO)⁻¹ s⁻¹). These data suggest that NO₂ diffusion over distances of ~100 μm weakly influences local NO₂ concentrations, which still inhibit NO oxidation and cause lower rates in the less intimate mixtures. Intrinsic NO₂ adsorption rates, rather than mass transport parameters, affect local NO₂ concentrations in intrapellet and co-impregnated mixtures in NO₃ trapping systems.

The absence of mass transfer artifacts in intrapellet mixtures implies that NO₂ can be treated as a reaction intermediate at pseudo-steady-state within intrapellet catalyst-adsorbent mixtures. NO₂ concentrations are then given by the balance between NO oxidation (r₈) and NO₂ adsorption rates (r₉a):

\[
0 = L_v r_a = L_{Ba} r_{Ba}
\]

(23)

Here, Lᵥ, and Lₛ represent the number of catalyst and adsorbent sites, respectively. Eq. (23) shows that NO₂ concentrations depend on the relative number of catalyst and adsorbent sites (\( \chi \)).

\[
\chi = \frac{L_{Ba}}{L_v}
\]

(24)

Fig. 7 shows the effects of \( \chi \) varied by changing the amount of catalyst and adsorbent in intrapellet mixtures, on NO oxidation rates at initial contact times. Initial NO oxidation rates were proportional to \( \chi^{-1/2} \) (dashed line). These effects are consistent with an adsorption rate expression that is first order in NO₂:

\[
r_{Ba} = k_{Ba}[NO₂]
\]

(25)

where \( k_{Ba} \) is constant for given inlet pressures and temperature. The combination of Eqs. (4) and (23)–(25) leads to an expression for NO₂ concentrations and observed NO oxidation rates in terms of \( \chi \), consistent with the results in Fig. 7:

\[
[NO₂] = \chi^{1/2} \left( \frac{k_{Ba}[NO][O₂]}{k_{Ba}} \right)^{1/2}
\]

(26)

\[
r_{r₈} = \chi^{-1/2} (k_{Ba}[NO][O₂])^{1/2}
\]

(27)

The beneficial effects of decreasing \( \chi \) on NO oxidation rates imply that the presence of more adsorption sites relative to catalyst sites results in lower NO₂ concentrations. Such low NO₂ concentrations still inhibit NO oxidation via the rate expression in Eq. (5) and the elementary steps in Scheme 1, consistent with the rapid dissociation of NO₂ on catalyst surfaces [39] and with the scarcity of vacancies that facilitate O₂ dissociation. Initial NO oxidation rates correspond to NO₂ pressures and O₂ between 0.04–0.2 Pa and 10⁻⁵–10⁻⁴ Pa, respectively, as determined by Eqs. (4) and (6) and the measured NO oxidation rate constant. These oxygen chemical potentials remain in the range where PdO is favored over Pd, which undergoes a phase transition at 5 × 10⁻⁶ Pa O₂ at 573 K [33,34]. Catalyst surfaces remain nearly saturated with chemisorbed O⁺ as a result of strong oxygen adsorption heats (220 and 330 kJ (mol O₂)⁻¹ on Pd clusters of 1 and 3 nm, respectively [47]), which remain relevant to the design of NO₂ trapping systems so long as NO₂ binding on adsorbents occurs with finite rates.

\[\text{Table 2}\]

<table>
<thead>
<tr>
<th>PdO−BaCO₃ distance (μm)</th>
<th>Initial NO oxidation rate (mol NO (mol PdO)⁻¹ s⁻¹)</th>
<th>Initial NO₂ elution rate (mol NO₂ (mol PdO)⁻¹ s⁻¹)</th>
<th>Initial NO oxidation rate (mol NO (mol PdO)⁻¹ s⁻¹)</th>
<th>Steady-state NO₂ oxidation rate (mol NO (mol PdO)⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;22( ^a )</td>
<td>0.079</td>
<td>&lt;0.001</td>
<td>0.2</td>
<td>0.005</td>
</tr>
<tr>
<td>77( ^a )</td>
<td>0.046</td>
<td>&lt;0.001</td>
<td>0.3</td>
<td>0.005</td>
</tr>
<tr>
<td>125( ^a )</td>
<td>0.038</td>
<td>&lt;0.001</td>
<td>0.4</td>
<td>0.005</td>
</tr>
</tbody>
</table>

\( ^a \) Rates measured at 573 K, 0.18 kPa NO, 1 kPa O₂ on mixtures of 10 mg Pd/Al₂O₃ (0.12 dispersion), 125 mg BaCO₃/Al₂O₃.

\( ^b \) Catalyst and adsorbent combined within pellets from particles sieved to <22 μm.

\( ^c \) Catalyst and adsorbent combined as mixtures of pellets with specified mean radii.

\[\text{Fig. 7. NO oxidation rates on intrapellet mixtures of Pd/Al₂O₃ (0.12 dispersion) and BaCO₃/Al₂O₃ as a function of \( \chi \) (Eq. (24)) at the initial contact time with 0.18 kPa NO and 1 kPa O₂ at 573 K.}\]
faces. The requirement for vacancies on PdO surfaces leads to NO₂ inhibition and to significantly higher NO oxidation rates when BaCO₃ sites that irreversibly bind NO₂ are present near catalyst sites in physical mixtures.

Acknowledgments

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References