NOX Interactions with Dispersed BaO: Adsorption Kinetics, Chemisorbed Species, and Effects of Oxidation Catalyst Sites

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Supporting Information

ABSTRACT: Infrared spectra and nitrate and nitrite formation rate data free of transport artifacts provide rigorous evidence for the identity of the adsorbed species and the elementary steps required for adsorption of NO, NO2, and CO2 on BaO/Al2O3 with and without Pt clusters that act as oxidation catalysts. NO/NO2 adsorption occurs via initial formation of nitrites and their subsequent oxidation to nitrates on samples presaturated with carbonates by exposure to CO2. Nitrites form much faster than nitrates at low NO2 pressures via displacement of carbonates and vicinal coadsorption of NO and NO2 molecules. As a result, the dynamics of nitrite formation and of their subsequent oxidation can be independently measured during exposure to NO/NO2 mixtures over a broad temperature range (453–673 K). Nitrites form rapidly upon exposure to NOx, but the presence of CO2 limits equilibrium NOx uptakes because of unfavorable thermodynamics, rendering nitrite formation an impractical strategy for NOx removal from CO2-rich combustion effluent streams. Nitrate thermodynamics is much more favorable, but the rate of nitrite oxidation to nitrates is limited by slow homogeneous NO2 dimerization to N2O4, which acts as the oxidant in nitrite conversion to nitrates on Pt-free Ba/Al2O3. This mechanism is consistent with nitrate formation rates that are second-order in NO2 pressure and essentially independent of NO pressure, sample temperature, and residual coverages of unreacted nitrates. Pt clusters present in close proximity to (but not atomic contact with) nitrite-saturated BaO domains provide a catalytic route for the formation of the N2O4 oxidant required to convert nitrites to stable nitrates and for the effective removal of NOx from CO2-containing streams. Nitrate formation rates on BaO/Pr/Al2O3 are proportional to NO2 pressures, inhibited by NO and proportional to the residual coverage of unreacted nitrites, consistent with rates limited by reactions between N2O4 molecules, in equilibrium with NO2 in steps mediated by Pt surfaces, and nitrates. These detailed kinetic and spectroscopic studies provide mechanistic details previously unavailable about the bifunctional character of NO2 reactions that form stable nitrates on BaO domains and about the essential role of oxidant formation on metal clusters in rendering such adsorption strategies practical for the removal of NOx from CO2-rich streams.

1. INTRODUCTION

BaO adsorbents, together with transition metal catalysts, can be used to trap smog-causing NO from combustion effluent streams that lack CO or residual hydrocarbons as reductants.1–3 Transition metals catalyze NO oxidation to NO2, a molecule that readily adsorbs on many porous solids4,5 but which also inhibits NO oxidation by tittering active sites on catalytic surfaces with oxygen atoms.6–8 As a result, NOx adsorption rates on BaO or BaCO3 strongly influence the effectiveness of the catalysts required to convert NO to NO2 as part of lean de-NOx removal strategies.7,8

Infrared and X-ray photoelectron spectroscopic studies suggest that NO2 initially adsorbs on BaO-containing solids as nitrites with either sequential5,9–16 or concurrent14–17 formation of nitrates. Nitrate formation can involve peroxides (BaO2)5,18,19 or direct interactions of NO25,8–23 or NO/O215,16,20 with BaO surfaces or with preformed nitrites. Nitrate and nitrate formation on BaO may also be mediated by intermediates formed on proximate metal clusters.15,16,20–22 The elementary steps for NOx adsorption processes and the transport pathways between Pt and BaO sites remain unclear and controversial, at least in part, because previous studies have been conducted at conditions leading to complete NO2 conversion, which preclude unequivocal interpretations of adsorption and reaction rates.

Here, we report infrared spectra and kinetic data under conditions of strict kinetic control to probe the nature of the
adsorbed species, reactions, and elementary steps involved in the competitive adsorption of CO₂ and NOₓ on BaO/Al₂O₃ and BaO/Pt/Al₂O₃. The formation of nitrates is slow at low NO₂ pressures (<9 Pa), and such conditions allow measurements of nitrite formation rates during contact with NO/NO₂ mixtures without concurrent nitrate formation. Consequently, we have prepared well-defined systems to study the rates of nitrite formation, the thermodynamics of nitrite—carbonate interconversion, and the dynamics of nitrite conversion to nitrates in the absence and presence of Pt catalysts. Our results indicate that the relative stabilities of nitrite and carbonate lead to low nitrite coverages in the presence of CO₂, making nitrites ineffective as adsorbed species in NOₓ trapping strategies. The sequential formation of more stable nitrates allows larger NO₂ uptakes, but nitrate formation rates in metal-free adsorbents are limited by slow NO₂ dimerization steps that form species required to oxidize nitrite. Intermediates formed on Pt sites present as coimpregnated mixtures with nitrite binding sites provide alternate and much faster nitrate formation pathways that allow for more efficient use of NO₂ adsorbents.

2. EXPERIMENTAL METHODS

2.1. BaO/Al₂O₃ and BaO/Pt/Al₂O₃ Synthesis. Materials were prepared by similar methods as in previous studies. γ-Al₂O₃ (Sasol, SBA-200, 180 m² g⁻¹) was heated to 1023 K at 0.06 K s⁻¹ in flowing dry air (Praxair, extra dry; 1 cm³ g⁻¹ s⁻¹) and held at 1023 K for 4 h. Pt/Al₂O₃ (2.1 wt % Pt) was prepared by methods described previously to achieve a material with 76% of Pt atoms exposed at cluster surfaces, which corresponds to Pt clusters with a mean size of 1.2 nm and a dispersion of 0.0059 Pt atoms per nm² assuming hemispherical geometries and a density equal to the bulk value (22 g cm⁻³). Either γ-Al₂O₃ or this Pt/Al₂O₃ was combined with an aqueous solution (0.45 cm³ (g Al₂O₃)⁻¹) of Ba(O₂C₂H₃)₂ (Sigma-Aldrich, 99.995%) to achieve loadings of 3.0 BaO nm⁻² (15 wt % BaCO₃). Impregnated samples were handled at 383 K for 6 h in ambient air and then heated to 823 K at 0.06 K s⁻¹ in flowing dry air (1 cm³ g⁻¹ s⁻¹) and held for 4 h. A portion of the BaO/Al₂O₃ adsorbent was pulverized in 1:3 ratios with either 2.1 wt % Pt/Al₂O₃ (0.76 Pt dispersion) or SiO₂ (Selecto, treated at 1123 K in flowing dry air (1 cm³ g⁻¹ s⁻¹) for 4 h).

2.2. CO₂ and NO₂ Adsorption Measurements. Adsorption thermodynamics and kinetics were measured on self-supported wafers (2–6 mg cm⁻², pressurized at 100 MPa) in an infrared cell described previously and on pellets (0.02–0.1 mm diameter; formed by pressurization of powders at 100 MPa) supported on a quartz wool plug within a quartz tubular reactor (4 mm diameter). Temperatures (423–673 K) were held constant using resistive heating and an electronic controller (Watlow 96 series). Mass flow controllers (Porter Instruments) and switching valves (Valco Instruments Co.) were automated using Labview software (National Instruments). Reactant gases (0.1% NO₂/He, 2% NO/He, 10% CO₂/He, He₂, and a He balance (Praxair; 99.999% purity) were metered to achieve 10⁻³–10⁻¹ kPa of NO₂, 10⁻¹–10⁻⁶ kPa of NO, 10⁻¹–10⁻¹⁶ kPa of CO₂, 3 kPa of He₂, and 10⁻³ kPa of total pressure. Reactor inlet and outlet concentrations of NO, NO₂, and CO₂ were measured by an infrared gas analyzer (MKS 2030, 2 cm cell, 2 cm path length), while adsorbates were detected by a Fourier-transform infrared spectrometer (Thermo-Nicolet 8700; transmission mode). BaO/Al₂O₃ adsorbents were discarded after their saturation with nitrate, but adsorption sites on nitrate-saturated BaO/Al₂O₃ were regenerated by treatment with 3 kPa of H₂ (473–573 K) for 0.5 h.

Adsorbate coverages were determined from infrared spectra by methods presented in the Appendix. NO and NO₂ conversions were kept below 15% for kinetic measurements by adjusting molar flow rates (9–400 mol (mol BaO)⁻¹ s⁻¹). Adsorption rates were normalized by the available surface area, the pore volume, or the number of accessible nitrite binding sites (denoted BₐO₂). Rates of the fastest process, nitrite formation on BaO/Al₂O₃ (5 Pa of NO₂, 75 Pa of NO, 503 K), were similar on 80 μm pellets of BaO/Al₂O₃ [5.3 × 10⁻³ mol (mol BaO₂)⁻¹ s⁻¹] and on 20 μm pellets [6.1 × 10⁻³ mol (mol BaO₂)⁻¹ s⁻¹] containing 1:3 mixtures of BaO/Al₂O₃ and SiO₂, confirming the absence of mass transfer artifacts.

3. RESULTS AND DISCUSSION

3.1. Adsorbed Species and Reactions Involved in CO₂ and NOₓ Adsorption on BaO/Al₂O₃ and BaO/Pt/Al₂O₃. In this section, we provide evidence for the identity of the adsorbed species and for the pathways involved in CO₂ and NOₓ adsorption on BaO/Al₂O₃ and BaO/Pt/Al₂O₃. The infrared spectra in Figures 1 and 2 show the main features of all infrared-active adsorbed species detected in this study. These spectra resemble those in previous reports, in which observed bands were assigned to carbonate27–29 (Figure 1a, 2a; 1250–1650 cm⁻¹), nitrite30 (Figure 1b, 2b; 1275–1500 cm⁻¹), and nitrate31,32 (Figure 1c, 2c; 1275–1500 cm⁻¹) on BaO structures. We note that the two antisymmetric carbonate stretches show different vibrational frequencies (Figures 1a, 2a), indicating that carbonates were formed only at BaO surfaces.27 Our infrared spectra (Figures 1d, 2b,f) also showed bands characteristic of nitrates on BaO and on γ-Al₂O₃,33 (1250–1350, 1500–1650 cm⁻¹). Unperturbed (3650–3750 cm⁻¹) and perturbed (3400–3600 cm⁻¹) hydroxyl groups34 were also present on γ-Al₂O₃. The respective frequencies of the carbonate, nitrite, and nitrate bands were similar on BaO/Al₂O₃ (Figure 1) and BaO/Pt/Al₂O₃ (Figure 2).
The interactions of CO$_2$ and NO/NO$_2$ mixtures with BaO/Al$_2$O$_3$ were examined by concurrent measurements of adsorbate coverages and NO$_x$ consumption and CO$_2$ evolution rates. Treatment of BaO/Al$_2$O$_3$ at 573 K with 1 kPa of CO$_2$ for 1 h led to surface carbonates (0.7 BaCO$_3$ nm$^{-2}$; Figure 3a, 0 ks). Subsequent treatment of this sample with a mixture of 30 Pa of NO$_2$ and 120 Pa of NO at 573 K caused nitrite coverages to increase and carbonate coverages to simultaneously decrease (Figure 3a, 0–0.5 ks), consistent with the displacement of carbonates by nitrites. The formation of nitrites occurred only when both NO and NO$_2$ were introduced, consistent with the equimolar consumption of NO and NO$_2$ (Figure 3b, 0–0.5 ks); CO$_2$ was concurrently evolved as nitrites formed, and the rate of CO$_2$ desorption was the same as the NO$_2$ (and NO) consumption rate (Figure 3b, 0–0.5 ks). Treatment of BaO/Al$_2$O$_3$ with 30 Pa of NO$_2$ and 120 Pa of NO eventually led to the formation of nitrates on BaO (Figure 3a, 1–12 ks), to the ultimate disappearance of nitrites and of all carbonate species, and to the consumption of NO$_2$ and the evolution of NO (Figure 3b, 1–12 ks). The amount of NO$_2$ consumed per NO evolved was 2.9 over the time period shown in Figure 3, consistent with previous reports on BaO/Al$_2$O$_3$ (3.0 NO$_2$ consumed per NO evolved$^{35,36}$). Nitrate formation was also observed on γ-Al$_2$O$_3$ (Figure 3a, 3–10 ks) and occurred concurrently with a decrease in the intensity of bands assigned to unperturbed OH groups on γ-Al$_2$O$_3$ (Figure 3a, 1–10 ks) and an increase in the intensity of a broad band at lower frequencies assigned to perturbed OH groups (Figure 1c,d). No other adsorbed species were evident in the infrared spectra (1100–1700 cm$^{-1}$) of BaO/Al$_2$O$_3$ during NO/NO$_2$ treatments (Supporting Information, Figure S1, with additional discussion in the Appendix).

We also investigated the interactions of NO/NO$_2$ mixtures with BaO/Pt/Al$_2$O$_3$ samples to determine any effects of Pt on adsorption reactions. Nitrites formed initially during contact of BaO/Pt/Al$_2$O$_3$ at 503 K with a mixture of 75 Pa of NO and 5.2 Pa of NO$_2$ (Figure 4, 0.0–0.2 ks) and occupied a large fraction of the accessible binding sites. These nitrite species were replaced by nitrites in slower sequential reactions (Figure 4, 0.2–6.0 ks). Carbonates were present initially on BaO and nitrate on Al$_2$O$_3$ were not detected during the treatment at 75 Pa of NO, 5.2 Pa of NO$_2$, 503 K.
The reactions in Scheme 1, which are not intended to describe elementary processes, account for the observed interconversions among the most abundant adsorbed species present on BaO/Al₂O₃ and BaO/Pt/Al₂O₃, as shown by the data in Figures 3 and 4. Scheme 1 includes reactions between carbonate (BaCO₃) and NO(NO₂)₂ to form CO₂ and nitrite [Ba(NO₂)₂] and between NO₂ and nitrite to form NO and nitrate [Ba(NO₃)₂]. The sequential replacement of surface carbonates by nitrates and ultimately by nitrites, taken together with the minor changes in the nitrite and nitrate infrared features during NO/NO₂ treatments (Supporting Information, Figure S1), indicates that infrared-active species were predominantly present at BaO surfaces. The conversion of hydroxyls on γ-Al₂O₃ [Al(O)OH] to nitrates [Al(O)NO₃] is also shown in Scheme 1 and is consistent with the consumption of three NO₂ molecules per NO released. We note that the slow formation of nitrates on both BaO and Al₂O₃ sites (Figures 3 and 4) allows measurements of nitrite formation rates (discussed next) before significant amounts of nitrate form and also allows subsequent measurements of nitrate formation rates on surfaces initially treated to form nitrites at saturation coverages (discussed in sections 3.4 and 3.5).

3.2. Nitrite Formation Rates on BaO/Al₂O₃. Nitrite formation rates were measured by holding BaO/Al₂O₃ at constant temperature (423–673 K) and treating each sample with 1 kPa of CO₂ for 1 h and then in flowing He [400 mol He (mol BaO)⁻¹ s⁻¹; 200 s] before introducing mixtures containing NO (0–100 Pa) and NO₂ (0–11 Pa). Nitrite formation rates were measured from CO₂ evolution rates, which were equal to nitrite formation rates (Figure 5) but were measured more accurately than differences in NO and NO₂ concentrations in the inlet and outlet streams. All rates were normalized by the number of nitrite binding sites (L₀) determined from the NO₂ uptake on BaO/Al₂O₃ treated with a mixture of 8 Pa of NO₂ and 560 Pa of NO (reported in the Supporting Information, Figure S2). We note that the steady-state coverage of adsorbed species measured by infrared spectroscopy varied weakly when the NO and NO₂ pressures were varied between 20 and 500 Pa of NO and 1–8 Pa of NO₂ (Supporting Information, Figure S3), but the NO₂ uptake decreased modestly with increasing treatment temperature (Supporting Information, Figure S2). These results suggest that all reactive BaO structures became saturated with nitrite when treated with a mixture of 8 Pa of NO₂ and 560 Pa of NO, but some BaO structures were converted to unreactive ones with increasing treatment temperature. As a result, a different value of L₀ was used to normalize rates at each temperature, using the uptake values measured at that temperature (Supporting Information, Figure S2).

Nitrite formation rates decreased almost linearly with increasing nitrite coverage as carbonates converted to nitrites with increasing contact time (Figure 5; 6 Pa of NO, 55 Pa of NO₂, 523 K). Nitrite formation rates were proportional to both NO (0–80 Pa) and NO₂ (0–11 Pa) pressures (Figure 6a) during initial contact of BaO/Al₂O₃ with NO/NO₂ mixtures; these rates were weakly influenced by temperature (423–673 K; Figure 6b), indicative of a very small apparent activation energy for nitrite formation (5 ± 2 kJ mol⁻¹). Previous studies of NO₂ adsorption rates on carbonate-saturated BaO/Al₂O₃ (NO₂ formed by NO oxidation on Pt/Al₂O₃ mixed with BaO/Al₂O₃) also showed that nitrite formation rates on carbonate-saturated surfaces increased linearly with NO₂ pressure and were not influenced by CO₂.

**Figure 5.** Nitrite formation rates normalized by BaO, and plotted as a function of nitrite coverage on BaO/Al₂O₃ (3.0 BaO nm⁻²) at 523 K treated with 6.0 Pa of NO₂ and 53 Pa of NO. Sample was treated at 523 K with 1 kPa of CO₂ for 1 h and then in flowing He for 200 s before introduction of NO/NO₂ mixtures. Dashed lines give the detected range for initial NO₂ adsorption rate [4.1 ± 0.8 × 10⁻³ mol (mol BaO)⁻¹ s⁻¹].
pressure (0.0–0.5 kPa),7 but kinetic dependences on NO pressures and temperatures were not reported.

The measured nitrite formation rates on BaO/Al2O3 surfaces initially saturated with carbonate species (r_{c-n}) are accurately described by the equation:

$$r_{c-n} = k_{c-n} [\text{NO}] [\text{NO}_2] (L_n - [\text{Ba(NO}_2]_{\text{a}})(1 - \eta)$$  \hspace{1cm} (1)

in which $L_n$ is the number of nitrite binding sites, $\eta$ (eq 2) accounts for the approach to equilibrium for the nitrite—carbonate interconversion (eq 3)

$$\eta = \frac{[\text{Ba(NO}_2]_{\text{a}}}{K_{c-n} [\text{BaCO}_3]/\psi}$$  \hspace{1cm} (2)

BaCO$_3$ + NO + NO$_2$ $\rightleftharpoons$ Ba(NO$_2$)$_2$ + CO$_2$  \hspace{1cm} (3)

and $\psi$ describes the thermodynamic driving force for this interconversion

$$\psi = \frac{[\text{NO}_2]/[\text{NO}]}{[\text{CO}_2]}$$  \hspace{1cm} (4)

The values of the equilibrium constant, $K_{c-n}$, for the nitrite—carbonate interconversion at BaO surfaces are reported and discussed in section 3.3. The measured rate constant for nitrite formation, $k_{c-n}$ [2.1 $\times$ 10$^{-5}$ mol (mol BaO)$^{-1}$ s$^{-1}$ Pa$^{-2}$ at 573 K], is similar to the NO$_2$ adsorption rate constant previously reported [1.4 $\times$ 10$^{-5}$ mol (mol BaO)$^{-1}$ s$^{-1}$ Pa$^{-2}$] on mixtures of Pt/Al$_2$O$_3$ and BaO/Al$_2$O$_3$ treated with 170 Pa of NO and 500 Pa of O$_2$ at 573 K. The nitrite formation rate constant from this previous study$^7$ was derived from reported values of the NO consumption rate [0.65 NO mol (mol Pt) s$^{-1}$], the Pt$_4$/BaO$_4$ ratio (5.6 $\times$ 10$^{-3}$), and the NO$_2$ pressure (0.8 Pa; determined from the NO oxidation kinetics). Our results therefore agree with previous measurements$^7$ of nitrite formation rates.

The measured kinetic responses described by eq 1 indicate that kinetically relevant nitrite formation steps involve species containing NO and NO$_2$. The linear decrease in rates with increasing nitrite coverage (eq 1) indicates that kinetically relevant nitrite formation steps occur on accessible binding sites that are not occupied by nitrites. The absence of inhibition of initial nitrite formation rates by CO$_2$ suggests that the formation of an unoccupied site via equilibrium CO$_2$ adsorption—desorption is not a prerequisite for NO/NO$_2$ adsorption, which must instead occur in a concerted manner with CO$_2$ desorption. The small apparent activation energy for nitrite formation (5 $\pm$ 2 kJ mol$^{-1}$) suggests that the reactants and transition state involved in nitrite formation have similar energies. This appears to reflect the concerted nature of the NO/NO$_2$ adsorption and CO$_2$ desorption steps, because sequential desorption of CO$_2$ before NO/NO$_2$ adsorption would involve an activation barrier commensurate with the CO$_2$ adsorption heat [230 or 272 kJ mol$^{-1}$ on BaO(100)$^{20}$ or bulk BaCO$_3$$^{23}$, respectively].

The individual presence of NO or NO$_2$ (Figure 6a) did not lead to NO$_x$ adsorption on carbonate-saturated BaO adsorbents. DFT-derived binding energies for vicinal NO and NO$_2$ adsorbed on BaO(100) are larger (by 80 kJ mol$^{-1}$) than for noninteracting NO and NO$_2$ adsorbates, suggesting that stabilization by coadsorbed NO$_2$ is required to bind NO or NO$_2$. Yet, even vicinal adsorption of NO and NO$_2$ as nitrites leads to species that are slightly more stable than adsorbed CO$_2$ (by 70 kJ mol$^{-1}$ on bulk BaO$^{24}$), which is present in very large excess in automotive exhaust (CO$_2$/NO$_x$ $>$ 10$^3$).

### 3.3. Thermodynamics of Nitrite and Carbonate Formation on BaO/Al$_2$O$_3$

We consider next the thermodynamics of competitive formation of nitrite and carbonate species over a broad concentration range. The rapid formation of nitrites during treatment of BaO/Al$_2$O$_3$ with NO/NO$_2$ mixtures (423–673 K) allowed efficient NO$_x$ trapping as nitrites, but the addition of CO$_2$ to NO/NO$_2$ mixtures significantly decreased equilibrium nitrite coverages (Figure 7). Equilibrium nitrite coverages on BaO/Al$_2$O$_3$ samples were similar for gas mixtures containing a constant value of $\psi$ ([NO])/([NO] + [NO$_2$]) but different individual NO, NO$_2$, and CO$_2$ pressures (Supporting Information, Figure S4), consistent with $\psi$ as the rigorous thermodynamic driving force for nitrite—carbonate interconversion. Equilibrium nitrite coverages decreased strongly with decreasing $\psi$ (Figure 7) over the range of NO (40–460 Pa), NO$_2$ (2.7–8.0 Pa), and CO$_2$ (0.1–9 kPa) pressures examined.

Equilibrium nitrite coverages were accurately described by an adsorption isotherm that involves three types of binding sites (eq 5; dashed curve in Figure 7). One site is saturated with nitrite, while another one remains occupied by carbonate over the reported range of $\psi$ values (0.01–30 Pa). The remaining sites, which account for most of the binding sites in these samples, exist at surfaces that reversibly adsorb NO and CO$_2$ according to a Langmuir isotherm with equilibrium constant $K_{c-n}$ (eq 3):

$$\frac{[\text{Ba(NO}_2]_{\text{a}}}{L_n} = \alpha + \beta \left( \frac{K_{c-n} \psi}{1 + K_{c-n} \psi} \right)$$  \hspace{1cm} (5)

$\alpha$ represents the fraction of sites that remain saturated with nitrite for $\psi$ above 10$^{-2}$ Pa, and $\beta$ represents the fraction of sites with equilibrium constant $K_{c-n}$. The three-site model (eq 5) represents a simplification of the true system, which likely contains BaO domains with a distribution of sizes and binding properties. Yet, previous computational results showed that the binding energies of isolated carbonates and nitrites have similar
sensitivities to the basicity of the substrate, and these calculations suggest that a single equilibrium constant describes the competitive binding of carbonate and nitrite on sites with different intrinsic basicities, in contrast with our observed results. The slight deviations that we observe from uniform site models may reflect repulsive interactions among adsorbed species, which can also influence their collective binding energies.

The parameters required to describe the data in Figure 7 and eq 5 indicate that a small fraction of sites [\( \alpha = 0.17 \pm 0.02 \text{ mol (mol BaO)}^{-1} \)] has a stronger affinity for nitrite than carbonate at values of \( \psi \) as low as \( 10^{-2} \text{ Pa} \). A majority of binding sites [\( \beta = 0.65 \pm 0.04 \text{ mol (mol BaO)}^{-1} \)] behave as a uniform ensemble with thermodynamic properties for the nitrite–carbonate interconversion that can be described by an equilibrium constant (\( K_{e-n} = 0.97 \pm 0.25 \text{ Pa}^{-1} \)) that resembles estimates (\( K_{e-n} = 0.35 \text{ Pa}^{-1} \) at \( 573 K \)) from DFT-derived nitrite (\( 360 \text{ kJ mol}^{-1} \)) and carbonate (\( 230 \text{ kJ mol}^{-1} \)) binding energies on BaO(100) and entropy changes for the nitrite—carbonate given by differences in the translational entropies of NO, NO2, and CO2 as gaseous molecules (\( -140 \) kJ mol\(^{-1} \) K\(^{-1}\)). Such low values of \( K_{e-n} \) cause carbonate to be preferred over nitrite in gas mixtures with values of \( \psi \) typically produced by combustion engines (\( \psi < 10^{-2} \text{ Pa}^{-1} \), \( \sim 10^{0} \text{ Pa of CO}_2 \), \( \sim 20 \text{ Pa of NO}_2 \)). The conversion of nitrite to carbonate is much more exothermic (\( -180 \) to \( -240 \) kJ mol\(^{-1}\)) than to nitrite (\( -70 \) to \( -130 \) kJ mol\(^{-1}\)), and the equilibrium constants for carbonate-to-nitrite conversion are therefore much larger (\( 10^{-1} \) to \( 10^{0} \text{ Pa}^{-1} \) at \( 573 K \)). As a result, the conversion of nitrites to nitrate becomes an essential requirement for the efficient removal of NOx from CO2-containing combustion effluent streams.

3.4. Nitrate Formation Rates on BaO/Al2O3. Nitrate formation rates were measured on BaO/Al2O3 samples (without Pt) previously treated with NO/NO2 mixtures (120/40 Pa) for 1 h at each reaction temperature (453–673 K) until the nitrite coverage reached a constant value (\( \sim 1 \text{ h on-stream} \)). Initial nitrate formation rates were unaffected by NO pressure and temperature (Figure 8) but increased strongly with increasing NO2 pressure with a dependence that was accurately described as proportional to \( (\text{NO}_2)^{3} \) (Figure 8a, dashed curve). Nitrate formation rates from pre-existing nitrites (\( r_{n-N} \)) remained essentially constant, even after significant amounts of nitrite were converted to nitrate (Figure 9). These nitrate formation rates were accurately described by the rate equation (Figure 9, dashed curves)

\[
r_{n-N} = k_{n-N}[\text{NO}_2]^2[\text{NO}]^0[\text{Ba(NO}_3)_2]^0
\]

but not by the alternate equation expected if rates were proportional to the remaining amounts of nitrite in the sample (Figure 9, solid curves)

\[
r_{n-N} = k’_{n-N}[\text{NO}_2]^2[\text{NO}]^0[\text{Ba(NO}_3)_2]^1
\]

The temperature dependence of the measured rate constant (\( k_{n-N} \) in eq 6) gave essentially no detectable activation energy (\( 0 \pm 5 \text{ kJ mol}^{-1} \)). We note that nitrite formation rates do not depend on coverage for values of nitrite coverage below 50% (Figure 9). Nitrate formation rates decrease with increasing nitrate coverage at higher nitrate coverages (as observed in Figure 3a). This decrease in rate reflects steps that are much slower than those limiting nitrite formation rates at low coverages; therefore, they are kinetically insignificant during the early stages of nitrate formation.

The functional form of eq 6 indicates that the oxidation of nitrite to nitrate species is mediated by intermediates containing two NO2 molecules, without detectable involvement of NO. This kinetic dependence suggests the participation of NO2 dimers (e.g., N2O4) whose equilibrium pressures are very low at these conditions (\( 10^{-9} \text{ to } 10^{-8} \text{ Pa} \)); thus, requiring their formation near BaO binding sites (i.e., within sample pores or intrapellet space). The weak effects of residual nitrite coverages on nitrate formation rates (eq 6) suggest that such rates are limited by steps that do not occur on Ba(NO3)2 surfaces. These data indicate that NO2 forms N2O4 via homogeneous dimerization pathways within the pore volume and that this step is rendered irreversible and rate-determining by the rapid subsequent reaction of N2O4 with nitrites to form nitrates with evolution of NO. NO2 dimerization...
Table 1. Nitrite and Nitrate Formation Rates on BaO/Al₂O₃ and BaO/Pt/Al₂O₃

<table>
<thead>
<tr>
<th>Material</th>
<th>Nitrite formation rate, 10⁻⁴ mol (mol BaO₂)⁻¹ s⁻¹</th>
<th>Nitrate formation rate, 10⁻⁴ mol (mol BaO₂)⁻¹ s⁻¹</th>
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<td>BaO/Al₂O₃</td>
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<td>Mechanically ground BaO/Al₂O₃ + Pt/Al₂O₃ (3:1 ratio)</td>
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<td>Coimpregnated BaO/Pt/Al₂O₃</td>
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<td>6.4⁴</td>
</tr>
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* Rates at 503 K, 5.2 Pa of NO₂, 75 Pa of NO. ² Loadings of 3.0 BaO nm⁻², 0.0059 Pt clusters nm⁻². ³ Rates extrapolated to initial saturated carbonate coverage on samples pretreated at 503 K with 1 kPa of CO₂ for 1 h. ⁴ Rates extrapolated to saturation nitrate coverage. ⁵ Samples pretreated at 503 K with a mixture of 5.2 Pa of NO₂ and 75 Pa of NO for 1 h. Samples pretreated at 503 K with 100 Pa of NO₂ for 0.5 h and then with 3 kPa of H₂ for 0.5 h.

Figure 10. Nitrate formation rates normalized by BaO and plotted as a function of nitrite coverage on BaO/Pt/Al₂O₃ treated with a mixture of 5.2 Pa of NO₂ and 75 Pa of NO at ( ) 473 K, (●) 503 K, and (■) 523 K. Samples were treated with 100 Pa of NO₂ (0.5 h) and then 3 kPa of H₂ (0.5 h) before introduction of NO/NO₂ mixtures. The nitrate coverage evolved from high to low values for the reported data.

molecules at much higher rates than homogeneous dimerization routes.

Nitrate formation rates on coimpregnated BaO/Pt/Al₂O₃ were much larger than on BaO/Al₂O₃ samples mixed with Pt/Al₂O₃ powders (3:1 ratio) by mechanical grinding (Table 1). These strong effects of the distance between Pt and BaO sites on nitrate formation rates suggest that the oxidant involved is unstable and present at very low concentrations and is therefore consumed near Pt sites that form this oxidant. Thus, Ba nitrite species are inaccessible to the oxidant unless Pt clusters are present within distances smaller than the micrometer dimensions of the physical mixtures.

Nitrites, however, were fully converted to nitrates on BaO/Pt/Al₂O₃ (Figure 4), suggesting that the distances between Pt and BaO sites in coimpregnated samples allow the oxidant to access all nitrite binding sites, not all of which are likely to reside within atomic distances of Pt clusters (present at 0.0059 Pt clusters nm⁻²). Nitrate formation rates on BaO/Pt/Al₂O₃ decreased linearly with decreasing nitrite coverage as nitrites were converted to nitrates (Figure 10), suggesting that nitrate formation via Pt-mediated pathways is limited by irreversible reactions on BaO sites and that the oxidant is formed at equilibrium concentrations on Pt sites and is present at the same concentration throughout all nitrite structures on BaO/Pt/Al₂O₃. The uniform nitrite reactivity is inconsistent with the requirement for atomic contact between Pt and BaO sites, in view of the much higher density of...
The kinetics of nitrate formation via Pt-mediated routes on BaO/Pt/Al2O3 (extrapolated to the initial saturated nitrite concentration of this Ba(NO2)(NO3), the product of N2O4 adsorption on BaO or Ba(NO2) sites, to the functional form of which cannot be rigorously reconciled with any sequence of elementary steps.

The different nitrate formation rate equations of BaO/Pt/Al2O3 (eq 8) and BaO/Al2O3 (eq 6) reflect corresponding differences in the kinetically relevant steps that form or consume the oxidants required to convert nitrites to nitrates. Nitrate formation rates via homogeneous pathways increased with [NO2]+ and were independent of coverage (eq 6) or temperature, consistent with nitrite oxidation steps that involve kinetically relevant N2O4 dimerization instead of direct NO2 reactions with nitrites. In contrast, rates via Pt-mediated routes were proportional to NO2 pressure and to residual Ba(NO2)2 concentrations and inhibited by NO (eq 8). Pt is unlikely to facilitate direct reactions between nitrite and O atoms or N2O4, because all BaO sites cannot plausibly be located in atomic proximity to a Pt cluster yet still convert nitrites to nitrates with uniform rates. Therefore, the effects of NO and NO2 pressures on nitrate formation rates on BaO/Pt/Al2O3 must reflect the formation of equilibrium concentrations of the relevant oxidant on Pt sites and the kinetic consequences of these oxidant concentrations on nitrite conversion to nitrates.

N2O4 intermediates are involved in nitrate formation via homogeneous pathways (section 3.4) and are plausible as nitrite oxidants formed on Pt sites. The thermodynamics of NO3−, an alternate strong oxidant, are known, but equilibrium NO3− pressures (4 × 10−12 Pa) are much smaller than for N2O4 (9 × 10−8 Pa under the conditions of these experiments (4 Pa of NO2, 70 Pa of NO, 503 K)); therefore, we consider NO3− a less plausible oxygen atom carrier than N2O4. Scheme 2 shows a sequence of elementary steps for nitrite oxidation to nitrate mediated by N2O4 species formed by equilibrated reactions on Pt (step 2a). Equilibrium N2O4 concentrations are proportional to [NO2]+, but the observed nitrate formation rates are first-order in NO2 (eq 8). This suggests that NO2 desorbs from a Ba(NO2)2 site in a quasi-equilibrated step (step 2b) to form a reactive intermediate [Ba(NO2)] on which N2O4 adsorbs (step 2d); the concentration of this Ba(NO2)2 intermediate is proportional to [NO2]+ on surfaces saturated by Ba(NO2)2. The NO inhibition evident from eq 8 suggests that NO desorption from Ba(NO2)2 (step 2c) also occurs before N2O4 adsorbs (step 2e). A final elementary step is required to convert Ba(NO2)(NO3), the product of N2O4 adsorption on BaO or Ba(NO2)2 sites, to Ba(NO3)2 (step 2f). The assumptions of irreversible N2O4 adsorption (by steps 2d and 2e) and of Ba(NO2)2 and Ba(NO3)2

The linear dependence of nitrate formation rates on nitrite coverage (Figure 10) suggests instead that reactions on Pt establish an equilibrium between the NO2 and NO reactants and the reactive oxidant species and that the proximity of BaO sites to Pt clusters is inconsequential to the formation rates on nitrite coverage (Figure 10). Differences in the kinetically relevant steps that form or consume the oxidant on Pt sites and the kinetic consequences of these oxidant concentrations on nitrite conversion to nitrates may have been related to the sequential formation of nitrites by NO/NO2 coadsorption and then nitrates by NO2 reactions with nitrites. In contrast, rates via Pt-mediated routes were proportional to NO2 pressure and to residual Ba(NO2)2 concentrations and inhibited by NO (eq 8). Pt is unlikely to facilitate direct reactions between nitrite and O atoms or N2O4, because all BaO sites cannot plausibly be located in atomic proximity to a Pt cluster yet still convert nitrites to nitrates with uniform rates. Therefore, the effects of NO and NO2 pressures on nitrate formation rates on BaO/Pt/Al2O3 must reflect the formation of equilibrium concentrations of the relevant oxidant on Pt sites and the kinetic consequences of these oxidant concentrations on nitrite conversion to nitrates.

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The kinetics of nitrate formation via Pt-mediated routes on BaO/Pt/Al2O3 (extrapolated to the initial saturated nitrite concentration of this Ba(NO2)(NO3), the product of N2O4 adsorption on BaO or Ba(NO2)2 sites, to Ba(NO3)2 (step 2f). The assumptions of irreversible N2O4 adsorption (by steps 2d and 2e) and of Ba(NO2)2 and Ba(NO3)2

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as most abundant surface species give nitrate formation rates
\( (r_{n,N,Pt}) \) as

\[
r_n - N_{n,Pt} = \left( K_{2d} [NO_2]^2 \right) \left( k_{2d} + K_{2e} K_{3e} [NO]^{-1} \right) \frac{[Ba(NO_2)_2]}{K_{2d} K_{2b} [NO_2]}
\]

(9)

\[
r_n - N_{n,Pt} = \lambda [NO_2] (1 + \mu [NO]^{-1}) [Ba(NO_2)_2]
\]

(10)

where \( \lambda \) represents \( K_{2d} K_{2b} k_{2d} \) and \( \mu \) represents \( K_{2e} (k_{2d}^{-1} k_{2e}^{-1}) \).

Equation 10 accurately predicts the first-order NO2 and Ba-
(NO2)2 dependences and NO inhibition of measured nitrate
formation rates (dashed curves in Figures 10 and 11a). The
apparent activation energy (68 kJ mol\(^{-1}\)) appears to reflect a
combination of the exothermic formation of N2O4 (\(-57 \) kJ
mol\(^{-1}\)), represented in \( K_{2d} \) and the endothermic desorption of
NO2 or NO from Ba(NO2)2 surfaces (147 kJ mol\(^{-1}\) on BaO-
(100)\(^{36} \) for each of NO2 and NO, represented in \( K_{2b} \) and \( K_{2e} \).

These results provide evidence for the synergistic roles of Pt
oxidation catalysts and BaO adsorbents in lean NOX trapping
strategies. Pt is necessary to catalyze NO oxidation to more
reactive NO2 molecules, but NO2 inhibits NO oxidation;\(^6,7\)
therefore, BaO sites must rapidly and irreversibly bind NO2 to
lower its concentration and increase NO oxidation rates.\(^7\) NO2
adsorption on BaO-containing solids in streams containing high
CO2 concentrations requires storage as stable nitrates that are
formed by reactions involving NO2 oxidants. These N2O4
oxidants are formed much faster by reactions of NO2 on Pt
surfaces than by homogeneous NO2 dimerization reactions. The
low stability and low equilibrium concentrations of N2O4 inter-
mediates, however, imply that Pt and BaO sites must be present
in nanometer-scale distances to increase nitrate formation rates
over levels achieved by homogeneous pathways; therefore, the
coimpregnation of metal and basic oxide substrates is required to
realize the synergistic effects that allow efficient NOX storage on
catalyst-adsorbent materials.

4. CONCLUSIONS

NO and NO2 adsorb on BaO/Al2O3 and BaO/Pt/Al2O3 to
initially form nitrates that are subsequently oxidized to nitrates by
NO2-derived intermediates. Nitrates are formed by a nonacti-
vated process when NO and NO2 bind molecularly at vicinal
positions on BaO surfaces. Nitrates readily displace preformed
surface carbonates when CO2 is absent from reactant streams,
but the addition of CO2 to NO/NO2 mixtures decreases steady-
state nitrite coverages because of competitive binding between
CO2 as carbonate and NO/NO2 as nitrite. A majority of BaO
binding sites behave as a uniform ensemble for nitrite—carbonate
interconversion reactions, with an equilibrium constant that
leads to low nitrite coverages at CO2/NO2 levels present in
combustion exhaust. Nitrates are more stable than nitrates,
but the oxidation of nitrates to nitrates on BaO/Al2O3 occurs slowly
and requires an oxidant in the form of NO2 that is produced by
nonactivated bimolecular collisions of NO2 molecules in the gas
phase. Nitrate formation becomes much faster when Pt sites are
present in close (but not atomic) proximity to Ba nitrite sites,
because reactions on Pt sites establish equilibrium concentra-
tions of N2O4 oxidants that react subsequently with nitrates on
BaO surfaces.

APPENDIX: DETERMINATION OF ADSORBATE
COVERAGES

Adsorbate coverages on BaO/Al2O3 were determined from
infrared spectra by assuming that coverages \( (\Theta) \) and spectra \( (\mathbf{Z}) \)
are related by response factors \( (\mathbf{F}) \):

\[
\mathbf{Z} = \Theta \mathbf{F}
\]

(A.1)

Here, \( \Theta \) and \( \mathbf{Z} \) are treated as matrices with each row of \( \mathbf{Z} \)
corresponding to an infrared spectrum and each row of \( \Theta \)
corresponding to the coverage of all adsorbates during an infrared
measurement. The response factors \( (\mathbf{F}) \) can also be treated as a
matrix when they are independent of coverage, which leads to
coverages described by

\[
\Theta = \Theta (\mathbf{F F}^T) (\mathbf{F F}^T)^{-1} = \mathbf{Z F}^T (\mathbf{F F}^T)^{-1}
\]

(A.2)

Equation A.2 involves matrix transpose, inverse, and multiplica-
tion operations.

The adsorbate coverages reported in this study were computed
from eq A.2, using response factors derived from matrix
representations of the spectra in Figures 1 or 2. The response
factors were normalized to reflect measured CO2, NO, and NO2
uptakes on BaO/Al2O3. Similar response factors were assumed
for BaO/Al2O3 and for BaO/Pt/Al2O3, and variation in the wafer
thickness was corrected by comparing the carbonate bands with the
CO2 uptake.

After the assumption that the response factors are independent of
coverage can be assessed from the effects of coverage on infrared
bandwidths and band centers or analyzed statistically by factor
analysis,\(^3\) which considers spectral features, \( E \), that are not
explained by the chosen response factors

\[
E = \mathbf{Z} - \Theta \mathbf{F}
\]

(A.3)

The spectral features that were unexplained by the deconvolu-
tion procedure that led to Figure 3a are shown in the Supporting
Information (Figure S1). The sum of squares of the unexplained
data was much less than the sum of squares of the explained data
(their ratio was \( 2 \times 10^{-5} \)), and no spectrally significant features
were observed in the unexplained data.

ASSOCIATED CONTENT

Supporting Information. Figure S1 (spectral residuals resulting
from deconvolution of infrared spectra), Figure S2 (carbonate, nitrite, and nitrate uptake versus temperature), Figure S3 (carbonate and nitrite coverage versus CO2, NO, and NO2 pressures), Figure S4 (equilibrium nitrite coverages at constant values of \( \psi \) ([NO]/[NO2][CO2]^{-1})), and section S.1 (effect of diffusion on reactive intermediate concentration). This
material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(38) Borrell, P.; Cobos, C. J.; Luther, K. J. Phys. Chem. 1988, 92, 4377.