

Mechanism and Site Requirements for NO Oxidation Catalysis and NO_x Adsorption on Dispersed Metal and Oxide Substrates

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Introduction

NO oxidation catalysts and NO₂ adsorbents based on BaO are used to remove NO_x from combustion effluents that lack CO or C_xH_y reductants [1]. NO_x trapping materials, however, inefficiently use costly active components because of persistent ambiguities about fundamental processes responsible for NO_x storage [1]. We address such matters by combining NO oxidation and NO_x adsorption rate data with infrared spectra of adsorbed species to identify elementary steps and active site requirements for NO oxidation and NO_x adsorption.

Materials and Methods

Supported clusters present as Pt, PdO, RhO₂, Co₃O₄, or BaO were dispersed on γ -Al₂O₃ by incipient wetness impregnation of precursor salts. Catalyst dispersions and cluster sizes were measured by H₂ or O₂ titrations at 313 K. BaO dispersions were determined from NO₂ uptakes as nitrites at 423-673 K. Rates were measured on pellets (80-240 μ m) in a flow reactor and on self-supported wafers (2-6 mg cm⁻²) in a flow infrared cell (423-673 K, 0-0.20 kPa NO, 0-0.10 kPa NO₂, 0-10 kPa O₂, 0-9 kPa CO₂). An infrared spectrometer (Nicolet 8700) and a gas analyzer (MKS 2030) were used to detect adsorbates on BaO and NO, NO₂, and CO₂ pressures.

Results and Discussion

NO oxidation rates on supported Pt [2, 3], PdO [4], RhO₂, and Co₃O₄ clusters increased linearly with NO and O₂ pressures and were inversely proportional to NO₂ pressures, consistent with a kinetically-relevant step involving the reaction of O₂ with an unoccupied site [2, 3, 4]. NO and NO₂ react in equilibrated steps to establish vacancy concentrations and oxygen chemical potentials at catalyst surfaces, resulting in near-saturation of active sites with oxygen atoms. NO oxidation rate constants were identical to those for ¹⁶O₂-¹⁸O₂ exchange on Pt [3] and PdO [4], confirming that O₂ activation on oxygen atom vacancies is kinetically-relevant and occurs without involvement of NO_x co-reactants. The prevalent oxygen chemical potentials established by NO/NO₂ pressures cause catalyst clusters to exist as Pt [3], PdO [4], RhO₂, and Co₃O₄ during NO oxidation catalysis, as confirmed by thermodynamic data, O₂ uptakes on reduced catalysts, and X-ray diffraction. NO oxidation turnover rates on both metal (Pt) and oxide (PdO, RhO₂) catalysts increased significantly with cluster size (Fig. 1a). Surface atoms become more coordinatively-unsaturated and electrons become localized within smaller domains as cluster size decreases, which both result in stronger metal-oxygen bonds, lower vacancy concentrations, and lower NO oxidation rates on small clusters.

NO₂ inhibits NO oxidation turnovers, but strongly binds on BaO surfaces that are present in NO_x trapping materials. As expected, NO oxidation rates were much higher when catalyst powders were combined with BaO/Al₂O₃ [2, 3]. NO oxidation turnovers increased as adsorbent sites became more abundant relative to catalyst sites, consistent with a model in which NO₂ is a reactive intermediate present at concentrations controlled by NO oxidation and NO₂ adsorption rates. Consequently, NO₂ adsorption rates critically influence NO oxidation turnovers.

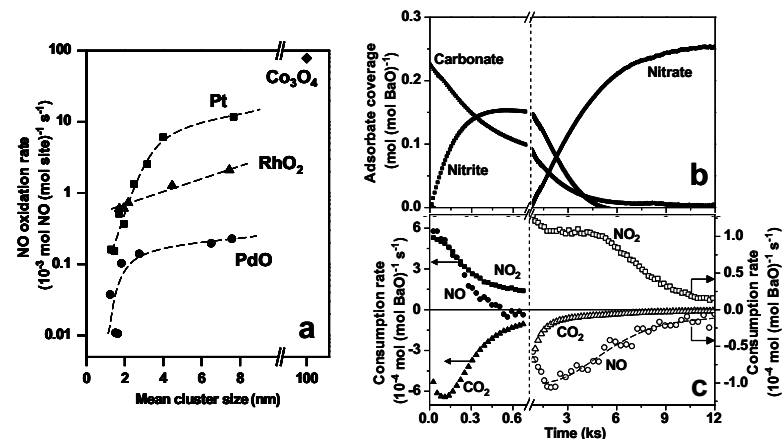


Fig. 1 (a) NO oxidation rates (603 K, 5 kPa O₂, 0.56 Pa NO₂, 110 Pa NO). (b) Coverages and (c) consumption rates on CO₂-pretreated BaO/Al₂O₃ (30 Pa NO₂, 150 Pa NO, 573 K).

NO₂ adsorption on dispersed BaO occurred concurrently with NO adsorption (Fig. 1c, 0-0.6 ks) and led to the initial formation of nitrites (Ba(NO₂)₂) that displaced pre-formed carbonates (Fig. 1b, 0-0.6 ks). Nitrite formation rates increased with NO and NO₂ pressures, but were independent of CO₂ pressure, consistent with concerted NO-NO₂ adsorption and CO₂ desorption. Nitrite and carbonate bind competitively, and equilibrium nitrite coverages were negligible at high CO₂/NO_x ratios (~10³), implying that nitrite oxidation to nitrate (Ba(NO₃)₂) is required for effective NO_x removal. Nitrate formation, however, occurs slowly in metal-free adsorbents (Fig. 1b, 1-9 ks); rates increased with [NO₂]² but were independent of NO pressure, nitrite/nitrate coverages, and temperature, suggesting N₂O₄ is a required oxidant that forms by a barrierless gas-phase NO₂ dimerization step. Pt clusters in close (but not atomic) proximity to nitrites facilitated faster nitrate formation; rates were linearly proportional to the residual nitrite coverage and the NO₂ pressure, were inhibited by NO, and depended strongly on temperature, consistent with a bifunctional mechanism in which Pt establishes equilibrium between NO₂ reactants and N₂O₄ intermediates that react subsequently on nitrite binding sites. Catalysts thus provide a crucial, yet unrecognized, pathway for converting nitrites to nitrates.

Significance

Synergistic reactions on catalysts and adsorbents allow efficient NO_x trapping. NO₂ adsorption on BaO increases NO oxidation rates on catalysts inhibited by NO₂; catalysts allow NO₂ adsorption in CO₂-rich streams by forming oxidants that convert nitrites to more stable nitrates.

References

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