NO Oxidation Catalyzed by Pt: Elementary Steps, Structural Effects, and Synergistic Effects of NO₂ Adsorption Sites

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Introduction

NO_x storage materials, containing noble metal catalysts and alkali or alkaline earth adsorbents, offer a promising strategy to remove toxic residues from the exhaust of lean combustion exhaust. NO oxidation rate data on Pt/Al_2O_3 are consistent with kinetically-relevant molecular adsorption of O_2 on Pt clusters nearly-saturated with chemisorbed oxygen (O*) [1]. Turnover rates were found to be higher on large clusters [1], but it remains unclear whether size effects reflect the formation of inactive oxides or the prevalence of stronger Pt-O bonds on surfaces of small clusters [1]. NO oxidation is inhibited by NO₂ products; therefore, the efficient use of NO oxidation catalysts in lean NO_x storage systems requires rapid NO₂ removal by adsorption sites, which occurs via the formation of nitrites and their subsequent oxidation to nitrates, but the identity of the oxidant remains controversial [2].

Materials and Methods

 Pt/Al_2O_3 catalysts and $BaCO_3/Al_2O_3$ adsorbents were prepared by incipient wetness impregnation. Metal dispersions were characterized by H_2 chemisorption (Quantachrome Analyzer). NO oxidation and NO₂ adsorption rates were measured on physical mixtures of catalysts and adsorbents at 553-673 K and 10-160 Pa NO, 10-120 Pa NO₂, and 250-7000 Pa O₂. Carbonates, nitrites, and nitrates bound on the adsorbents were detected from their infrared spectra at during adsorption and reaction.

Results and Discussion

Kinetic measurements suggest that NO oxidation rates on Pt catalysts are proportional to prevalent O_2 pressures and the concentration of vacancies within chemisorbed oxygen monolayers. NO2 inhibits NO oxidation catalysis by reacting with vacancies to form NO and chemisorbed oxygen in quasi-equilibrated steps. The resulting O* coverage is in equilibrium with a virtual oxygen pressure, given by $[NO_2]^2 [NO]^{-2} K_R^{-1}$, where K_R is the equilibrium constant for the overall NO oxidation stoichiometric reaction. The elementary steps governing O_2 activation and formation on surfaces nearly saturated with O* were probed by comparing reverse rates of NO oxidation and ¹⁶O₂-¹⁸O₂ isotopic exchange. Rates of both reactions are similar at identical (virtual) O₂ pressures, confirming that O₂ dissociates on only surface vacancies during NO oxidation and that these virtual pressures rigorously describe oxygen chemical potentials. NO oxidation and ¹⁶O₂-¹⁸O₂ exchange rate constants are consistent with immobile O* species and transition states; apparent activation energies reflect predominantly the adsorption enthalpy of dissociated O* on Pt surfaces. Rate constants for NO oxidation, NO₂ decomposition, and O₂ isotopic exchange increase as the Pt dispersion decreases (Figure 1), because of the prevalence of coordinatively unsaturated atoms, with high oxygen binding energy, on small clusters. These size effects on the reactivity of clusters for oxidation reactions are general and reflect metal-adsorbate binding energies that determine the

concentration of vacancies on metal or oxide clusters saturated with oxygen [3,4]. Oxygencovered Pd metal clusters show lower reactivity than PdO clusters for CH₄ combustion, suggesting that bulk oxidation weakens metal-oxygen bonds at surfaces and increases vacancy concentrations during catalysis, consistent with bond order conservation concepts [4].

The initial NO oxidation rates after exposure of reactants to fresh catalyst-adsorbent mixtures depend inversely on Pt_s/Ba atomic ratios (Figure 2), because adsorption site decrease prevalent NO_2 concentrations. The proximity of sites for adsorption and catalysis favors NO oxidation rates, up to distances that eliminate NO_2 concentration gradients between these sites (~400 µm). Infrared spectra for $BaCO_3/Al_2O_3$ (573 K, 4 Pa NO_2 , 410 Pa NO) showed that surface nitrites (1210 cm⁻¹) rapidly displace carbonates (1392, 1440 cm⁻¹). Nitrate formation occurs on relevant time scales for NO_2 pressures (~100 Pa) above those prevalent during NO_x storage.



Figure 1. Rate constants for NO oxidation on Pt/Al₂O₃ at 603 K from this work (\blacktriangle), and from [1] (\blacksquare); and for ¹⁶O₂-¹⁸O₂ isotopic exchange extrapolated to 603 K (\blacklozenge).

Figure 2. Initial NO oxidation rates and implied NO₂/NO ratios at 573 K, 160 Pa NO, 500 Pa O₂ over 1.2 wt% Pt/Al₂O₃ (1-10 mg) and 17 wt% BaCO₃/Al₂O₃ (125 mg) mixed within pellets (\blacklozenge , \diamondsuit) and as separate pellets, 250-425 µm (\blacksquare , \blacksquare).

Significance

These results demonstrate the consequences of metal-oxygen binding energies on oxidation rates and show the importance of the synergistic effects adsorption sites for NO oxidation.

References

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