Mechanistic assessments of NO oxidation turnover rates and active site densities on WO_3-promoted CeO_2 catalysts

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A B S T R A C T

The effects of NO, NO_2 and O_2 pressures on NO oxidation rates and UV-visible spectra are used here to assess the elementary steps and the number and type of redox-active sites involved in NO oxidation on CeO_2 promoted by contact with WO_3 domains. The reversible chemisorption of O_2 on vacancies (*) and the subsequent dissociation of O_2^* assisted by NO to form O^* and NO_2 are the kinetically-relevant steps on surfaces with O^* coverage set by $NO-NO_2$ equilibration. $O_{2p} \rightarrow Ce_{4f}$ ligand-to-metal charge transfer (LMCT) bands probe the rate constants for O_2^* formation and desorption at catalytic conditions; their comparison with those derived from rate data confirms the mechanistic conclusions and the involvement of CeO_2 surfaces promoted by contact with WO_3 domains. These data allow an accurate assessment of the number and type of redox-active sites, thus allowing reactivity comparisons among catalysts based on turnover rates. The number of redox-active sites increased with increasing W surface density (2.1–9.5 W/nm^2), but NO oxidation turnover rates were essentially unchanged. These elementary steps and active structures differ markedly from those that mediate NO oxidation on Pt, PdO, RhO_2 and Co_3O_4 catalysts. Turnover rates are similar on WO_3/CeO_2 and Pt-based catalysts at practical temperatures of diesel exhaust treatment ($\sim$500 K), but WO_3/CeO_2 catalysts exhibit much higher rates based on catalyst mass (>10-fold), thus rendering useful as less costly and more resilient alternatives to noble metals. These findings illustrate a method to probe the number and type of redox-active sites and conceptual insights into the pathways that mediate the chemisorption and activation of O_2 by isolated vacancies and the subsequent dissociation of O=O bonds by assistance from co-reactants.

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1. Introduction

Nitrogen oxides [NO_x (NO and NO_2)] from hydrocarbon combustion exhaust cause photochemical smog, acid rain, and stratospheric ozone depletion [1,2]. NO_x can be converted into dinitrogen (N_2) via reactions with ammonia (NH_3) in the presence of dioxygen (O_2) via selective catalytic reduction (SCR) processes [3]. The presence of equimolar $NO-NO_2$ mixtures leads to faster reactions ("fast SCR" ($NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$)) than in the absence of NO_2 ($2NO + \frac{1}{2}O_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$) [4]. The prevalence of NO in effluent streams thus requires NO oxidation to NO_2 for the efficient performance of NH_3-NO_x processes. Metals (Pt [5,6]) and their oxides (PdO [7], RhO_2 [8], Co_3O_4 [8,9], MnO_x

[10]) catalyze these reactions at relevant exhaust conditions; their active sites and reaction mechanism are well understood and involve O_2 activation on vacancies present at surfaces nearly saturated with oxygen adatoms as the kinetically-relevant steps [5–8]. These catalysts, however, are also effective in NH_3 oxidation to NO_x, thus degrading the effectiveness of SCR abatement strategies [11,12].

Recently, Cu cations exchanged into small-pore molecular sieves with chabazite (CHA) frameworks (SSZ-13, SAPO-34) have been found to exhibit excellent SCR activity and hydrothermal stability [13–15]. Theory and experiments have suggested that NO oxidation proceeds via (i) molecular O_2 adsorption on Cu dimers to form $Cu-O_2-Cu$ as a side-on peroxide (η^2-O_2), (ii) NO(g) reactions with these species to form $Cu-O-Cu$ and NO_2(g), and (iii) O-atom removal from $Cu-O-Cu$ by NO(g) to form another NO_2 molecule, with step (ii) as the kinetically-relevant step [16].

Tungsten (W) and niobium (Nb) oxides dispersed on ceria (CeO_2) also exhibit high SCR activity, as well as excellent N_2 selectivity and resistance to sulfur dioxide (SO_2), over a broad temper-

ature range (473–723 K) [17–26]. These catalyst systems are based on non-toxic elements and include WO_3-CeO_2 [17–19], WO_3-CeO_2-TiO_2 [20,21], WO_3-CeO_2-ZrO_2 [22,23], Nb_2O_5-CeO_2 [24,25], and Nb_2O_5-WO_3-CeO_2-TiO_2 compositions [26]. The requirement for acid and redox sites, proposed for SCR on V_2O_5-TiO_2 [27], may also account for the promotional effects of WO_3 on CeO_2, via the formation of acid centers in WO_3 domains [19]. SCR reactions are likely to require acid sites, but such sites do not catalyze NO oxidation at relevant SCR conditions (473–723 K), thus preventing the involvement of fast-SCR pathways that require NO_2 molecules [28,29]. The redox properties of CeO_2 lead to low but detectable NO oxidation reactivity; such properties have been implicated in its promotion of the SCR-reactivity of TiO_2 [30]. Hence, NO oxidation reactivity measurements provide an effective probe of the presence and reactivity of redox sites in these catalysts.

Intrapellet physical mixtures of ZrO_2-supported WO_3 (denoted WO_3/ZrO_2), a prototypical acid catalyst, with CeO_2 led to higher SCR rates but did not influence NO oxidation rates [31]. The dispersion of WO_3 domains onto CeO_2 (WO_3/CeO_2), however, increased both SCR and NO oxidation rates over those on pure CeO_2 [31], suggesting that redox-active sites form via atomic contact between WO_3 domains and CeO_2 surfaces. The mechanistic details of NO oxidation and the nature of such sites on these catalysts remain unclear and are the subject of the present study.

Here, we report NO oxidation turnover rates (normalized by the number of redox-active sites) under conditions of strict kinetic control on WO_3/CeO_2 (2.1–9.5 W nm^{-2}) and CeO_2 to assess the identity and kinetic relevance of the elementary steps involved. We provide evidence for the kinetic relevance of steps involving the reversible molecular adsorption of O_2 followed by the irreversible dissociation of the chemisorbed oxygen molecules (O_2^*) assisted by interactions with NO(g). These conclusions are consistent with UV-visible spectra acquired at steady-state and transient conditions, which detected reversible changes in the ligand-to-metal charge transfer (LMCT) band shifts corresponding to O_2^* species. The number and reactivity of such O_2^* species, formed at reduced Ce centers promoted by interactions with WO_3 domain, were determined from these spectroscopic data and used to normalize rates, thus allowing an accurate determination of active site densities by comparing kinetic parameters obtained from NO oxidation rate data and from LMCT spectral features. These data allowed the first rigorous assessment of the number of active sites involved in catalytic turnovers through the analysis of transient spectra to obtain intrinsic rate constants (i.e. per site) for the kinetically-relevant O_2 activation steps. The quantitative interpretation of the effects of W density on the number of active sites provides fundamental and conceptual insights into the type and genesis of the redox-active sites that form by atomic contact between CeO_2 surfaces and WO_3 domains.

2. Experimental methods

2.1. Catalyst preparation and characterization

CeO_2 powders (Rhodia, 150 m^2 g^{-1}) were heated to 873 K at 0.08 K s^{-1} in flowing air (0.3 cm^3 s^{-1} g^{-1}) and held for 10 h. These CeO_2 powders (75 m^2 g^{-1}, BET surface area) were impregnated to incipient wetness using aqueous ammonium metatungstate solutions ((NH_4)$_6$$H_2$$W_{12}$$O_{40}$, Strem Chemicals, 99.9%) containing the desired amount of W, treated in static ambient air at 383 K overnight, and then, treated in flowing dry air (0.8 cm^3 s^{-1} g^{-1}) at 823 K (0.08 K s^{-1}) for 3 h. WO_3/CeO_2 samples prepared with 4, 8 and 13 wt% WO_3 gave BET surface areas of 49, 39 and 35 m^2 g^{-1}, corresponding to 2.1, 5.3 and 9.5 W-atom nm^{-2} surface densities, respectively. BET surface areas were determined using the single-

point method (Micro Data, Micro Sorp 4232II) after treatment at 523 K for 0.33 h in N_2 flow (0.4 cm^3 s^{-1}).

WO_3/ZrO_2 samples were also prepared in a similar manner to WO_3/CeO_2. ZrO_2 powders (Daiichi Kigenso Kagaku Kogyo, RC-100, 114 m^2 g^{-1}) were impregnated using an (NH_4)$_6$$H_2$$W_{12}$$O_{40}$ aqueous solution and treated using the same protocols as for WO_3/CeO_2. Samples with 10 and 15 wt% WO_3 concentrations gave BET surface areas of 101 and 93 m^2 g^{-1}, leading to 2.6 and 4.2 W-atom nm^{-2} surface densities, respectively.

2.2. Steady-state NO oxidation rate measurements

The reactant gases (Praxair, 3% NO/He, 1% NO_2/He, 20% O_2/He) and the He diluent (Praxair, 99.999%) were metered using electronic controllers (Porter Instruments) to give the desired reactant pressures (0.03–0.43 kPa NO, 0.01–0.23 kPa NO_2, 1–18 kPa O_2). The inlet and outlet NO and NO_2 concentrations were measured with an infrared analyzer (MKS Multi Gas Analyzer 2030, 2-cm^3 cell; 2-cm path length, 353 K).

Catalyst samples were pelleted and sieved to retain particles 125–180 μm in diameter and then diluted with quartz powder (Fluka; 125–180 μm) at quartz/catalyst mass ratios of 0.3–10 for WO_3/CeO_2 and 0–3 for CeO_2. Samples were held on a porous quartz frit within a U-shaped quartz tube (10 mm) kept at constant temperature (±0.3 K) by a resistively heated furnace. Temperatures were measured using K-type thermocouples placed at the outer reactor wall and controlled electronically (Watlow Series 96). The catalyst samples (WO_3/CeO_2; 0.035–0.9 g, CeO_2; 0.3–1.4 g, WO_3/ZrO_2; 1.4 g) were heated to 673 K at 0.08 K s^{-1} in flowing 5% O_2/He (3.3 cm^3 s^{-1}) and then exposed to the reactants (0.1 kPa NO, 0.05 kPa NO_2, 5 kPa O_2, 3.3 cm^3 s^{-1}) at 673 K for 2 h before rate measurements. The rates were measured at a standard condition (0.1 kPa NO, 0.05 kPa NO_2, 5 kPa O_2, 3.3 cm^3 s^{-1}) after each experiment at different conditions to ensure that changes in structure or reactivity with time did not influence the measured kinetic responses. NO_2 formation was not detected on the quartz powder used as diluent or in any transfer lines (Figs. S1 and S2 in Supplementary Information (SI)).

Intrapellet concentration or temperature gradients were ruled out by mixing WO_3/CeO_2 with fumed SiO_2 (Fluka) and then pelleting and sieving to retain 125–180 μm aggregates (intrapellet SiO_2/catalyst = 3; quartz/catalyst = 24). NO oxidation rates were unaffected by intrapellet or bed dilution (Figs. S2 and S3; SI), indicating that the local concentrations and temperatures are identical to those measured in the fluid phase; therefore, the rates reported here reflect the intrinsic chemical reaction rates devoid of transport artifacts.

2.3. Diffuse reflectance UV-visible spectroscopy

Diffuse reflectance UV-visible spectra were collected using a Cary 4 Varian spectrophotometer with a Harrick Scientific diffuse reflectance attachment (DRP-XXX) and a reaction chamber (DRA-2CR). The reaction cell was modified with a quartz frit to support catalyst samples and to improve flow and temperature uniformity. Spectra were acquired in the 1.55–6.2 eV range (0.0002–0.015 eV step, 360 s per spectrum) in 2.5–70 kPa O_2 in He, 5 kPa H_2 in He, or pure He streams. The Kubelka–Munk function [32] was used to convert reflectance (R_{sample}) into pseudo-absorbances ($F(R_\infty)$) using the reflectance of quartz powder (Fluka) as a reference white reflector ($R_{reference}$).

$$R_\infty = R_{sample}/R_{reference} \tag{1}$$

$$F(R_\infty) = (1 - R_\infty)^2/2R_\infty \tag{2}$$