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Structure sensitivity via decoration of low-coordination exposed metal atoms: CO oxidation catalysis on Pt clusters

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ABSTRACT

The effects of CO and O_2 concentrations on turnover rates and $^{18}O_2$–$^{16}O_2$ exchange rates during catalysis are used to assess the relevant elementary steps and the consequences of Pt coordination for CO oxidation catalysis at moderate temperatures (700–800 K) on supported Pt clusters 1.8–25 nm in diameter. Turnover rates, measured under conditions of strict kinetic control, are proportional to O_2 pressure and inhibited by CO; these data are consistent with kinetically-relevant O_2 dissociation steps on cluster surfaces covered partially by chemisorbed CO (CO^*). O_2 dissociation also limits CO oxidation rates at higher temperatures, which lead to bare Pt surfaces, and at lower temperatures, where saturation CO^* coverages require O_2 dissociation to be assisted by CO^* because of a dearth of vacant sites. At the intermediate temperatures used here, kinetic coupling between irreversible O_2 activation and CO^* reactions with O^* causes edge and corner atoms to become decorated by unreactive O^* species; consequently, turnovers occur predominantly on exposed low-index planes, which account for a decreasing fraction of exposed atoms with increasing metal dispersion. These decoration effects confer the appearance of structure sensitivity to the prototypical structure insensitive reaction by rendering only a fraction of exposed metal atoms able to turnover. These active sites, residing at exposed low-index planes, show similar CO^* binding energies on large and small Pt clusters, but their relative abundance decreases as clusters become smaller, leading to a sharp decrease in turnover rates with increasing Pt dispersion. These trends stand in marked contrast with the absence of cluster size effects on CO oxidation rates at low temperatures, where high CO^* coverages dampen the intrinsic site non-uniformity of metal clusters, and at high temperatures, where all Pt atoms remain accessible irrespective of coordination and active for catalytic turnovers.

1. Introduction

The catalytic oxidation of CO has been widely studied at low temperatures (360–473 K) because of its relevance in the removal of CO from H_2-rich streams [1–3] and from automotive exhaust [4,5]. Fewer studies are available at higher temperatures, in spite of its importance in the oxidation of trace CO components in combustion effluent streams [6,7]. Its molecular simplicity and detectable rates over a wide temperature range have made this reaction a ubiquitous choice in probing fundamental concepts in heterogeneous catalysis and specifically the effects of cluster size and surface coordination on catalytic reactivity [1,3].

At low temperatures, CO oxidation occurs on surfaces nearly saturated with chemisorbed CO (CO^*), but CO^* coverages decrease with increasing temperature and unoccupied surface atoms ($*$) ultimately replace CO^* as the most abundant surface intermediates (MASI). On surfaces covered with CO^*, turnover rates depend weakly on Pt cluster size [3,8], because CO^* monolayers appear to dampen the consequences of the intrinsic non-uniformity of small Pt clusters, which would be expected to cause strong size effects [9]. Such non-uniformity is likely to become increasingly influential as surface atoms with varying coordination and binding properties become accessible at lower CO^* coverages.

Kinetic, isotopic, and infrared data and their mechanistic interpretation indicate that CO oxidation at low temperatures (350–450 K) on Pt proceeds via kinetically-relevant O_2 activation steps assisted by CO^* [3], consistent with the effects of CO and O_2 concentrations on turnover rates:

$$r_{CO} = \frac{K_{O_2} k_{O_2^*-CO^*}}{K_{CO}} \frac{[O_2]}{[CO]} = k_{eff} \frac{[O_2]}{[CO]} \tag{1}$$

In this equation, $k_{O_2^*-CO^*}$ is the rate constant for the activation of O_2^* assisted by interactions with vicinal CO^* species and K_{O_2} and K_{CO} are the equilibrium constants for the molecular adsorption of O_2 and CO, respectively. At low O_2/CO ratios, CO^* can instead react with another CO^* to form CO_2 and chemisorbed carbon (C^*) [10]. At these

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low temperatures, turnover rates and activation energies depend only weakly on Pt cluster size (1.2–20.0 nm) [3,8], in spite of marked differences in the average coordination of exposed Pt atoms in clusters within this size range. It appears that the binding properties of isolated vacancies within dense CO* overlayers depend strongly on intermolecular interactions but much more weakly on the coordination of exposed metal atoms [3].

At high temperatures (800–900 K), Pt clusters remain essentially uncovered during CO oxidation and turnover rates become proportional to O_2 pressure and insensitive to CO pressure [11]:

$$r_{CO} = K_{O_2} k_O [O_2] = k_{eff} [O_2] \tag{2}$$

as first proposed by Langmuir [12] on bare Pt wires at high temperatures. In this kinetic regime, O_2 dissociation on bare Pt clusters limits CO oxidation rates and measured rate constants (k_{eff}) reflect the product of the equilibrium constant for molecular O_2 adsorption (K_{O_2}) to form O_2^* and its dissociation rate constant (k_O) on essentially bare Pt clusters. Their product, as it appears in k_{eff}, reflects differences in enthalpy (and entropy) between O_2(g) and the transition state that mediates O_2 dissociation elementary steps on such surfaces. O_2 dissociation is essentially barrierless (<3 kJ mol^{-1}) on bare surfaces and independent of the coordination of exposed atoms [13], as expected for the early nature of the transition states involved in these very exothermic steps; such transition states exhibit little if any product character and cannot sense changes in O* binding energy caused by concomitant changes in the size of metal cluster or in the average coordination of metal atoms exposed at their surfaces. As in the case of CO*-covered surfaces at low temperatures, CO oxidation turnover rates and activation barriers are insensitive to cluster size at high temperatures [13], albeit for mechanistic reasons that differ markedly in these two extreme kinetic regimes.

The mechanism and site requirements for catalytic CO oxidation on Pt at intermediate temperatures remain unclear and reported rate equations differ significantly among several studies. Rates are proportional to O_2 pressures in most of the studies reported, but kinetic orders in CO range from −0.3 (Pt supported on fiber glass; 475–650 K; [14]), to −0.5 (Pt monolith; 475–650 K; [15]) and even −1 (Pt(100) single-crystal; above 550 K; [8]).

Here, we report CO turnover rates measured under conditions of strict kinetic control on Pt clusters (1.8–25 nm mean cluster diameter) in this intermediate temperature range (723–793 K) and interpret the observed kinetic response and effects of cluster size in mechanistic terms. Measured turnover rates are consistent with kinetically-relevant O_2 dissociation on cluster surfaces partially covered by CO*. The rate constants for these O_2 dissociation steps are much smaller on small than on large Pt clusters, but without concomitant changes in measured CO adsorption equilibrium constants. We conclude that small clusters retain a smaller fraction of their exposed atoms available during catalysis than larger clusters, but that these active regions, residing at low-index planes with more highly coordinated exposed atoms, are similar in binding and reactivity on clusters of different size.

CO oxidation on Pt clusters occurs predominantly on low-index planes, which are more prevalent on larger clusters, because low-coordination sites, such as corners and edges, become decorated by strongly-bound and less reactive chemisorbed oxygen atoms. Such phenomena, often cited without direct evidence to account for cluster size effects, are shown here to account for the similar binding of CO* species on clusters that differ in size (1.8–25 nm) and in CO oxidation turnover rates. Residual undecorated surface regions account for the observed CO oxidation reactivity; these regions consist of low-index planes, where O* and CO* bind more weakly than on Pt atoms with lower coordination at corners and edges.

2. Experimental methods

2.1. Catalysts synthesis procedures

Supported Pt catalysts (0.2–0.5% wt.) were prepared by incipient wetness impregnation of SiO_2 (Davisil LS150A, Grace Davison; 100–150 μm; 340 m^2 g^{-1}) with aqueous hexachloroplatinic acid ($H_2PtCl_6(H_2O)_6$, Aldrich, CAS #16941-12-1). Silica supports were treated in flowing dry air (Praxair, 99.99%, 0.8 cm^3 g^{-1} s^{-1}) by heating at 0.083 K s^{-1} to 1073 K and holding for 3 h before contacting SiO_2 powders with the impregnating solutions. After impregnation, samples were treated overnight at 373 K in stagnant ambient air and individual portions were treated in flowing dry air (Praxair, 99.99%, 0.8 cm^3 g^{-1} s^{-1}) to different temperatures (823–973 K; 0.083 K s^{-1}) for 5 h; the intention and the observed effects of these treatments was to vary the Pt dispersion and cluster size over a range that is expected to cause significant changes in the coordination of exposed metal atoms (1.8–25 nm). Samples were then cooled to ambient temperature in flowing dry air, flushed with He, and exposed to 10% H_2/Ar (Praxair, certified standard, 0.8 cm^3 g^{-1} s^{-1}) by heating to 823 K (at 0.083 K s^{-1}) and holding for 3 h. This treatment was followed by cooling in He (Praxair UHP grade, 0.8 cm^3 g^{-1} s^{-1}) to ambient temperature and exposing samples to 1% O_2–He flow (Praxair certified standard, 0.8 cm^3 g^{-1} s^{-1}) for 4 h to passivate cluster surfaces before exposure to ambient air.

The number of Pt atoms exposed at cluster surfaces was measured from volumetric uptakes of strongly chemisorbed H_2 at 313 K (Quantasorb Chemisorption Analyzer; Quantachrome Corp.) by extrapolating isotherms (1–50 kPa H_2 pressure) to zero H_2 pressures, as reported elsewhere [16]. Mean cluster diameters were estimated from dispersion values by assuming hemispherical clusters with the bulk density of Pt metal (21.5 g cm^3; [17]).

2.2. Turnover rate and selectivity measurements

Catalytic CO oxidation rates were measured at 453–793 K using a quartz tube (8.1 mm inner diameter) with a K-type thermocouple at its external wall. Catalysts (0.2–0.5% wt. Pt/SiO_2) were diluted with inert SiO_2 (Davisil LS150A) to form mixtures with SiO_2/catalyst intraparticle mass ratios (λ) of 100–300 and then pelleted and sieved to retain 100–250 μm aggregates. These aggregates were then diluted with acid-washed quartz granules (100–250 μm, Fluka, #84880) at quartz/catalyst mass ratios (α) of 8000–30,000. Before dilution, SiO_2 (Davisil LS150A) and acid-washed quartz (Fluka) diluents were treated in dry air (Praxair, 99.99%, 0.8 cm^3 g^{-1} s^{-1}) at 1123 K (for 5 h) and 1173 K (for 2 h), respectively. Diluents alone were tested at the conditions of catalytic measurements and did not show detectable reaction rates.

Reactants were metered using electronic flow controllers (Porter, type 201) using 1% CO/He (Praxair certified standard), 5% O_2/He (Praxair certified standard), 1% O_2/He (Praxair certified standard), O_2 (Praxair UHP grade), and He (Praxair UHP grade). Samples were treated in 5% H_2/He (Praxair UHP grade; 1.67 cm^3 s^{-1}) by heating to 773 K at 0.083 K s^{-1} and holding for 600 s before rate measurements, and the lines were purged with He before introducing reactants. Reactant and product concentrations were measured using an Agilent 3000A Micro GC equipped with Poraplot Q and Mol Sieve 5A columns and thermal conductivity detectors.

2.3. Isotopic exchange measurements

$^{16}O_2$–$^{18}O_2$ exchange rates were measured using the same reaction system and treatment protocols as in the case of CO–O_2 reactions. A mixture of 5% $^{18}O_2$/He (Isotec, 97% at. ^{18}O) was used to carry out CO–$^{16}O_2$–$^{18}O_2$ and $^{16}O_2$–$^{18}O_2$ reaction experiments. The concentrations of the various dioxygen and carbon dioxide isotopologues