

Oxidation

Catalytic Oxidation of CO with N₂O on Gas-Phase Platinum Clusters**

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Herein we report the observation of the full catalytic cycle of CO oxidation with N₂O on cationic platinum clusters for Pt_n⁺, *n* = 6–8, in the gas phase studied by Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry. Platinum is

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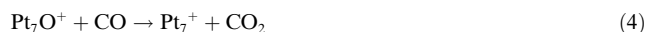
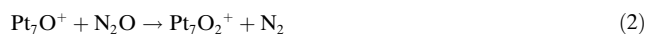


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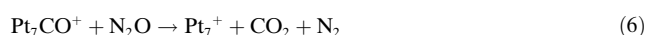
the key catalytic metal for a variety of industrial and environmental applications, for example, it catalyzes the oxidation of CO with O₂ in catalytic converters. This reaction has been studied in detail on surfaces.^[1] In the present study, N₂O was chosen as oxidant because small platinum clusters can undergo loss of platinum atoms by formation of PtO₂ by reaction with O₂.^[2] Gas-phase reactivity studies with bare transition-metal ions and clusters have been a useful tool to elucidate elementary steps in catalysis.^[3–6] Irion and co-workers demonstrated the catalytic formation of benzene from ethylene catalyzed by Fe₄⁺ in the gas phase,^[7] during which collision-induced desorption of C₆H₆ from the cluster was necessary to close the catalytic cycle. Ervin and co-workers demonstrated that the elementary steps of the catalytic cycle of the oxidation of CO with N₂O are possible on anionic platinum clusters.^[8–11] Schwarz and co-workers showed that the platinum cation Pt⁺ already exhibits catalytic activity, including full cycles of CO and methane oxidation.^[12–18] Andersson and Rosén provided strong evidence for catalytic oxidation of H₂ with O₂, forming H₂O on neutral platinum clusters in a flow reactor, albeit without resolving the detailed kinetics of the reaction.^[19] Previous studies of gas-phase platinum clusters^[1,8–11,19–28] were limited in size range and mass resolution by the use of platinum targets with natural isotope distribution. A laser vaporization source requires only minor amounts of materials, permitting work with isotopically enriched samples.^[29] We recently showed that full kinetic information of gas-phase reactions of cationic and anionic platinum clusters with up to 24 atoms can be obtained by using nearly pure ¹⁹⁵Pt.^[30] This size range is vital for comparison with the reactivities of size-selectively deposited clusters on surfaces, as studied for example, by Heiz et al.^[31,32]

When platinum cluster cations in a size range from 5 to 10 are stored in the ICR cell together with a 1:6 mixture of CO and N₂O, for some cluster sizes sequential addition of CO is observed, while for others, a steady state between the bare platinum cluster and its oxides is established. Although Pt₅⁺ forms Pt₅O⁺ and Pt₅O₂⁺, it efficiently reacts by attaching CO molecules. Pt₆⁺ reaches a steady state with Pt₆O⁺, and, to a small extent, Pt₆O₂⁺ and Pt₆O₃⁺ are also visible. Pt₇⁺ establishes a steady state with Pt₇O⁺ and Pt₇O₂⁺ in a ratio of about 1:2:4. Pt₈⁺ behaves somewhat similarly to Pt₇⁺, with Pt₈⁺ and Pt₈O⁺ as dominant species. Pt₉⁺ and Pt₉O⁺ keep a constant branching ratio, but their intensities decrease, because Pt₉⁺ sequentially attaches CO ligands. Pt₁₀⁺ efficiently attaches CO without any indication of catalytic activity.

Mass-selection experiments confirm that a steady state is indeed established for the Pt₇⁺ group. When Pt₇O⁺ was mass selected after 2 s, the constant intensity ratio between Pt₇⁺, Pt₇O⁺, and Pt₇O₂⁺ is again established within 3 s after mass selection, which proves that catalytic oxidation of CO takes place, involving the four reactions [Eqs. (1)–(4)]:



After very long reaction delays of 150 s, Pt₇CO_{8–10}⁺ species are observed to a very small extent. Evidently, by addition of multiple CO molecules, some bare Pt₇⁺ ions are removed from the catalytic cycle. To learn more about this process of catalyst poisoning, and to establish the number of CO molecules necessary to quench the oxidation reaction, we changed the experimental conditions in favor of poisoning. A 5:3 mixture of CO and N₂O was used in the ICR cell, and Pt₇CO⁺ was mass selected after 1 s. Subsequently, Pt₇CO⁺ is (with almost equal probability) either converted back into Pt₇⁺, which becomes available for the catalytic cycle described above, or it attaches a second CO molecule to form Pt₇(CO)₂⁺ [Eqs. (5)–(7)]:



Mass selection of Pt₇(CO)₂⁺ under otherwise similar conditions shows efficient addition of further CO molecules, whereas Pt₇CO⁺ is barely visible over the full course of the reaction. This observation unambiguously shows that a second CO ligand effectively poisons the cluster, although a minor contribution of CO₂ formation, at most 10 % of the efficiency for Pt₇CO⁺, cannot be fully excluded. The cluster then presumably adds CO molecules until the surface is fully saturated [Eq. (8)]:

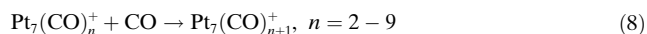


Figure 1 shows the kinetics of the Pt₇⁺ catalytic cycle when using a 1:6 mixture of CO and N₂O without mass selection, as this yields the best signal to noise ratio. To decrease the number of fit parameters, we have used the previously published absolute rate constants of Equations (1) and (2).^[30] In addition, the rate constant of Equation (6) was taken from the mass selection of Pt₇CO⁺. Absolute rate constants and reaction efficiencies of Equations (1)–(7) are summarized in Table 1. As seen in Figure 1, the steady state between Pt₇⁺, Pt₇O⁺, Pt₇O₂⁺, and Pt₇CO⁺ is established within 5 s. Towards longer reaction times, the intensities slowly decrease, and the poisoned clusters become more and more intense. By extrapolating the exponential decrease of the ions involved in the catalytic cycle, the active lifetime of a cluster in the cycle is estimated to be 750 s. From the reaction rate constants and the intensities of the reactant ions in Equations (3), (4), and (6), one can estimate that each Pt₇⁺ cluster converts 0.687 CO molecules into CO₂ per second. Over the lifetime of the cluster in the cycle, this amounts to a total of 515 CO₂ molecules formed.

The full catalytic cycle together with the poisoning mechanism is summarized in Scheme 1. Efficient catalytic conversion of CO into CO₂ is achieved in three different ways, either by CO colliding with the oxide species Pt₇O⁺ or Pt₇O₂⁺ (Equations (3) and (4)), or by N₂O oxidizing preadsorbed CO

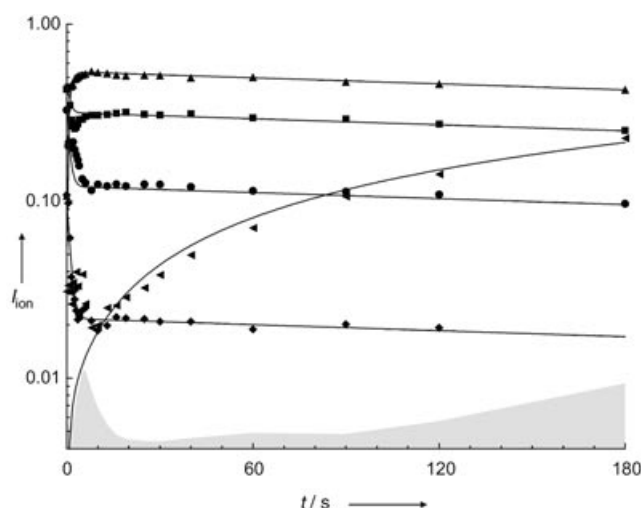
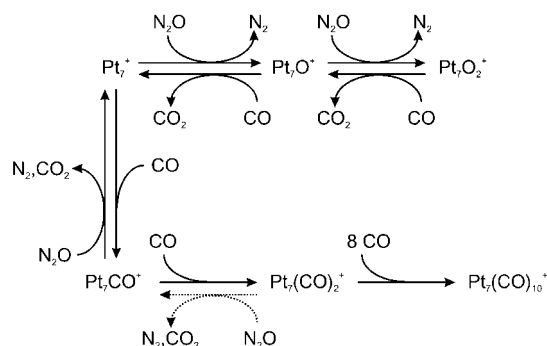


Figure 1. Kinetic fit of the Pt_7^+ reactions with a 1:6 mixture of CO and N_2O . Pt_7^+ (●) reacts very fast to form Pt_7O^+ (■) and Pt_7O_2^+ (▲). The described steady state is established between the three species within 5 s. Pt_7^+ also reacts efficiently with CO to form Pt_7CO^+ (◆), which, in turn, can either revert back to Pt_7^+ (●) or can very slowly attach a second CO molecule to form $\text{Pt}_7(\text{CO})_2^+$. Additional CO molecules are then attached until the cluster is fully saturated. The final product of CO attachment is $\text{Pt}_7(\text{CO})_{10}^+$. The visible $\text{Pt}_7(\text{CO})_n^+$, $n = 2, 8, 9, 10$, are summed together for clarity. Owing to the low intensity of $\text{Pt}_7(\text{CO})_2^+$, it was not possible to include it separately in the fit. The gray area denotes the noise level.

Table 1: Absolute rate constants k_{abs} and efficiencies calculated from ADO theory^[37,38] for the reactions of Pt_7^+ .

Reaction	$k_{\text{abs}} [10^{-11} \text{ cm}^3 \text{ s}^{-1}]$	Efficiency [%]
[Eq. (1)]	96.2	154.1 ^[a]
[Eq. (2)]	48.9	78.4
[Eq. (3)]	179.8	287.9 ^[a]
[Eq. (4)]	231.1	370.1 ^[a]
[Eq. (5)]	71.9	115.1 ^[a]
[Eq. (6)]	61.7	98.8
[Eq. (7)]	15.4	24.7

[a] Efficiencies above 100% are obtained because the collision rate is calculated by using a point-charge model, whereas the cluster has a finite size.



Scheme 1. Catalytic cycle of the Pt_7^+ ion in a 1:6 mixture of CO and N_2O . The catalytic cycle is running efficiently between Pt_7^+ , Pt_7O^+ , Pt_7O_2^+ , and Pt_7CO^+ . Additional CO molecules increasingly poison the cluster. Conversion of $\text{Pt}_7(\text{CO})_2^+$ back into Pt_7CO^+ might contribute to a minor extent to the catalytic cycle.

on Pt_7CO^+ (Equation (6)). A minor contribution from $\text{Pt}_7(\text{CO})_2^+$ to CO_2 formation is possible, but the absence of $\text{Pt}_7(\text{CO})_n^+$ with $n = 3-7$ and the appearance of the $n = 8-10$ species in the mass spectra clearly indicate that CO addition is the only significant process for $n = 3-9$.

If N_2O is present in sufficient excess, the concentration of Pt_7^+ in the steady state is small, and the catalytic cycle runs mostly through Equations (2) and (3) between Pt_7O^+ and Pt_7O_2^+ . Very few Pt_7CO^+ ions are formed and these are, in turn, almost entirely converted back into Pt_7^+ , before attachment of a second or third CO molecule can occur. This gas-phase catalytic cycle thus exhibits a typical characteristic of large-scale catalytic processes: The partial pressures of the reactants can be adjusted to suppress catalyst poisoning.

Our preliminary data for other cluster sizes indicate that the catalytic activity with respect to CO oxidation by N_2O is determined by the reactivity of the bare cluster with N_2O .^[30] This seems eminently reasonable: A high reactivity with N_2O shifts the cluster intensities in the steady state in favor of the oxide species and thus hinders the poisoning reaction by sequential CO addition to the bare cluster. For larger clusters, however, the picture becomes more complicated. Owing to their larger surface, adsorption of CO on Pt_nO^+ becomes feasible, presumably at a site that is remote from the oxygen atom. For example, for Pt_{20}^+ , it seems that $\text{Pt}_{20}\text{OCO}^+$ becomes an observable intermediate in the catalytic cycle. Such larger clusters, as well as anionic species, are currently under investigation.

Experimental Section

The experiments were performed on a modified Bruker/Spectrospin CMS47X mass spectrometer, equipped with an Apex III data station and an external homebuilt laser vaporization source described previously.^[33-36] Platinum clusters Pt_n^+ were produced by laser vaporization of a solid platinum target with the 5-ns pulse of a frequency-doubled Nd:YAG laser (Continuum Surelite II, 10 Hz, 5-mJ pulse energy), followed by supersonic expansion of the hot plasma entrained in a 50- μs helium pulse. The Pt_n^+ ions formed were transferred by a series of electrostatic lenses through four stages of differential pumping, decelerated, and stored in the ICR cell. To minimize problems associated with the isotope pattern of larger clusters, isotopically enriched platinum (97.3% ^{195}Pt , Oak Ridge National Laboratories) was used as described previously.^[30] The reactant gases CO (99.98%) and N_2O (99.8%) were admitted through two needle valves into the UHV region of the FT-ICR instruments at constant partial pressures. In the 1:6 mixture, $p(\text{CO}) = 1.6 \times 10^{-8}$ mbar and $p(\text{N}_2\text{O}) = 9.9 \times 10^{-8}$ mbar. In the 5:3 mixture, $p(\text{CO}) = 1.6 \times 10^{-8}$ mbar and $p(\text{N}_2\text{O}) = 9.8 \times 10^{-9}$ mbar. Relative rate constants were obtained by fitting the experimental data to pseudo-first-order reaction kinetics and converted into absolute rate constants and reaction efficiencies by using average dipole orientation (ADO) theory.^[37,38]

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