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Nanoparticles

“Oxidationless” Promotion of Rapid Palladium Redispersion by Oxygen during Redox CO/(NO+O_2) Cycling[**]

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The study of the behavior of palladium, and noble metals in general, in respect of fundamental gas–metal interactions and reactive chemistry, has attracted a great deal of attention over a great many years.[1–15] The intrinsic importance of a range of commercial applications of palladium—not least of which being automotive exhaust catalysis—coupled to a fundamental desire to understand the basic physics and chemistry of such interactions, are the prime drivers for this interest. In the exhaust catalysis application, the catalyst has to operate in conditions wherein the redox potential of the feedstock can change in a highly dynamic manner. Further, the interplay between oxidized and reduced phases of palladium is of central importance to palladium activity in methane oxidation catalysis.[8–10] As such, a comprehension of the dynamic redox behavior of Pd and other noble metals is of considerable importance.

Recently, we demonstrated the presence of a highly dynamic size/shape variation occurring during CO/NO cycling over 1 wt% Pd/10% (Ce,Zr)O_x/Al_2O_3 catalysts.[16] Part of this phenomenon comprises a non-oxidative, palladium-redispersion mechanism. Herein we contrast the behavior of chloride-free 2 wt% Pd/Al_2O_3 catalysts at 673 K during redox cycling using CO as the reductant, and in the absence (NO only) and presence (5 O_2:1 NO) of O_2 during the oxidizing part of the cycle. We show that, even in the presence of a relatively large amount of oxygen, oxidation cannot compete kinetically with the redispersion events. On the contrary, significant levels of O_2 in the oxidizing feed greatly enhance the degree of palladium redispersion possible before any formal oxidation of Pd^0 to Pd^{2+} can be observed.

Figure 1 shows the variation in observed Pd–Pd coordination number (CN) derived from analysis of energy-dispersive EXAFS (EDE) data (EXAFS = extended X-ray absorption fine structure spectroscopy; see also Supporting Information) in the two cases studied: the first (Figure 1, open circles) is obtained during cycling of a 2 wt% Pd/Al_2O_3 sample between flows of 5% CO/He and 5% NO/He at 673 K. The second (Figure 1, filled circles) shows results obtained when the total flow in the oxidizing cycle now comprises a mix of 5 O_2:1 NO. Figure 2 shows the result of translating this raw CN data into an average number of Pd atoms per particle. This translation is done within the framework proposed by Jentys[17] and, as such, a constant particle morphology and 0% Pd oxidation is assumed.

The overall behavior during CO/NO cycling over a 2 wt% Pd/Al_2O_3 sample is as observed previously.[16] The presence of the CeZr phase is therefore not a prerequisite and these transformations appear intrinsic to Pd nanoparticles. It further appears that, even though there are considerable error

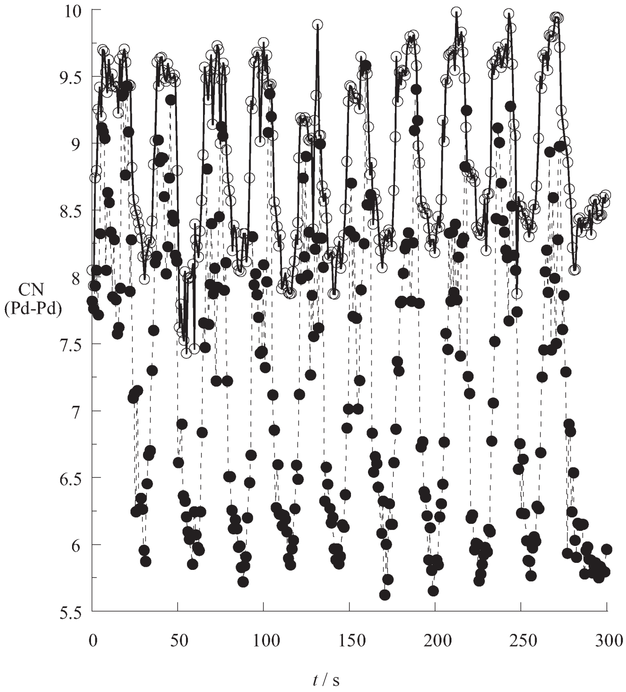

Figure 1. Variation of Pd–Pd coordination number (CN) derived during cycling experiments over 2 wt% Pd/Al_2O_3 catalysts at 673 K. ○ cycling between 75 mL min^{-1} 5% CO/He and 75 mL min^{-1} 5% NO/He; ● cycling between 75 mL min^{-1} 5% CO/He and 75 mL min^{-1} 5% (5 O_2:NO)/He.

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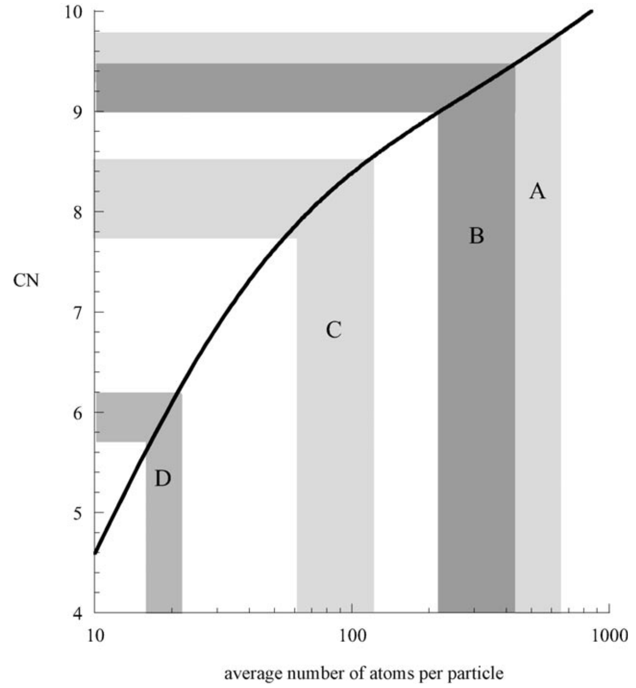

Figure 2. Implied changes in average particle atomicity during CO/NO and CO/(NO+O_2) cycling. The solid black line relates CN to an average number of atoms within a particle.[17] The shaded areas correspond to average positions within: A) CO/NO, reducing phase; B) CO/(NO+O_2), reducing phase; C) CO/NO, oxidizing phase; D) CO/(NO+O_2), oxidizing phase.

bars to be considered at the upper end of the CN scale (see Supporting Information), the presence of a considerable amount of O_2 in the oxidizing phase greatly increases the degree of redispersion obtainable from the cycling experiment. Starting from essentially the same (CN) state at $t = 0$ the two cases can be seen to diverge rapidly. In the absence of O_2 a typical cycle appears to involve particles of up to approximately 600 atoms (CN ≈ 9.5) reversibly dispersing in a few seconds into entities of approximately 100 atoms (CN ≈ 8); in the presence of an excess of O_2 in the oxidizing cycle the redispersion yields particles of around 20 atoms (CN ≈ 6).

The data contained in Figure 1 cannot, however, specifically exclude that CN changes in the oxidation cycles could be due to "static" oxidation of the outer layers of the Pd particles. Such mechanisms are well established for noble-metal particles of a wide variety of sizes and situations.[18–20] In such a case, the variation in CN can simply reflect a progressively smaller metallic Pd core surrounded by a progressively larger oxide layer. To be sure of what we are actually observing we turn to a quantitative principle component analysis (PCA)[21] using the XANES (X-ray absorption near-edge structure) region of the dispersive EXAFS to elucidate the levels of oxidation to Pd^{2+} that are found in each case during the oxidizing cycle. The results of such an analysis for a single oxidizing cycle are shown in Figure 3. Even in the presence of five-times more O_2 than NO, and within the time frame of the cycling experiment, a maximal level of approximately 15% Pd oxidation is indicated. Moreover, by far the majority of the change in CN (and in the first approximation, particle size/shape) occurs before ($<$ 3–4 seconds after the switch to an oxidizing feed) the XANES data offers any significant evidence for the presence of Pd^{2+} in the system (see Supporting Information for normalized XANES spectra and further analyses).

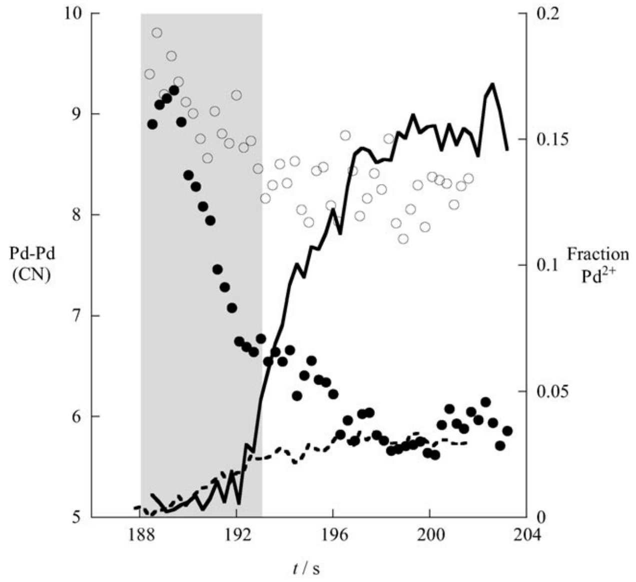

Figure 3. Temporal variation in Pd–Pd coordination (from dispersive EXAFS analysis; symbols) and %Pd^{2+} (from XANES PCA analysis; lines) observed within a single redispersion cycle. ●/—— (O_2+NO), ○/----- NO only. Within the shaded region, and with O_2 present, the Pd–Pd CN drops from around 9 to 6.5 within 2 seconds and with no obvious Pd^{2+} formation.

The simple conclusion is that, even in a 5 O_2:1 NO feed, significant Pd particle redispersion occurs before the relatively slow process of particle oxidation can begin. This situation does not rule out that further redispersion may also occur at $t > 3$ seconds as a PdO phase starts to appear—Ruckenstein and Chen[11–13] have speculated that interfacial strain between the growing PdO and metallic Pd was the source of the particle splitting and flattening that they, and more recently, Penner et al.[14] have observed. Our results show, however, that another route to the majority splitting or flattening of the Pd nanoparticles exists, and that it can precede the formation of observable levels of oxidized Pd.

As a potentially important consequence, the oxidation (and kinetics thereof) observed, do not pertain to the starting Pd particles, but to much smaller/flatter entities created as a result of the redispersion. The combination of Figures 1 and 3 shows that a rapid sintering/redispersion of Pd nanoparticles proceeds unimpeded by the presence of excess O_2; indeed the redispersion is very significantly promoted in its extent compared to the O_2-free case.

Recent X-ray scattering study of Pd supported upon MgO surfaces,[15] have also shown size and shape variation occurring at $T > 500$ K and $p_{O_2} > 10^{-6}$ mbar. Qualitatively speaking, these observations, and those made using TEM,[11–14] are in accord with the data we have obtained dynamically from a local structure point of view. Kasper et al.[15] suggested a role of oxygen spillover to "loosely bound" Pd atoms, (those at, for instance, corners of the Pd particles), as central to inducing size change in the Pd particles prior to or during oxidation: it is within this notion that a possible explanation for the enhanced magnitude of Pd redispersion in the presence of excess O_2, presents itself.

Studies of NO dissociation on model Pd/Al_2O_3 catalysts have identified a relatively stable ($600 < T_{\mathrm{desorption}} < 700$ K) atomic nitrogen species, N_a, that can be formed as a result of NO dissociation.[2,3] This atomic N_a has also been associated with adsorption at low-coordinate Pd sites. This being the case we can hypothesize that such an N_a species, formed by rapid initial dissociation of NO, can compete with O_a for adsorption at low coordinate Pd sites. As such, the degree of particle disruption that may be initiated by this mechanism may be attenuated simply as a result of the N_a species being less effective in initiating redispersion. This situation may arise as any atomic N is efficiently sequestered by adsorbed CO in the absence of O_2 and moved onto the support as transient NCO species,[16] or lost by direct recombinative desorption to yield N_2; there is also the simple possibility that the atomic N simply blocks these sites completely within the residence time of this species on the surface.

In summary we have used in situ dispersive EXAFS to show that the very rapid oxidationless dispersion of Pd/Al_2O_3 nanoparticles, of up to about 30 Å diameter, during CO/NO cycling is considerably enhanced in the presence of oxygen. At 673 K oxidation of the Pd nanoparticles only occurs after the Pd particles have undergone significant size/morphological alteration (this occurring within two seconds). Indeed, in this particle size regime, it appears that redispersion in the absence of significant Pd oxidation can be regarded as a precursor to the mechanism of oxidation (of the subsequently much smaller Pd particles) itself. As such we might place this new observation within the framework of mechanisms already proposed on the basis of static measurements,[5,7,11–15] as an initiation step that considerably redisperses Pd in its own right, and paves the way for the formation of PdO/Pd interfaces that, on a longer timescale, complete the particle splitting and redispersion process. Our results imply that, in the absence of other factors, and if the kinetics of redispersion and oxidation can be quantified and understood, the dispersion catalytic properties of such systems, can potentially be manipulated and controlled dynamically within the framework of a working process by appropriate management of the environment experienced by the catalyst.

Experimental Section

2 wt% Pd/Al_2O_3 samples were synthesized from as described elsewhere.[22] Approximately 40–50 mg of sample, sieved to a 112–80 µm fraction, are used per experiment and loaded into a DRIFTS cell modified for the synchronous collection of transmission EXAFS.[23]

Experiments were carried out on ID24 at the European Synchrotron Radiation Facility (ESRF) using a Si(311) polychromator in Bragg configuration and yielding a focal spot of approximately 150 × 300 µm.[24] A 16-bit FReLoN detector was used to collect the dispersive EXAFS data. A palladium-free "reference" sample, sieved to the same particle size fraction and presented to the X-rays in the same manner as the sample itself was used as the reference measurement.[25,26]

Samples were heated under a flow of He to 673 K and then subjected to cycles comprising alternate (CO first) flows (75 mL min^{-1}) of 5% CO/He (13.8 s) and 5% NO/He or 5% (5 O_2:NO)/He (13.8 s) whilst dispersive EXAFS was collected at a rate of 3–4 Hz. After finishing the cycle with an exposure to NO the flow is returned to He before cooling under to 300 K. Principle component (PCA) and iterative transformation factor analyses (IFTA) were made according to the methods outlined elsewhere[21] Reduction and analysis of the dispersive EXAFS data was made using PAXAS[25] and EXCURV.[26]

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