In Situ X-ray Absorption Spectroscopy Studies on Chemical Oscillations in the CO/O$_2$ System on Supported Pd Catalysts

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The combustion of carbon monoxide on transition metals is known to exhibit an intriguing oscillatory behavior in reaction rate as well as reaction temperature under certain conditions. Chemical oscillations during the oxidation of CO at atmospheric pressure on supported Pd catalysts were studied *in situ* by employing X-ray absorption spectroscopy (XAS) in an energy-dispersive mode. Self-sustained thermokinetic oscillations with a period of about 12 min were found in both reaction temperature and carbon dioxide partial pressure. Energy-dispersive XAS experiments were carried out *in situ* at the Pd K-edge (24.35 keV) during the occurrence of chemical oscillations with a time resolution of several seconds. An elliptically bent, rectangular Si(400) crystal in transmission geometry was used. From the Pd absorption spectra, a constant phase correlation of edge position (threshold energy) with respect to the observed temperature oscillations could be revealed. This points toward a periodic oxidation/reduction process accompanying the deactivation/activation cycles of the catalyst. Furthermore, an oscillatory behavior in height and position of the first Pd peak was found in the radial distribution function FT($\chi(k)$). From a comparison with theoretical cluster calculations, it can be deduced that the evaluated oscillations in Pd coordination number and Pd−Pd distance indicate an oscillatory change of the oxygen surface coverage as well as the ratio of linearly and bridged bonded carbon monoxide. Taking these surface-coverage oscillations and the periodic oxidation/reduction process into account, a surface activation/deactivation mechanism for chemical oscillations during CO oxidation on supported Pd catalyst can be confirmed. The activity of the catalyst appears to be decreased by a surface oxidation leading to an increasing concentration of linearly bonded CO molecules. Thereafter, an increasing amount of bridging CO and a decreasing amount of linearly bonded CO accompany the reduction of the catalyst and subsequently the return to the high activity branch of the reaction.

Introduction

Self-sustained oscillations in a heterogeneous catalytic reaction were first observed in 1972 in the oxidation of CO on Pt catalysts[1,2] and in the oxidation of hydrogen on nickel catalysts in 1973.[3] A close connection of the oscillations with the reaction mechanism has been proved, excluding the influence of sample or gas impurities, pressure oscillations, or temperature variations. Since then the investigation of chemical oscillations was intensively extended, and oscillatory behavior in many heterogeneous oxidation reactions has been found. Detailed reviews on this large field of interest are given by Schüth *et al.*,[4] by Slin'ko and Jaeger,[5] and by Imbihl and Ertl.[6]

Chemical Oscillations during the Oxidation of CO on Pd Catalysts. Although already extensively studied in the past, the kinetic mechanism of oscillations in the CO oxidation on supported Pd catalysts remains to be subject to controversial discussions. Kinetic oscillations in the oxidation of CO on Pd catalysts were investigated on Pd(110) single-crystal surfaces by Ehsasi[7] *et al.* and Ladas *et al.*[8] These authors suggested the slow formation and removal of subsurface oxygen as the driving mechanism for these oscillations. The same mechanism was proposed for chemical oscillations on polycrystalline Pd wires in a pressure range of $0.05 < P_{CO}/P_{O2} < 2.0$.[9]

Oscillations involving supported Pd catalysts have been investigated by Wicke *et al.*[10,11] The mechanism of these oscillations has been studied by *in situ* IR absorption measurements of two bridged and one linearly bonded form of CO. It was found that the absorbance of all chemisorbed species decreases along the ascending branch of the reaction rate and again increases along the descending branch. Therefore, the authors considered that the observed oscillations are not necessarily connected with oxidation−reduction processes.

Oscillations in the oxidation of CO on Pd supported on zeolites have been studied by Jaeger *et al.*[12,13] The authors suggested a periodic oxidation−reduction process as the driving mechanism. In the high-rate branch of the reaction a surface oxide may form on the heated surface leading to a decrease in the catalysts' activity and the reaction temperature. Thereafter, CO accumulates on the oxidized surface and initiates the reduction of the catalyst. Temperature and rate increase again, the desorption of CO is accelerated, and the system returns to the high-activity branch.

A theoretical model for chemical oscillations in the CO/O$_2$ system on Pt, Pd, and Ir has been developed by Sales, Turner, and Maple.[14] In this model two branches of a Langmuir−Hinshelwood type reaction mechanism were assumed. A slow oxidation and reduction of the metal surface layer induces the transition between these two branches. From a comparison of model calculations and experimental results, the oscillatory characteristics observed on Pt could be quantitatively reproduced.

Energy Dispersive X-ray Absorption Spectroscopy. Since the first observation of a fine structure behind an absorption edge, X-ray absorption spectroscopy (XAS) has been proven

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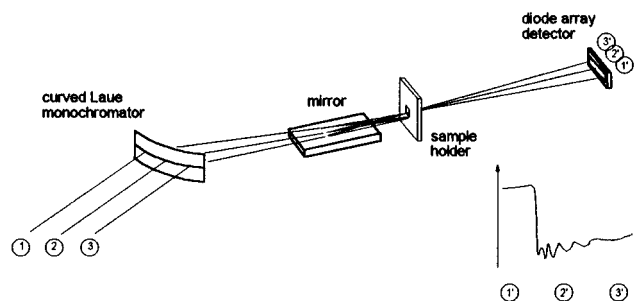*J. Phys. Chem. B, Vol. 101, No. 34, 1997* **6681**

Figure 1. Schematic representation of the dispersive XAS spectrometer at HASYLAB employing transmission monochromator optics.

to be a valuable tool for structure determination, complementary to many standard methods such as X-ray diffraction or infrared spectroscopy. The introduction of electron/positron storage rings as dedicated synchrotron radiation sources makes this method widely available as well as reduces the measuring time per absorption spectrum from several hours down to several minutes. Nevertheless, this time scale hardly allows the investigation of fast dynamic processes such as, for instance, *in situ* homogeneously or heterogeneously catalyzed reactions. These studies may benefit from the development of *energy-dispersive* X-ray absorption spectroscopy and the specific advantages of a dispersive setup compared to the standard XAS setup. In contrast to the double-crystal monochromator, where the required energy range is scanned stepwise by changing the Bragg angle of both crystals, the dispersive spectrometer applies a bent monochromator crystal in either reflection or transmission geometry. The variation of the diffraction angle over the crystal's surface can be assumed to be linear, and depending on illuminated length and Bragg angle a specific energy range is diffracted. The sample under investigation is located at the focal point of the monochromator, and the intensity of the different diffracted wavelengths is measured on a position sensitive detector (Figure 1).[15,16] Owing to the fixed energy−position correlation on the detector, a complete absorption spectrum can be obtained from measuring the intensity distribution on the detector with and without a sample. For the energy-dispersive setup, the minimum measuring time per absorption spectrum is mainly restricted by the read-out time of the detector and usually amounts to several milliseconds at most currently available dispersive spectrometers.

Many different experimental methods have been applied in order to study oscillatory behavior in chemical reactions on supported catalyst or single-crystal surfaces. Several requirements must be met by the experimental technique of choice, such as it must be an *in situ* method, it has to be sufficiently fast, and it must not disturb the system under investigation. Infrared spectroscopy and low-energy electron diffraction (LEED), for instance, are suitable experimental techniques and have been applied frequently in the past. An overview is given by Schüth *et al.*[4] and Slin'ko and Jaeger.[5]

The objective of this work is to further elucidate the kinetics that accompany chemical oscillations on supported Pd catalysts at atmospheric pressure, in particular structural alterations and changes in the oxidation state of the Pd. For our investigations we have chosen energy-dispersive X-ray absorption spectroscopy. Owing to its element specificity, XAS allows direct access to structural and electronic changes on the catalytic metal and provides insight into the behavior of the catalyst during the occurrence of chemical oscillations. Moreover, XAS at higher photon energies is a very suitable *in situ* method. It can easily be employed at a large pressure range from vacuum to high pressure without requiring a complex experimental setup. The available energy range at the Pd K-edge (24.5 keV) amounts

to about 1.5 keV, which is certainly sufficient for a reliable structural analysis from XAS data.

Experimental Section

Data Reduction and Analysis. The analysis of XAS data measured in an energy-dispersive mode requires several preliminary steps, which will be shortly described in the following. For every energy-dispersive XAS investigation the I_0 signal (without sample), the dark current of the photodiode array (I_D), and a reference sample (I_R), most often a metal foil, are measured at the beginning and the end of each experiment. Afterward the sample under investigation, e.g. a catalyst pellet, is placed at the focal point of the bent monochromator and successive absorption spectra (I_S) are recorded in predetermined time intervals.

The next step in the treatment of dispersive XAS data includes the energy calibration of the measured absorption spectra, which are obtained during the experiment as a function of photodiode number. For this purpose a polynomial has to be calculated representing the energy−position correlation on the detector and converting the measured absorption spectra into photon energy. A deviation from linearity can be often observed, and thus a second order polynomial was applied in all cases. The polynomial coefficients were determined by calibration using a standard metal foil spectrum recorded on a conventional point-by-point scanning EXAFS beam line.

Data reduction of absorption spectra followed standard procedures already described elsewhere[17−21] employing the XAS analysis software package WinXAS.[22,23] Energy-calibrated absorption spectra were background-corrected with a zero-order polynomial and normalized to an edge jump equal to one. The inflection point of each spectrum was taken as threshold energy. Afterward, a cubic spline, representing the atomic absorption $\mu_0(k)$, was refined to the k^2-weighted spectrum in a range from $k = 2.2$ to 13.5 Å^{-1}, and the EXAFS function $\chi(k)$ was calculated using the refined $\mu_0(k)$. In order to obtain the radial distribution function FT($\chi(k)$), the experimental $\chi(k)$ was weighted with k^2, multiplied by a Bessel window, and Fourier transformed into the R space.

Sample Treatment and Activation. One hundred and thirty milligrams of a palladium on carbon (Pd/C) catalyst (10 wt % Pd, as-purchased from Alfa-Johnson Matthey GmbH) were pressed into a self-supporting pellet and installed in a flow reactor.[24] Energy-dispersive XAS experiments were carried out at the DEXAFS beam line at the Hamburger Synchrotronstrahlungslabor HASYLAB with DORIS operated at 4.45 GeV and a positron injection current of 90 mA. Absorption spectra were measured *in situ* at the Pd K-edge (24.35 keV) with a time resolution of several seconds in order to improve the counting statistics. An elliptically bent, rectangular Si(400) crystal in transmission geometry was used with a horizontal focal point size of 200 μm and a vertical size of about 500 μm.[16] Reaction temperature and exhaust gas composition were continuously monitored with a thermocouple directly attached to the catalyst pellet and a quadrupole mass spectrometer included in the exhaust gas system, respectively.

The Pd/C catalyst was activated at 450 °C in air for 30 min. Afterward, the resulting PdO/C phase was reduced with CO at 180 °C, and oxidation of CO was started by adding an excess of oxygen. In Figure 2 the evolution of Pd K-edge spectra during reduction and starting CO combustion is shown. Evidently, reduction of the catalyst with CO at 180 °C leads to Pd clusters, which can be seen from the appearance of typical Pd metal near-edge features in Figure 2 (feature A, "reduction"). Adding oxygen to the reduced catalyst at 180 °C results in a
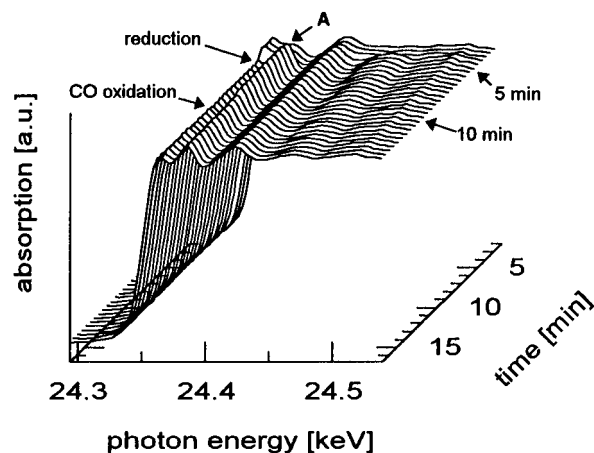
Figure 2. Evolution of the Pd K-edge spectra during the reduction of PdO/C with CO (@ 5 min) and the starting oxidation of CO on Pd/C at 180 °C (@ 10 min) (integration time per spectrum: 15 s).
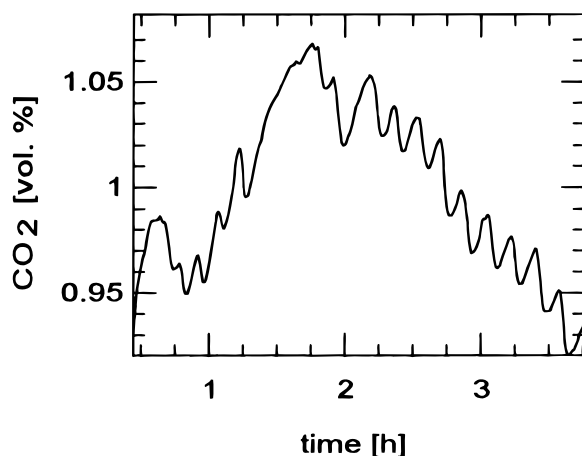

Figure 4. Temperature (solid) and CO_2 partial pressure (dashed) oscillations during CO oxidation on Pd/C catalyst.

Figure 3. CO_2 partial pressure oscillations during CO oxidation on Pd/C.

Figure 5. Evolution of the Pd K-edge spectra during CO oxidation on Pd/C (integration time per spectrum: 15 s).

slight decrease of the second feature of the Pd K near-edge structure (Figure 2, "CO oxidation"). An EXAFS analysis points toward a surface oxidation of the Pd clusters with a cluster size of about 10 Å. The pretreatment procedure and its results at different reaction temperatures are additionally described in refs 16, 22, 25, and 26.

A constant flow of 200 mL/min of nitrogen was added in order to dilute the reactant mixture. For less diluted gases, the catalyst temperature might increase and the system moves away from a kinetic toward a diffusion-controlled region.[5] Chemical oscillations have been observed at a constant flow of carbon monoxide of 10 mL/min (equal to 4.2 vol % CO) and air of 30 mL/min (equal to 2.5 vol % O_2), where the duration of the oscillations amounted to several hours with a period of about 12 min.

Results and Discussion

Macroscopic Oscillations in CO_2 Partial Pressure and Reaction Temperature. Oscillations in CO_2 partial pressure in the exhaust gas measured during CO oxidation on Pd/C are shown in Figure 3. In addition to CO_2 oscillations in the exhaust gas, temperature oscillations within the range of 2 K were measured in a constant phase correlation with respect to the corresponding change in CO_2 partial pressure (Figure 4). The measured temperature oscillations within the range of a few degrees indicate a kinetically controlled regime (i.e. thermokinetic oscillations[4]).
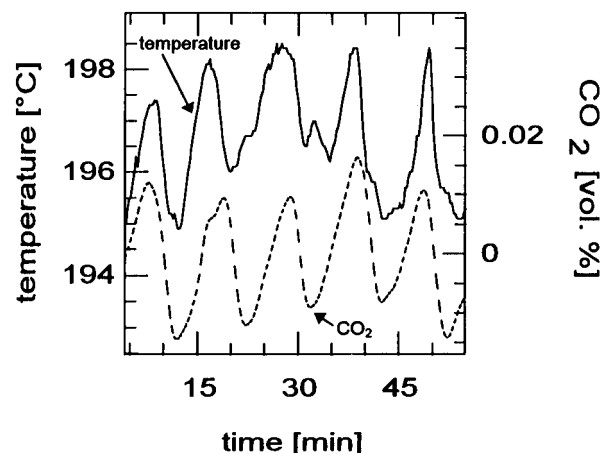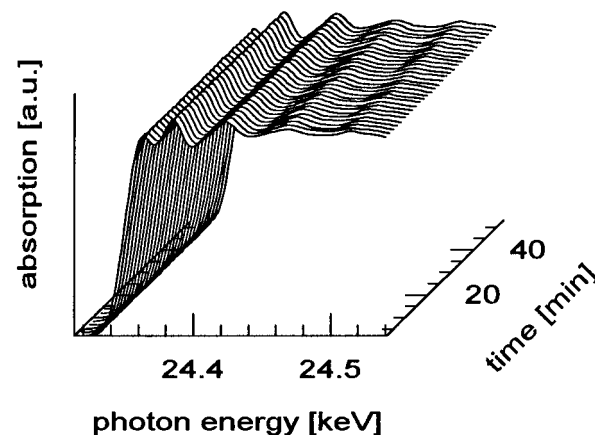
Oscillations in Absorption Spectra Near-Edge Region (XANES). Figure 5 displays X-ray absorption spectra measured during CO oxidation on Pd/C with an integration time of 15 s each. The spectra were energy calibrated as described above, background corrected with a zero-order polynomial, and normalized to an edge jump equal to one. The absorption spectra plotted in Figure 5 correspond to the temperature and rate behavior in Figure 4. Evidently, the observed temperature oscillations are not accompanied by large changes in the XANES region of the Pd K-edge spectra. Alteration in the catalytic activity that manifests itself in macroscopic oscillations of temperature and reaction rate is not caused by a periodic phase transition from a palladium oxide to a palladium cluster phase. Despite the fact that the catalyst appears to be deactivated by formation of a PdO phase, which was observed for CO oxidation at 230 °C,[25] a similar mechanism apparently does not hold for the oscillatory behavior of CO oxidation. A phase transition should have been recognized immediately from a change in the typical XANES features of the Pd K-edge. Hence, conversion of CO is continuously taking place on the cluster's surface, and a kinetic mechanism suggested for the oscillation on a microscopic scale has to take this into account.

Nevertheless, small changes in the XANES as well as in the EXAFS region of the palladium absorption spectra could be revealed from a more detailed analysis and correlated to the observed temperature oscillations. In Figure 6 the variation of the Pd K-edge position relative to a Pd metal foil is displayed together with the reaction temperature. The inflection point of the spectrum was taken as the edge position. Oscillations in the edge position of several tenths of an electronvolt can be
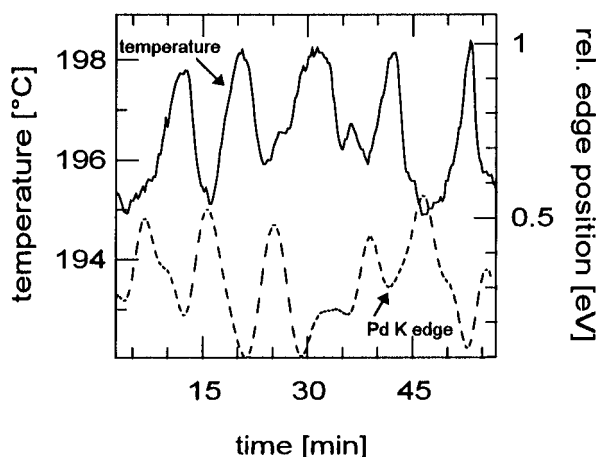
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Figure 6. Change of the Pd K-edge position (solid) relative to the position of a Pd metal foil together with the observed temperature oscillations (dashed) during CO oxidation.
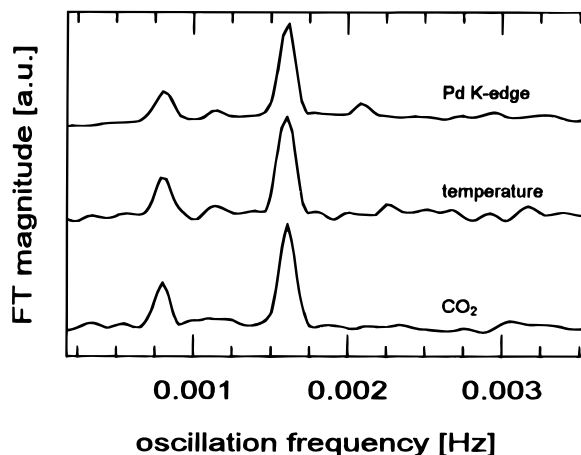

Figure 7. Frequency analysis of CO$_2$ partial pressure (bottom), reaction temperature (center), and Pd K-edge position (top) oscillations during CO oxidation on Pd/C.

Figure 8. Fourier-transformed theoretical $\chi(k)$ of a 13-atom Pd cluster (solid) coordinated to oxygen (dash−dot) or η^1- (dash) and μ- (dot) carbon monoxide.

TABLE 1

cluster type	1st Pd FT peak	
	ΔR (Å)	rel. CN
Pd$_{13}$	0.0	1.0
Pd$_{13}$ + η^1-CO	−0.025	1.31
Pd$_{13}$ + η^1-CO + μ-CO	−0.033	1.13
Pd$_{13}$ + μ-CO	−0.040	0.88
Pd$_{13}$ + O + η^1-CO	−0.022	0.93
Pd$_{13}$ + O	−0.006	0.98

seen with a constant out-of-phase correlation of π with respect to the temperature variation. The shift in the edge position indicates an oxidation/reduction cycle counterphase to the measured temperature oscillations. Deviations from an ideal single-period oscillations may be due to the existence of a second superimposed frequency that could not be experimentally resolved but influences the accuracy of the edge determination. The Fourier transform (Figure 7) of the observed oscillations in temperature, partial pressure, and Pd K-edge position reveals the same frequency for all three parameters.

Calculations of Theoretical $\chi(k)$ for Pd Clusters. In order to obtain a quantitative estimation of the influence of the adsorbed reactants on the experimentally derived Pd EXAFS functions, theoretical XAS functions were calculated using the *ab initio* code FEFF.[21] Different Pd clusters were generated with carbon monoxide, oxygen, or a mixture of both bonded to the surface atoms (Pd−O distance 2.0 Å, Pd−C distance 2.1 Å, C−O distance 1.15 Å). The clusters consisted of 13 Pd atoms assuming the structure of metallic Pd (*fcc*, $a_0 = 3.8898$ Å[27]). This cluster size was already sufficient to exhibit the effect of the reactants on the theoretical Pd EXAFS function. Structural changes due to the finite cluster size have not been taken into account. Calculations were carried out for both linearly (in the following referred to as η^1-CO) as well as bridged coordinated CO (μ-CO).

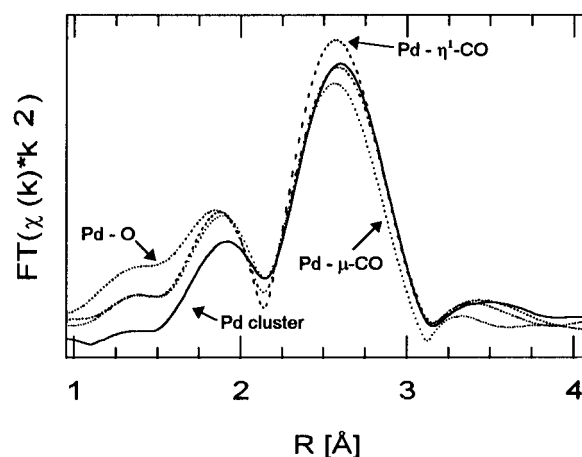Figure 8 displays four theoretical Fourier transforms calculated for 1 surface atom of the 13-atom Pd cluster. The solid curve represents the pure Pd cluster, the dash-dotted curve was obtained for a surface Pd atom bonded to one oxygen atom, and the dashed and dotted curves were calculated for the Pd cluster coordinated to μ-CO and η^1-CO, respectively. It can be seen from Figure 8 that the presence of oxygen or carbon monoxide on the surface of small Pd clusters should be discernible from their different influence on the first Pd peak in the FT($\chi(k)$). Whereas the coordination of oxygen shows only little effect on the prominent Pd peak (2.5 Å, not phase shift corrected), the coordination of carbon monoxide exhibits significant influence on Pd peak height as well as position. Moreover, the existence of linearly or bridged bonded carbon monoxide appears to be perceptible from their contrary effect particularly on the first Pd peak height. Whereas the linear coordination of carbon monoxide results in an increase in peak height, bridged CO leads to a decrease in peak height. A shift toward a smaller distance can be observed in both cases.

Various theoretical EXAFS functions have been calculated and Fourier transformed in the way described above. For all calculated mixtures of CO and oxygen, the peak height and position of the first Pd FT peak at about 2.35 Å were determined and normalized with respect to height and position of the free Pd cluster. Table 1 shows a quantitative estimate of the changes in Pd FT peak height and position that can be expected for different reactants coordinated to the surface of a Pd cluster. It can be seen that the presence of linear CO on the Pd surface results in a significant increase in peak height and a small shift toward lower distances. The presence of bridged CO leads to a decrease in Pd peak height and an even larger shift toward smaller distances. The effect seems to scale with the amount of CO or oxygen bonded to the Pd cluster. Oxygen coordinated to the cluster's surface gives rise to only marginal decrease in peak height and shift.

The origin of the different effects of oxygen and CO on the first Pd peak in the FT($\chi(k)$) can be understood from an analysis of the various scattering paths contributing to the total EXAFS function $\chi(k)$ of a Pd catalyst under reaction conditions. Besides
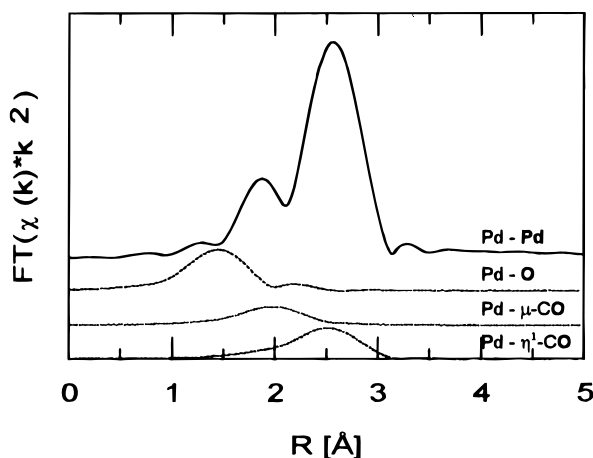
Figure 9. Fourier-transformed theoretical $\chi(k)$ of a 13-atom Pd cluster (solid) together with various contributing scattering paths from different reactants (dashed, oxygen; dotted, μ-CO; dash-dotted, η^1-CO).

the Pd−Pd and Pd−O or Pd−C backscattering, Pd−CO multiple scattering paths for linearly and bridged bonded CO add significantly to the entire $\chi(k)$. Figure 9 illustrates the different Pd−CO scattering paths for μ- and η^1-CO that have to be considered. The contrary effect of μ- and η^1-CO in particular on the Pd peak height is caused by the phase relationship between the corresponding EXAFS functions. Whereas the η^1-CO EXAFS function interferes constructively with the first Pd shell $\chi(k)$ and leads to an increase in FT peak height, the μ-CO function adds destructively to Pd $\chi(k)$ and results in a decrease in FT peak height.

As a result of the analysis of theoretical $\chi(k)$ for different Pd clusters coordinated to either oxygen or carbon monoxide, the following conclusions can be drawn:

From a comparison of the effect caused by oxygen and carbon monoxide, it turned out that the influence of both reactants is remarkably different. Carbon monoxide present on the surface of a Pd cluster influences the first-shell Pd peak in the FT(χ-(k)) significantly, whereas oxygen does not. Therefore the analysis of the first Pd shell of a real Pd catalyst under reaction conditions opens the possibility to monitor reactions taking place on the catalyst surface. Although the coordinated atoms or molecules do not appear as distinct shells in the Fourier transform and can hardly be separated by Fourier filtering, a change in the surface coverage of the catalyst clusters can be distinguished. It must be emphasised that the described alterations in height or distance of the first Pd shell of a real catalyst under reaction conditions do not indicate a change in cluster size or distance but a contribution of other scattering paths. Fortunately, they can be used to make assumptions about surface coverage and reactions taking place on the catalyst. The discernible extent of a change in the Fourier-transformed $\chi(k)$, however, depends essentially on the surface to bulk ratio (dispersion) determined by the Pd cluster size. Therefore, small clusters with a narrow size distribution shall be preferable for *in situ* XAS investigation in transmission.

Oscillations in the Experimental FT($\chi(k)$). In addition to the above-described alteration in the Pd K-absorption edge position, an oscillatory behavior could indeed be found in the experimental FT($\chi(k)$). Figure 10 shows the Fourier-transformed $\chi(k)$ of the Pd K-edge spectra. Significant changes in the peak height of the first Pd−Pd shell can be seen. The alterations in peak height are larger than the expected error obtained from measurements of the catalyst under stable reaction conditions. A change in the catalyst temperature of a few degrees can also be excluded as the source for the observed height oscillations.
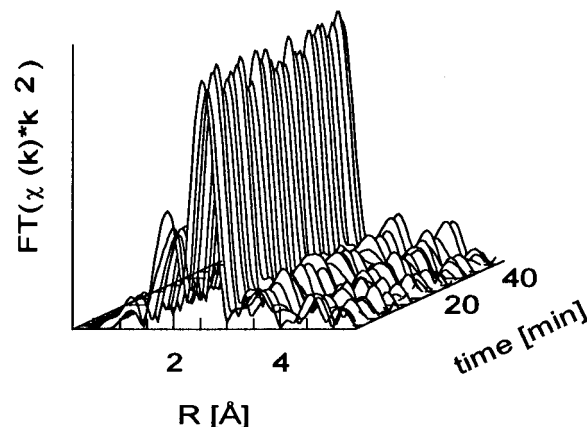

Figure 10. Fourier-transformed experimental $\chi(k)k^2$ of the Pd K-edge during CO oxidation on Pd/C.
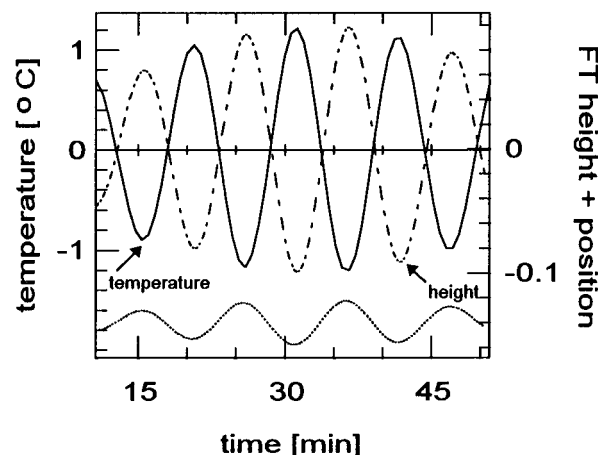

Figure 11. Oscillations of first Pd peak height (dashed) and position (dotted) in experimental FT($\chi(k)$) during CO oxidation on Pd catalyst together with reaction temperature variation (solid). Obtained from back-transformation of the main peak in the corresponding FT (Figure 7).

Moreover, a periodic shift in the imaginary part of the Fourier transform could be found, confirming multiple scattering contributions from the reactants to the first Pd shell.

Similar to the procedure described above for theoretical EXAFS functions obtained from FEFF calculations of various Pd clusters, peak height and position of the first Pd peak in the Fourier-transformed experimental $\chi(k)$ were determined. In Figure 11 the obtained periodic alterations in height and position are plotted together with the measured reaction temperature oscillations. It can be seen that Pd peak height and position oscillate with the same frequency and with a phase shift of π with respect to the reaction temperature. According to the theoretical calculations and the expected influence of adsorbed CO and oxygen on the Pd $\chi(k)$, an oscillatory change in CO and oxygen surface coverage during the reaction has to be assumed. Moreover, the phase relationship between reaction temperature and peak height and position allows a more detailed assumption about the reactions taking place on the cluster's surface. A phase correlation of π between peak position and reaction temperature clearly points toward a relatively higher population of CO molecules during the high-activity branch of the reaction and a lower population of CO during the low-activity branch of the combustion. Furthermore, the phase relationship between peak height and temperature can only be explained by an alternating relatively higher concentration of linearly bonded and bridged CO counterphase to the reaction temperature.

Multiple-Shell EXAFS Refinement and Difference File Technique. Since no definitive conclusion about the kinetics

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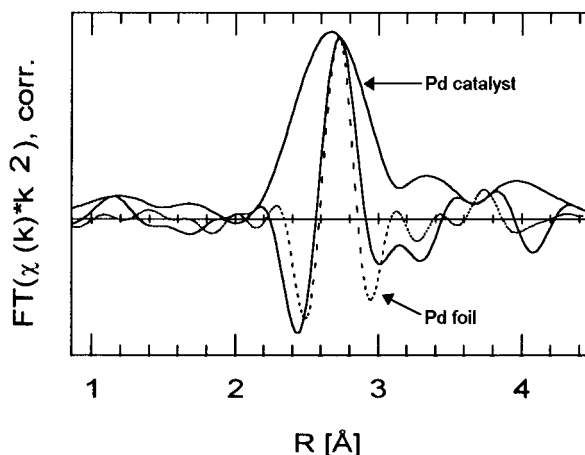*J. Phys. Chem. B, Vol. 101, No. 34, 1997* **6685**

Figure 12. Normalized Fourier-transform of Pd/C catalyst (solid) under reaction conditions and a Pd metal foil (dotted) (Pd–Pd phase and amplitude corrected).

Figure 13. Fourier-transformed residual $\chi(k)$ of a Pd/C catalyst in the high- (solid) and low- (dashed) activity stage of the oscillatory reaction.

of the oscillatory behavior in the CO combustion could be made only from the observed FT peak alterations, a three-shell EXAFS refinement to the experimental Pd $\chi(k)$ of the catalyst in the high- or low-activity branches of the reaction was carried out. Theoretical phase shifts, amplitudes and "mean free photoelectron paths" obtained from the above-mentioned FEFF calculations were employed. One Pd shell and two oxygen shells for η^1- and μ-CO were refined with three parameters each (coordination number, distance, Debye–Waller type disorder parameter) and an overall E_0 shift. The fit was performed in R space in a range from 1.7 to 3.0 Å.

In order to justify the effort of refining three scattering paths, the refinement was also tried with only one Pd shell as well as one Pd shell plus either η^1- or μ-CO. None of these trials resulted in satisfying fits. Neither the height of the Pd FT peak nor the small shoulder at about 1.9 Å could be refined with adequate accuracy. This clearly indicates the necessity to consider more than one type of carbon monoxide coordinated to the Pd cluster surface, which was previously reported from IR measurements, too.[10,11,28] Moreover, from a comparison of the experimental FT($\chi(k)$) and a single Pd shell (Figure 12), differences in the imaginary parts in the region at about 2.4 Å as well as at about 3.1 Å can be observed. This points to a contribution of light elements to the entire $\chi(k)$ (oxygen and/or carbon lower than 2.0 Å and carbon monoxide at about 2.6 and 3.0 Å).

Although a three-shell XAS refinement leads to reasonable residuals, no consistent results could be obtained for different k weighting. This is mainly due to the extremely heterogeneous composition of the system, which would require the consideration of several reactants on the catalyst's surface at the same time. Owing to the limited available k range, a refinement of all necessary shells would exceed the number of free parameters.

In order to extract information on the contribution of the C and O backscatterer on the Pd FT peak, difference spectra were calculated and Fourier transformed. A detailed description of the "difference file technique" and the underlying theory can be found in refs 29–31. A single Pd shell was refined to the experimental $\chi(k)$ in a range from $k = 6$ to 13.5 Å⁻¹ using experimental Pd phase and amplitude obtained from a Pd metal foil. This Pd shell was then subtracted from the whole $\chi(k)$ and the residual spectrum thereafter Fourier transformed. Figure 13 shows two residual FT for the catalyst in the high- and low-activity branches of the reaction. Additionally, the residual obtained from a Pd metal foil is shown. Apparently, three additional shells can be distinguished. The first shell corre-
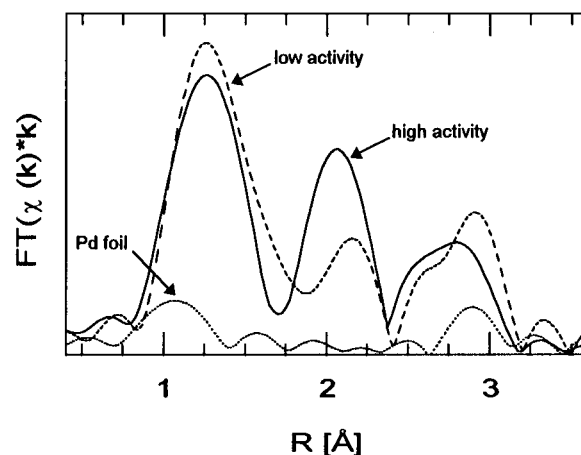
sponds to either C or oxygen from the reactants or the support. The second and third shell correspond to bridged and linearly bonded CO on the Pd cluster's surface, respectively.

For comparison, the difference file technique was tested with a theoretical $\chi(k)$ obtained from the above-described FEFF calculations. A single Pd XAS function was refined to a theoretical $\chi(k)$, consisting of a Pd–Pd backscatterer as well as of Pd–O, Pd η^1-CO, and Pd μ-CO contributions. From the residual FT it could be concluded that a nonnegligible part of the CO contribution appears to be removed together with the Pd shell. Therefore, the difference file technique was used in this work only to obtained a qualitative estimate of the behavior of η^1- and μ-CO during the chemical oscillations. No attempt was made to refine XAS functions with the calculated residual FT. Nevertheless, an obvious relationship between the concentration of η^1- and μ-CO on the cluster's surface could be found. In the high-activity branch of the reaction μ-CO seems to accumulate on the surface, whereas in the low-activity branch the concentration of η^1-CO appears to be increased. Although both CO species show periodic concentration alterations with a constant phase relationship with respect to the reaction temperature, the degree of change during the different stages of the oxidation seems to be higher for the concentration of η^1-CO than for μ-CO.

Moreover, the increased concentration of oxygen during the low-activity stage on the Pd cluster can be seen from a slightly higher shell at about 1.3 Å (Figure 13). The presence of oxygen and carbon monoxide on the surface of the Pd cluster additionally points toward a Langmuir–Hinshelwood type kinetic mechanism for CO oxidation, which of course has already been assumed for most of the transition metals being catalytically active in CO combustion. Our results obtained from the EXAFS refinement are consistent with the observed oscillations in the Pd K-edge position as well as the described periodic alterations in the experimental first Pd FT peak height and position.

Conclusions

Proposed Model. On the basis of our results, a reaction scheme for the oscillatory behavior in the CO oxidation on supported Pd catalysts at atmospheric pressure is proposed. The observed alterations in the EXAFS parameters are in good agreement with the results obtained from theoretical Pd K-edge $\chi(k)$, assuming that the state of the catalyst alternates between an oxygen-covered and a carbon monoxide-covered surface during the observed chemical oscillations. Taking into account the phase relation between temperature and edge position on one side and between temperature and EXAFS parameters on
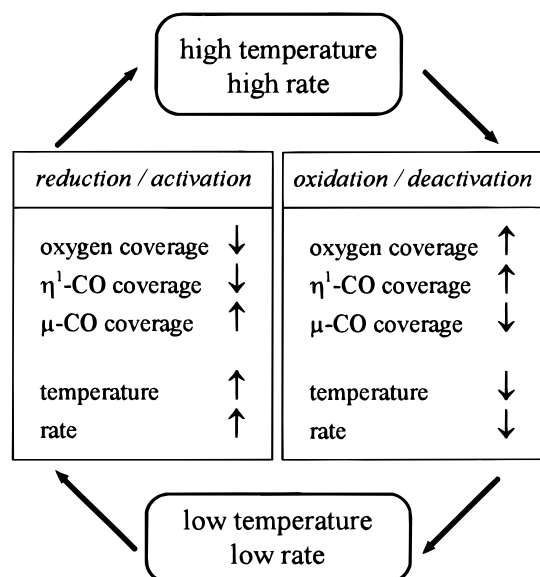
Figure 14. Schematic representation of the reaction mechanism of chemical oscillations occurring during CO oxidation on supported Pd catalysts. (Up and down arrows indicate an increase or decrease of each parameter, respectively.)

the other, the following kinetic mechanism for the oscillations on a Pd cluster is proposed (Figure 14).

The chosen model represents a nonisothermal surface blocking/reactivating mechanism[4,13] assuming a Langmuir−Hinshelwood type reaction kinetic. The different steps of one reaction cycle appear to be the following. Starting with an active catalyst in a *high-temperature/high-rate* stage, the heated surface of the catalyst becomes more and more covered by oxygen (slow oxidation[14]). This step coincides with a higher concentration of linearly bonded CO and a lower concentration of bridging CO on the Pd surface. Further adsorption of carbon monoxide seems to be hindered, conversion rate as well as reaction temperature decrease, and the cycle reaches the *low-rate/low-temperature* stage. At this point CO adsorbs to the catalyst surface again and reacts with the oxygen leading to an increase in reaction rate and temperature (slow reduction[14]). Additionally, a higher concentration of bridging CO and a lower concentration of linearly bonded CO can be observed. The *high-rate/high-temperature* stage is reached again, and a new cycle can start.

The expected influence of this reaction cycle on *in situ* measured X-ray absorption spectra corresponds very well to the measured and described changes in energy threshold and the Pd K-edge EXAFS functions. The increasing oxygen coverage leading to the low-activity stage is visible as a shift of the absorption edge to higher photon energies with decreasing reaction temperature. A higher concentration of linearly bonded CO results in an increased first Pd peak height and a shift toward larger distances with respect to the high-activity stage. An increasing CO coverage can be regarded as a reduction step and results in a shift of the absorption edge to smaller photon energies with an increasing reaction temperature. In contrast to the oxidation step, the increased concentration of bridging CO in the high-activity stage results in a decreased first Pd peak height and a shift toward smaller distances. All described changes could be found from the analysis of the measured absorption spectra and therefore confirm the suggested reaction scheme.

From a comparison of our results with the kinetic mechanism suggested for chemical oscillations on Pd single-crystal surfaces[1−4] or polycrystalline[5,6] catalysts, it can be stated that apparently a

similar mechanism can be applied on supported catalysts as well. However, the formation of "subsurface oxygen" on small Pd clusters corresponds to a further oxidation and should be visible particularly in the XANES region of the experimental X-ray absorption spectra. Moreover, the formation of "subsurface oxygen" on small clusters should result in a decreasing first Pd shell FT peak height in the low-activity region of the oscillatory cycle, which could not be observed.

In our analysis we did not consider significant changes in the cluster size during the occurrence of chemical oscillations. The Pd clusters were assumed to maintain their average size with the CO oxidation taking place on the cluster's surface. Since the available experimental data can sufficiently be interpreted without considering a periodic change in cluster size, we restricted our interpretation on the as-described mechanism.

Compared with results obtained from Jaeger *et al.*[12,13] for oscillations on Pd supported in zeolites, a good agreement can be found. Both proposed mechanisms assume an oxidation−reduction process as the driving force for oscillations in the kinetic regime. In both cases the catalyst exhibits a decreasing activity with increasing oxygen coverage and a restoration of catalytic activity with an increasing carbon monoxide accumulation on the catalyst's surface. Moreover, our results fit very well into predictions based on the theoretical model of Sales, Turner, and Maple.[14] In addition to their assumptions, differences in the coordination type of carbon monoxide during the oscillations could be found. No conclusions though could be made about reasons leading to a slow oxidation and reduction of the catalyst that is apparently responsible for the occurrence of chemical oscillations.

The suggested mechanism describes very well the occurrence of chemical oscillations on single Pd clusters. The observed temperature and rate oscillations as well as the periodic alteration of the measured X-ray absorption spectra, however, indicate a synchronization of a certain number of clusters. This question is not addressed in this paper. A recent overview concerning the synchronization of catalytically active centers can also be found in ref 5.

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