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***In Situ* XAS Investigations of Chemical Oscillations in the Oxidation of Co on Supported Pd Catalysts**

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Abstract. Self-sustained temperature as well as rate oscillations during the oxidation of CO at atmospheric pressure on supported Pd catalysts were studied *in-situ* at the Pd K edge by employing energy-dispersive XAS. From the absorption spectra a phase transition from palladium oxide to palladium clusters can be excluded as driving force of the observed oscillations. Nevertheless, a constant phase correlation between edge position and the observed temperature oscillations could be revealed. This points toward a periodical surface oxidation / reduction process in phase with deactivation / activation cycles of the catalyst. Furthermore, an oscillatory behaviour in height and position of the first Pd peak could be seen in the radial distribution function. From theoretical cluster calculations using FEFF6 it can be deduced, that the evaluated oscillations in Pd coordination number and Pd-Pd distance indicate an oscillatory change of surface coverage from CO to oxygen and *vice-versa*. Taking these surface-coverage oscillations and the periodical oxidation / reduction into account, a surface activation / deactivation process is proposed as kinetic mechanism for the observed chemical oscillations.

1. Introduction

The carbon monoxide combustion on transition metals is known to exhibit an intriguing oscillatory behaviour with respect to reaction rate as well as reaction temperature under particular conditions. Self-sustained oscillations were first observed in 1972 in the oxidation of CO on Pt catalysts [1]. Oscillations involving supported Pd catalysts have been thoroughly investigated by Wicke *et al.* [2] by employing *in-situ* IR spectroscopy of two bridged and one linearly bonded form of CO. From their results, 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.* [3]. The authors suggested a periodical oxidation-reduction process as the driving mechanism. Detailed reviews on this large field of interest are given by M.M. Slin'ko and N.I. Jaeger [4] and by R. Imbihl and G. Ertl [5].

2. Data reduction

Data reduction of absorption spectra followed standard procedures already frequently described elsewhere [6] employing the XAS analysis software package WinXAS [7]. Energy calibrated absorption spectra were background corrected with a zero order polynome and normalised to an edge jump equal to one. The inflection point of each spectrum was taken as threshold energy. Afterwards, 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 $13.5 \text{ \AA}^{-1}$. 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 R space.

3. Sample treatment and activation

130 mg of a Palladium on Carbon (Pd/C) catalyst (10 weight-% Pd, as-purchased from *Alfa-Johnson Matthey GmbH*) were pressed into a self-supporting pellet and installed in a flow-reactor. The described energy-dispersive XAS experiments were carried out at the DEXAFS beam line at the Hamburger Synchrotronstrahlungslabor HASYLAB. 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 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 [8]. 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. Afterwards, 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 Fig. 1 the evolution of Pd K edge spectra during reduction and starting CO combustion is shown at different reaction temperatures (180 °C and 230 °C).

Fig. 1: 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) (left) and 230 °C (right) (integration time per spectrum : 15 s).

Evidently, the near edge region of absorption spectra measured under reaction condition at 180 and 230 °C (last five minutes of each experiment) exhibit significant differences. Reduction of the catalyst with CO leads to small Pd clusters in both cases, which can be seen from the appearance of the typical Pd metal near edge features in Fig. 1. Adding oxygen to the reduced catalyst at 180 °C results only in a slight decrease of the second feature of the Pd K near edge structure (Fig. 1, left). An EXAFS analysis points towards a surface oxidation of the Pd clusters. In contrast, starting the CO oxidation at 230 °C leads to a further oxidation of Pd clusters and finally to a Palladium oxide phase, which is remarkably less active as a CO combustion catalyst. Transition from small Pd clusters to PdO can clearly be seen from the appearance of typical PdO features in the XANES region of the measured absorption spectra (Fig. 1, right).

3.1 Macroscopic oscillations in CO₂ partial pressure and reaction temperature

A constant flow of 200 ml/min of nitrogen was added in order to dilute the reactant mixture. 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. % O₂), where the duration of oscillations amounted to several hours with a period of about 12 minutes. Oscillations in CO₂ partial pressure measured during the oxidation of CO on Pd/C are shown in Fig. 2 together with observed temperature oscillations. The measured temperature oscillations in the range of a few degrees indicate a kinetically controlled regime (thermo-kinetic oscillations [4]).

Fig. 2 : Temperature (solid) and CO₂ partial pressure (dashed) oscillations during the oxidation of CO on Pd/C catalyst.

Fig. 3 : 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 the oxidation of CO.

3.2 Oscillations in XANES and EXAFS

From the XANES region of *in-situ* measured X-ray absorption spectra during the occurrence of chemical oscillations no periodical transition from Pd clusters to a Palladium oxide phase could be found. Nevertheless, a small periodical shift in the Pd K edge position could be determined, counterphase to the observed temperature oscillations (Fig. 3). These energy threshold oscillations indicate, that the reaction takes place on the surface of small Pd clusters that are periodically surface oxidised and reduced. During the high activity branch of the reaction the Pd catalyst appears to be reduced, whereas the change of the

catalyst towards the low activity branch coincides with a slight surface oxidation of Pd clusters. Furthermore, periodical variations of first Pd peak height and position in the Fourier transformed experimental $\chi(k)$ were found. In order to interpret these changes in the FT($\chi(k)$) and to estimate the influence of carbon monoxide and oxygen coordinated to the clusters' surface on Pd EXAFS function, theoretical XAS calculations were carried out using the *ab-initio* code FEFF6 [9]. From an analysis of the obtained theoretical XAS functions and particularly the different scattering paths that contribute to the total $\chi(k)$, it was found, that coordination of CO and oxygen appears to be distinguishable from their effect on the first Pd peak in the FT($\chi(k)$). Whereas the coordination of oxygen shows only little effect on peak height and position, linearly bonded CO results in a significant increase of first Pd peak height and a small shift towards lower distances. Bridged coordinated CO on the clusters surface leads to an even larger peak shift towards lower distances and, contrary to linear CO, a decrease in FT peak height.

Fig. 4 : Fourier transformed theoretical $\chi(k)$ of a 13 atoms Pd cluster (solid) coordinated to oxygen (dash-dot) linearly (dash), and bridged bonded (dot) carbon monoxide.

Fig. 5 : Fourier transformed experimental $\chi(k) * k^2$ of the Pd K edge during the oxidation of CO on Pd/C.

3.3 A kinetic model for oscillations in the CO oxidation on Pd catalysts at atmospheric pressure

Provided that the state of the catalyst alternates between an oxygen covered and a carbon monoxide covered surface during the observed chemical oscillations, the alterations in the EXAFS parameters are in good agreement with results obtained from theoretically calculated Pd K-edge $\chi(k)$. Taking phase relation between temperature and edge position on one side, and between temperature and EXAFS parameters on the other, the following kinetic mechanism for chemical oscillations on Pd clusters can be confirmed.

The chosen model represents a non-isothermal surface blocking / reactivating mechanism [10] assuming a Langmuir-Hinshelwood type reaction kinetic. Starting with an active catalyst in a *high temperature, high rate* phase the heated surface of the catalyst becomes more and more covered by oxygen. This step coincides with a higher concentration of linearly bonded CO and a lower concentration of bridged bonded CO on the Pd surface. The further adsorption of carbon monoxide seems to be hindered and conversion rate as well as reaction temperature decrease and the cycle reaches a *low rate, low temperature* phase. At this point CO adsorbs to the catalyst surface again and reacts with the oxygen leading to an increase in reaction rate and temperature. Additionally, a higher concentration of bridged bonded CO and a lower concentration of linearly bonded CO can be observed. The *high rate, high temperature* phase is reached again and a new cycle can start.

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