Catalysis Letters 28 (1994) 373–381

Experimental evidence for an oxidation / reduction mechanism in rate oscillations of catalytic CO oxidation on Pt / SiO_2

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Received 16 February 1994; accepted 13 July 1994

In situ X-ray diffraction experiments have been conducted during rate oscillations of catalytic CO oxidation on a supported Pt catalyst, EuroPt-1. The measurements which were carried out at atmospheric pressure with flow rates of ~ 200 ml/min showed that the non-isothermal oscillations in the reaction rate were accompanied by periodic intensity variations of a Bragg peak. A Debye function analysis of beam profiles recorded at the two extrema of the oscillations revealed that the Pt catalyst undergoes a periodic oxidation and reduction during rate oscillations. The diffraction experiments are therefore considered to be the first experimental proof that the oxide model proposed originally by Sales, Turner and Maple to explain rate oscillations in the $CO + O_2$ reaction at atmospheric pressure is in fact correct.

Keywords: catalytic CO oxidation; kinetic oscillations; in situ X-ray diffraction; supported catalysts

1. Introduction

Kinetic oscillations in CO oxidation on Pt catalysts have been studied with various forms of catalysts over a wide range of conditions [#1]. While the origin of the oscillations which occur on Pt single crystal surfaces under isothermal low-pressure conditions ($p < 10^{-3}$ mbar) has been unambiguously identified as being due to periodic structural changes of the substrate, the driving force for the high pressure ($p > 10^{-3}$ mbar) oscillations is still a matter of debate. For these high pressure oscillations, which are non-isothermal and which have been studied with foils, wires or supported Pt catalysts, a large number of different mechanisms have been discussed [3–14]. Neglecting all models without experimental support, the

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[#1] Experiments with single crystal surfaces are reviewed in refs. [1,2], while the results of experiments with polycrystalline material are summarized in refs. [3,4].

number of possible mechanisms is reduced to only three: the reconstruction model adopted from the single crystal experiments [8,14], the carbon model [11,12] and the oxide model [5,6,10,13], with the latter two assuming a periodic deactivation of the surface by carbon and by oxide formation, respectively.

Of the three "realistic" models the so-called oxide model introduced by Sales, Turner and Maple has gathered the widest support [5]. However, aside from some experiments showing the formation of Pt oxide under oscillatory conditions, there have been to date no conclusive experiments demonstrating that a periodic oxidation and reduction of the Pt catalyst actually takes place as it is required by the proposed mechanism [6,13]. In this letter we report on in situ X-ray diffraction (XRD) experiments that show that the amount of Pt oxide periodically varies during rate oscillations thus verifying the proposed oxide model. These experiments have been conducted with a supported Pt catalyst (EuroPt-1) which has been extensively characterized in previous investigations and whose small particles of $\sim$ 10–15 Å diameter exhibit a large surface to volume ratio (dispersion $65 \pm 5\%$) [15–18].

2. Experimental

The in situ X-ray measurements were conducted in a specially designed reactor cell as described in ref. [19], a sketch of which is reproduced in fig. 1. The cell was mounted onto a commercial Guinier diffractometer (HUBER) using monochromatized Cu $K_{\alpha 1}$ radiation in a 45° transmission geometry. The cell, which has a volume of 115 cm^3 and which could be evacuated down to 10^{-7} mbar, was connected to three flow controllers supplying CO (purity 4.7), O_2 (purity 4.5) and He (purity 4.6). All experiments were conducted at atmospheric pressure. He was added in some cases in order to regulate the thermal conductivity of the gas atmosphere.

For preparing the samples, 40 mg of the catalyst EuroPt-1 consisting of 6.3% Pt supported on SiO_2 were pressed with 2×10^7 N/m^2 to self-supporting pellets of $15 \times 12 \times 0.3$ mm^3 size. The sample holder could be heated resistively up to 1000 K. Two chromel–alumel (K-type) thermocouples, one of them attached directly to the sample, served for measuring the temperature of the sample and of the gas phase. A differentially pumped quadrupole mass spectrometer (QMS) was used for monitoring the CO_2 partial pressure in the cell.

3. Results and discussion

For following continuously the state of the catalyst during experiments the intensity of the 111 Bragg peak was recorded at the fixed Bragg angle $\vartheta = 19.9°$ and a receiving slit set to $\Delta\vartheta = \pm 1$ with counting intervals of 5 s. Alternatively under sta-

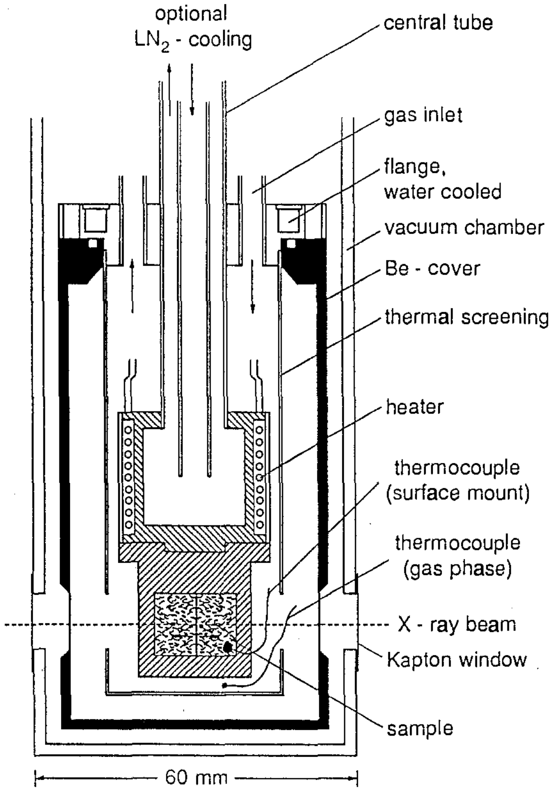

Fig. 1. Sketch of the in situ reaction chamber for X-ray diffraction.

tionary conditions, angular profiles of the diffracted intensity were measured with high resolution in a step scanning mode. These intensity profiles can be used to obtain a cluster size distribution of the catalyst by fitting theoretical curves calculated with Debye functions to the experimental ones. The scattered X-ray intensity $I_N(b)$ of randomly oriented clusters of N atoms has been shown to be described by Debye functions [17]:

$$I_N(b) = \sum_{m,n=1}^{N} f_m f_n [\sin(2\pi b r_{mn})]/(2\pi b r_{mn})$$

with $b = 2\sin\vartheta/\lambda$. In this expression f_m and f_n represent the atomic scattering amplitudes and r_{mn} the distance of pairs of atoms m and n. In the expression for the scattering vector b, ϑ denotes the Bragg angle and λ the wavelength. The usefulness of this so-called Debye function analysis (DFA) has been demonstrated in this lab with the EuroPt-1 catalyst [17].

The kinetics of the $CO + O_2$ reaction were typically studied by cycling the oven temperature with fixed flow rates of the gases. Since the reaction is strongly exothermic the increase of the sample temperature can serve as a good indicator for the catalytic activity, i.e. of the CO_2 production rate provided that spatial inhomogeneities do not play a dominant role [9]. In the present case it has been verified by parallel measurements of the CO_2 production rate and the sample temperature that the latter follows in fact the variations in the reaction rate. As observed before, one finds ignition/extinction phenomena during such a cycle associated with the removal and the build-up, respectively of a CO poisoned catalyst surface [9]. A typical experiment showing the variations in the Bragg intensity and in the sample and gas-phase temperature is displayed in fig. 2. One notes that the ignition of the reaction at point A in fig. 2 is accompanied by (1) a positive spike in the sample temperature and (2) a steep decrease of the background corrected Bragg intensity by 18%. After the He flow has been switched off the intensity drops further reaching a total decrease of 31.5%.

At flow rates below 50 ml/min the reaction displayed merely bistability but as the flow rates were increased to ~100 ml/min oscillatory behavior was observed, too. This is demonstrated in fig. 2, where rate oscillations develop after slowly cooling the sample to ~ 375 K (point D in fig. 2). The plot shows oscillations in the sample temperature of ~50 K amplitude (peak to peak) that accompany the variations in the reaction rate (not shown here). In the period where the oscillations develop, the Bragg intensity rises continuously until the X-ray intensity starts to oscillate coincident with the beginning of the rate oscillations. The phase relationship between the temperature oscillations (T oscillations) and the oscillations in the

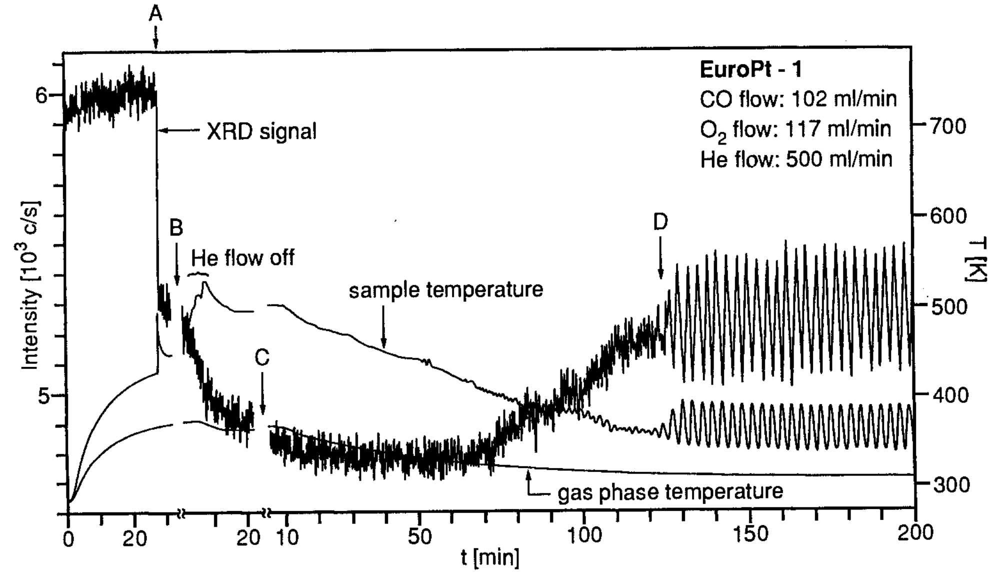

Fig. 2. Time dependent integral Pt(111) intensity (noisy signal) during a heating/cooling cycle leading to oscillatory reaction behavior in the CO/O_2/He mixture. After ignition of the reaction at point A the external heating of the sample was reduced. The He flow was switched off after B. Intensity profiles were taken at points A, B and C, while D marks the onset of the rate oscillations.

Bragg intensity (*I* oscillations) is illustrated by fig. 3. One notes that the X-ray intensity oscillates with a phase angle of ~ 120° ahead of the *T* oscillations.

One can rule out that the observed oscillations of the Bragg intensity are caused by temperature oscillations via the Debye–Waller factor for two reasons: (1) the time delay of the sample temperature to variations in the catalytic activity is estimated from the ignition behavior to be on the order of several seconds. Accordingly there should practically be no phase shift in the *T* signal and the *I* signal in contrast to what is observed in fig. 3. (2) The magnitude of the *I* oscillations (11%) would require unrealistically high bulk temperature variations of the platinum particles of a magnitude of ~ 1000 K [20]. Since sintering was observed to occur for $T \geqslant 750$ K, such a strong temperature effect would cause irreversible changes in the catalyst in contradiction to the experimental results showing complete reversibility.

In order to relate the variations in the Bragg intensity to changes in the state of the catalyst, angular scans of the diffracted intensity were recorded before and after the transition from the inactive to the active state corresponding to points A and B in fig. 2. The angular profiles together with the results of a DF analysis are reproduced in figs. 4 and 5. First, one realizes that the two angular scans shown in figs. 4a and 5a exhibit quite pronounced differences. Compared to fig. 4a the first peak in fig. 5a is broadened with an asymmetric wing at low angles and the high order peaks are strongly damped. Similar observations have been made by Liang, Laderman and Sinfeld, who used differential anomalous X-ray scattering (DAXS) on a Pt/Al_2O_3 catalyst [21].

The experimental curves were fitted with curves calculated for discrete cluster distributions using Debye functions, as has been demonstrated in detail earlier [17]. The discreteness of the cluster distribution is based on theoretical calculations showing that clusters with certain magic numbers of Pt atoms exhibit an enhanced

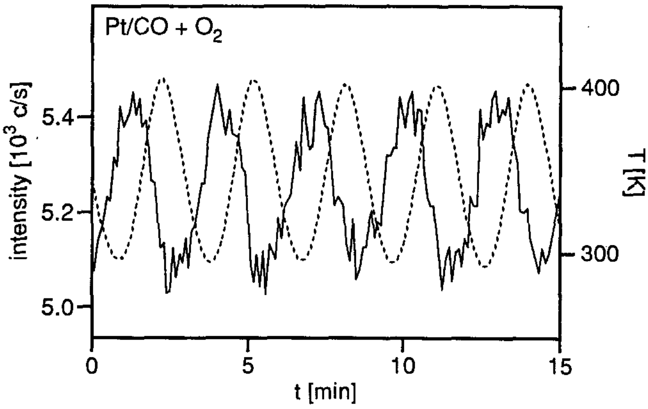

Fig. 3. Enlarged plot of the oscillations seen in fig. 2 demonstrating a phase shift between the sample temperature (dashed curve) and Pt(111) intensity.

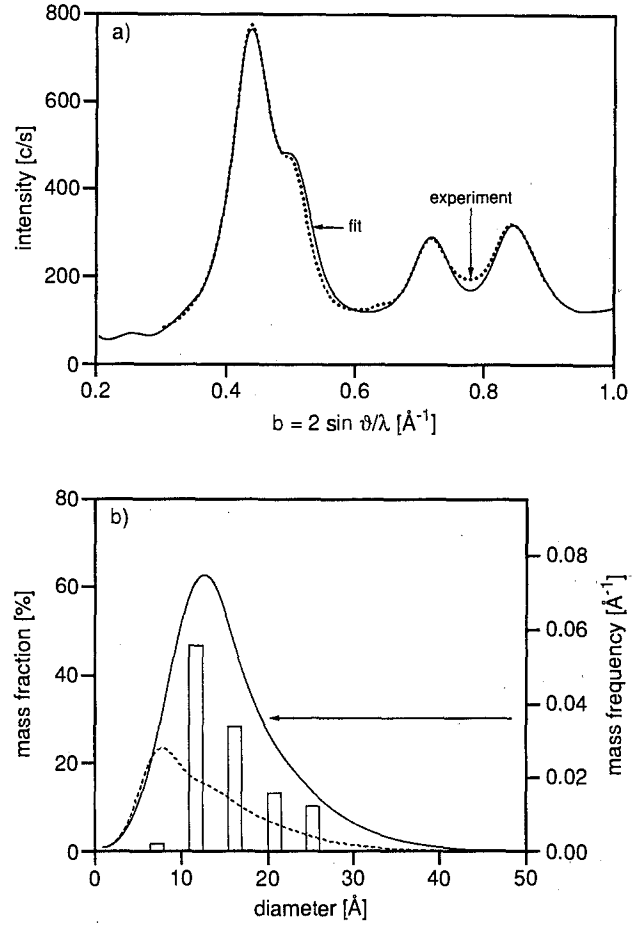

Fig. 4. (a) Intensity profile after background subtraction and angular corrections (dots) and corresponding DFA fit (full line), measured in the reduced state preceding point A in fig. 2. (b) Cluster size distribution belonging to the fit shown in (a). The bars represent mass fractions of closed shell fcc-clusters Pt$_N$ with $N = 13, 55, 147, 309$ and 561 atoms, which are plotted versus cluster diameter. A continuous mass frequency function (solid line) is deduced from the discontinuous distribution and fits equally well to the experiment. The dashed curve corresponds to a hypothetical size distribution obtained by removal of all outer atomic shells.

stability [22]. The results, however, remained essentially unchanged when the discrete distribution functions were replaced by continuous functions. A cuboctahedral shape was assumed for the Pt clusters, which means that the Pt particles are almost of spherical shape. Calculations have also been conducted with other geometrical shapes, but, quite generally, it turned out that the diffracted Bragg intensity is rather insensitive to the shape of the clusters.

The cluster distribution which gave the best fit to the angular scan of the inactive CO covered catalyst (state A) is shown in fig. 4b. The histogram, which corresponds to a mean cluster diameter of 15.5 Å, yields a quite good fit to the experi-

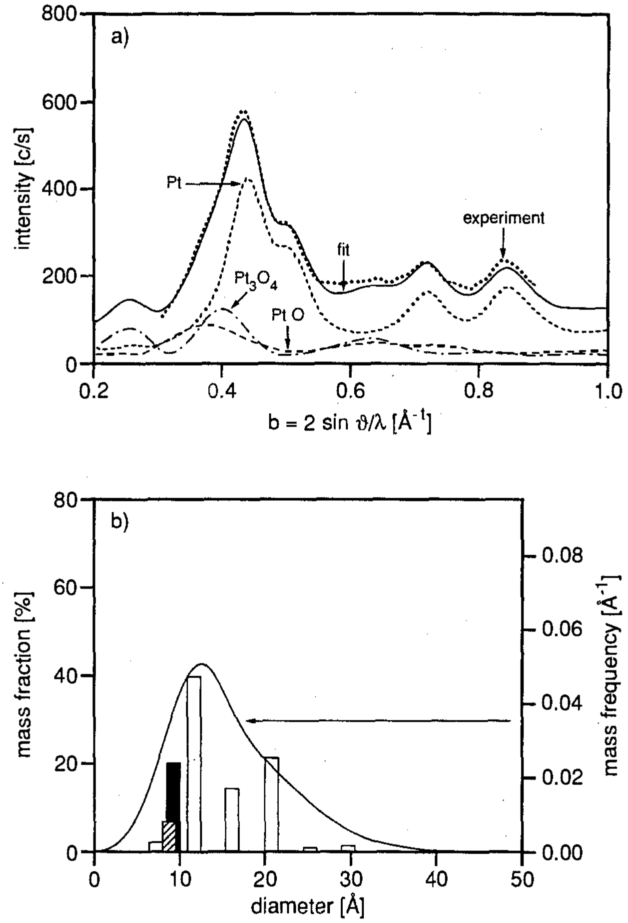

Fig. 5. (a) Intensity profile as in fig. 4, measured at point B in fig. 2. A reasonable DFA fit can only be achieved by addition of the Debye functions of platinum oxide clusters as indicated. (b) Cluster size distribution belonging to the fit shown in (a). The bars represent mass fraction as in fig. 4b including PtO (black bar) and Pt_3O_4 (dashed bar). The solid line stands for the mass frequency of the metallic platinum phase alone.

mental data as demonstrated by the comparison fit/experiment in fig. 4a. Attempts to fit the angular scan recorded at point B in fig. 2 with pure metallic Pt clusters failed. A successful fit to the experimental data was, however, possible with a distribution consisting of a mixture of metallic clusters and PtO and Pt_3O_4 clusters. The histogram and the resulting fit are reproduced in figs. 5a and 5b, respectively. The formation of PtO_2 has not been included in the histogram because its inclusion substantially worsened the quality of the fit [15–17].

The above results demonstrate that the transition from a predominantly CO covered surface at A to a predominantly oxygen covered surface at B in fig. 2 is accompanied by oxide formation. The degree of oxidation, which can be taken from the histogram in fig. 5b, is roughly 20–30% of the metal atoms. Repeated scans showed that the transition from A to B and subsequently to C is reversible and that no sintering occurs if a sufficiently high amount of the carrier gas He is used at the ignition point. The data indicate that smaller particles exhibit a higher tendency for oxidation than larger particles. Consistent with the experimental data and with the reversibility of the oxidation process is a shell model in which partial oxidation of the larger particles takes place such that a core of metallic Pt is surrounded by a shell of oxide. With the high dispersion of 65% of the catalyst such a model is practically equivalent to stating that only the surface atoms are being oxidized. The hypothetical cluster distribution curve one obtains for complete oxidation of the surface atoms is represented by the dashed curve in fig. 4b.

Since the transition from A to B is reversible and since the Bragg intensity during kinetic oscillations varies between the intensity levels corresponding to points A and C in fig. 2, one has to conclude that the rate oscillations are associated with a periodic oxidation and reduction of the Pt catalyst. In earlier studies it had already been demonstrated that during oxidation of the EuroPt-1 catalyst, the intensity of the Pt(111) peak varies anticorrelated to peaks belonging to Pt O [16]. Such a periodic oxidation and reduction has been proposed as the driving force for rate oscillations by Sales, Turner and Maple, and the present data apparently represent the first direct experimental evidence for the correctness of the oxide model [5]. The phase difference of 120° between T oscillations and X-ray intensity oscillations seen in fig. 3 is consistent with this model because first the catalyst should become deactivated by oxidation and only then should the temperature decrease as a consequence of a reduced catalytic activity. Reactivation of the catalyst takes place as the oxidized inactive surface becomes covered by CO leading to a reduction of the oxide.

Some experimental support for the oxide model has already been gathered in earlier investigations. In a Fourier transform infrared (FTIR) study Lindstrom and Tsotsis found, in addition to oscillatory changes in the intensity of the CO stretching frequency at 2070 cm^{-1}, a second band at 2120 cm^{-1}, which exhibited oscillatory changes on a slow time scale [10]. They attributed this band to CO adsorbed on the oxidized Pt surface and since the catalyst they used was Pt supported on Al_2O_3 their interpretation is consistent with our results. In a CO oxidation study in which oxygen was electrochemically pumped onto a Pt film evaporated on a solid-state electrolyte, Vayenas et al. concluded that PtO_2 is formed under oscillatory conditions [13]. In none of these studies, however, has it been proven that a periodic oxidation and reduction of the catalyst takes place under oscillating conditions.

In order to really substantiate the proposed oxide model one has to rule out other sources for the observed changes in the X-ray intensity during rate oscillations. Since the reconstructions of Pt(100) and Pt(110) can be lifted in the presence of an adsorbate one could argue that a similar mechanism also holds for the small Pt cluster possibly associated with a structural rearrangement of the whole cluster [1,2]. The observed variations of Bragg intensity could thus be caused entirely by structural changes of the metal substrate without any involvement of an oxidation/

reduction cycle. Such a mechanism, however, can be excluded because cluster calculations with fixed mass and varying shape and surface geometries demonstrated that the resulting intensity variations are too small to explain the experimentally observed oscillations in the Bragg intensities.

In summary, it has been demonstrated by in situ X-ray diffractometry that the rate oscillations observed in catalytic CO oxidation on supported Pt catalysts are accompanied by a periodic oxidation and reduction of the surface. These results therefore demonstrate the validity of the oxide model for rate oscillations on supported Pt catalysts. Whether the oxide model is also applicable to kinetic oscillations on Pt foils or Pt wires needs to be verified in future experiments, since small Pt clusters presumably have a much higher tendency to form oxides than massive Pt metal.

Acknowledgement

The authors would like to thank I. Heinrichs for designing the in situ cell used in the experiments.

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