

Platinum deactivation: *in situ* EXAFS during aqueous alcohol oxidation reaction

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With a new set-up for *in situ* EXAFS spectroscopy the state of a carbon-supported platinum catalyst during aqueous alcohol oxidation has been observed. The catalyst deactivation during platinum-catalysed cyclohexanol oxidation is caused by platinum surface oxide formation. The detected Pt–O co-ordination at 2.10 Å during exposure to nitrogen-saturated cyclohexanol solution is different from what is observed for the pure oxidised platinum surface (2.06 Å).

Keywords: platinum, EXAFS, catalysis, catalyst deactivation, oxidation

1. Introduction

Selective oxidation of alcohols and carbohydrates provides useful products and intermediates for fine chemistry. The main oxidation products of primary alcohols are aldehydes and carboxylic acids, secondary alcohols yield ketones. Under some conditions total oxidation towards carbon dioxide occurs, which is useful for waste treatment.

For more than 150 years noble-metal-catalysed aqueous-phase oxidation using dioxygen has been studied. An oxidative dehydrogenation mechanism on a reduced metal surface has been generally accepted (figure 1). Platinum and palladium proved to be the most promising catalysts, but fast catalyst deactivation has prevented large-scale use of this process [1]. Several mechanisms for the deactivation of platinum have been proposed:

- Formation of strongly adsorbing by-products, including coke deposition. During oxidation of primary alcohols the most common poison is carbon monoxide [2].
- Oxidation of the platinum surface, also known as over-oxidation. The platinum surface is either covered with strongly adsorbed oxygen species or a surface platinum oxide is formed. Both mechanisms lead to inactive surface sites [3,4].
- Corrosion and Ostwald ripening of the platinum particles. High temperature and high pH promote these mechanisms, leading to a smaller reactive surface [5].

Recent work by Vleeming et al. [3] on the aqueous-phase oxidation of methyl glucoside with graphite-supported platinum showed a decrease in reaction rate of 80% in 2 h. The

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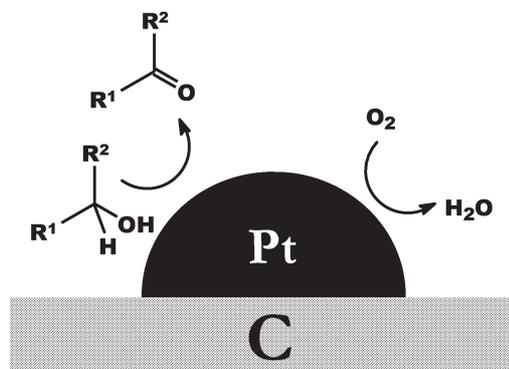


Figure 1. Alcohol oxidation on supported platinum.

activity of the catalyst was completely recovered by *in situ* replacement of oxygen by nitrogen for 1000 s (figure 2). Hence, catalyst over-oxidation is the most probable cause of deactivation.

In the past much work has been done to discover the nature of platinum over-oxidation. Electrochemical methods such as cyclic voltammetry proved the existence of several types of adsorbed oxygen. The reduction characteristics of oxidised platinum indicated restructuring of the platinum surface. No bulk-platinum oxidation was established at potentials below the oxygen evolution region [6,7].

It is obvious that the state of platinum during an aqueous oxidation reaction is different from that under ultra-high vacuum conditions. However, the small size of the catalytic platinum particles (typically below 2 nm) and the low platinum to background ratio hinder the *in situ* use of most catalyst characterisation techniques. Extended X-ray absorption fine structure (EXAFS) spectroscopy is a very powerful and versatile characterisation technique [8]. The technique can be applied *in situ* (at reaction conditions and in the presence of reactants) and gives information that has proved

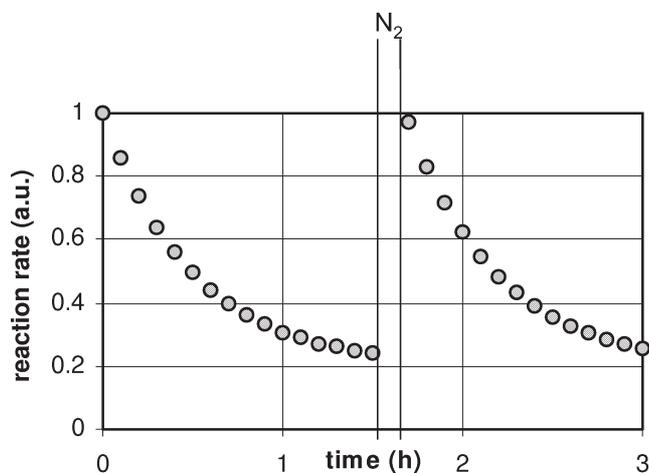


Figure 2. Platinum catalyst deactivation and reactivation by *in situ* replacement of oxygen by nitrogen.

to be very suitable for the characterisation of supported catalysts. Because X-ray absorption at the platinum L_{III} edge is much more sensitive to platinum than to other elements it is possible to work with supported catalysts in water.

Previous work on γ - Al_2O_3 -supported platinum [9] and iridium [10] particles indicated the existence of three different Pt–O distances: an oxidic distance at 2.05 Å, a metal–support distance at 2.20 Å, which is also found for adsorbed oxygen at 77 K, and a metal–support distance at 2.66 Å after low-temperature reduction. The different types of distances including the experimental conditions necessary to create the different types of Pt–O bonds are extensively discussed in [11]. The Pt–O distance of 2.20 Å occurs for interfacial platinum atoms in direct contact with support oxygen ions. The longer distance of about 2.6 Å can be detected if hydrogen is present in the metal–support interface.

So far, no platinum EXAFS measurements under aqueous reaction conditions have been reported. Exposure of small (less than 0.7 nm) supported platinum particles to gaseous oxygen leads to total oxidation towards PtO_2 , whereas bigger particles show surface oxide formation [12]. Van den Tillaart [13] and Pinxt [14] used EXAFS to characterise carbon-supported platinum catalysts in water after various oxidative and reductive treatments.

The scope of the present work is characterisation by EXAFS of a carbon-supported platinum catalyst during aqueous alcohol oxidation. Changes in particle morphology and different types of Pt–O distances have been observed dependent on the applied reaction conditions.

2. Experimental

The reactants used for this EXAFS investigation are cyclohexanol and oxygen. The reaction products are cyclohexanone and water. Poisoning of the catalyst by carbon monoxide or coke formation is unlikely using cyclohexanol

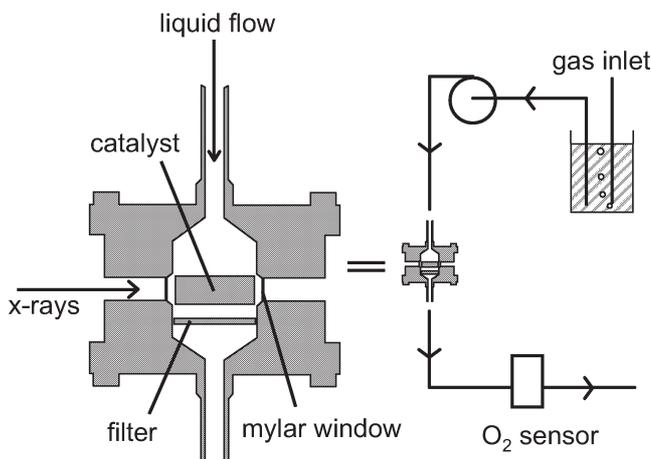


Figure 3. Cell for *in situ* EXAFS measurement during platinum-catalysed alcohol oxidation.

as a reactant [2]. The reactor is operated at room temperature.

The EXAFS cell we used (figure 3) is a modification of a cell described in detail in a previous paper by Pinxt et al. [14]. A continuous liquid flow is now led through the cell during pretreatments and measurements. The cell consists of a reactor chamber with an X-ray beam path of 3 mm, a liquid supply tube and a liquid outlet tube. The reactor is filled with a packed bed of carbon-supported platinum, which is kept in the reactor by a paper filter and a thin layer of quartz powder. A flow of water or aqueous cyclohexanol solution is led through the cell. Before it is fed to the cell, the liquid is saturated with hydrogen, nitrogen or oxygen.

The low oxygen solubility (typically 1.3 mol/m³) and diffusion rate set strict demands upon the *in situ* EXAFS cell and the catalyst. In order to obtain a homogeneous sample, the oxygen concentration should be uniform throughout the cell. This implies that large microporous catalysts should be avoided, because oxygen gradients are likely to occur in the inner regions of the particles, causing inhomogeneous reaction conditions. Small particles cannot be used due to the high pressure drop. Carbon fibrils are not porous, but do have a high surface area, which makes them very suitable for EXAFS purposes.

The catalyst, 5.7 wt% platinum on carbon fibrils, was prepared by Vleeming [15] by ion exchange using a tetramineplatinum(II) hydroxide ($Pt(NH_3)_4(OH)_2$) solution. The characteristics of the catalyst are described in the same paper [15]. The surface area averaged platinum particle diameter, as determined, with transmission electron microscopy (d_s^{TEM}), is 1.8 nm. The platinum fraction exposed, as measured with CO chemisorption, is 0.53.

The packing density of the catalyst bed is typically 200 kg/m³. The catalyst content of the cell is between 50 and 100 mg. The pressure drop over the catalyst bed (typical height 4 mm, typical superficial velocity 1.5 mm/s) is below 0.3 bar. The residence time is about 3 s, which infers a very low conversion of reactants and near-homogeneity of

Table 1

EXAFS analysis results for carbon-fibrils-supported platinum. The accuracies of the results are: Pt co-ordination number (N) 5%, C and O co-ordination number 10%, Debye–Waller factor ($\Delta\sigma^2$) 5%, atomic distance (R) 0.01×10^{-10} m and energy correction (E_{corr}) 10%.

	Shell	N	$\Delta\sigma^2$ ($\times 10^{-22}$ m ²)	R ($\times 10^{-10}$ m)	E_{corr} (eV)	Fit variance (im, abs)
Hydrogen in water	Pt	8.4	0.4	2.76	2.7	0.375
	C	0.8	0.2	2.57	11.2	0.244
Oxygen in water	Pt	5.3	0.7	2.75	1.5	0.378
	O	2.1	0.5	2.06	4.4	0.277
Nitrogen in 0.05 M cyclohexanol	Pt	7.6	0.6	2.75	1.8	0.253
	O	1.1	0.6	2.09	2.2	0.176
Nitrogen in 0.01 M cyclohexanol	Pt	7.8	0.5	2.74	1.9	0.380
	O	0.8	1.0	2.10	1.2	0.271
Oxygen in 0.2 M cyclohexanol (ox)	Pt	6.6	0.6	2.75	1.6	0.186
	O	1.5	0.6	2.06	4.4	0.128
Oxygen in 0.2 M cyclohexanol (red)	Pt	7.5	0.6	2.76	0.7	0.396
	O	1.5	0.8	2.08	2.6	0.207
Oxygen in 0.05 M cyclohexanol (ox)	Pt	7.0	0.6	2.75	1.2	0.379
	O	1.4	0.9	2.09	1.6	0.235
Oxygen in 0.05 M cyclohexanol (red)	Pt	6.8	0.6	2.75	1.2	0.142
	O	1.4	0.5	2.07	3.8	0.093
Oxygen in 0.01 M cyclohexanol (ox)	Pt	5.7	0.5	2.75	0.9	0.289
	O	1.8	0.7	2.08	3.0	0.183
Oxygen in 0.01 M cyclohexanol (red)	Pt	6.6	0.6	2.75	1.2	0.315
	O	1.5	0.8	2.07	3.4	0.188

the liquid stream. The oxygen concentration of the effluent is measured. The maximum oxygen conversion is 21%.

An EXAFS measurement consists of six scans of 30 min each. Prior to measurement, all catalyst samples have been reduced *in situ* by feeding hydrogen-saturated water at ambient for 1 h. This state corresponds with the “hydrogen in water” measurement in table 1. After this treatment the hydrogen is purged using nitrogen. For measurement of an oxidised catalyst (“oxygen in water”) the reduced catalyst sample is treated with a feed of oxygen-saturated water for 90 min prior to measurement. The interaction between platinum and cyclohexanol under non-reaction conditions is measured while feeding nitrogen-saturated cyclohexanol solution to a reduced catalyst sample (“nitrogen in 0.05 or 0.1 M cyclohexanol”).

There are two types of measurements under reaction conditions, indicated “ox” and “red”. Prior to the “ox” measurements the reduced catalyst sample is exposed to a feed of oxygen-saturated water for 90 min. After this treatment the feed is changed to oxygen-saturated cyclohexanol solution. After 2 h a steady state is assumed and EXAFS measurement starts. This procedure is called an oxidative start-up, indicated “ox” in table 1. Prior to the reductive start-up measurements, indicated “red”, a nitrogen-saturated cyclohexanol solution is fed to the reduced catalyst sample for 3 h. After this an oxygen-saturated cyclohexanol solution is fed and after 2 h the “red” EXAFS measurement starts.

EXAFS measurements were performed at station 9.2 of the SRS at Daresbury (UK) with an electron beam energy

of 2 GeV and a stored current varying between 140 and 250 mA. The wiggler was operated at 5.0 T. Data were collected in transmission mode at the Pt L_{III} edge from 11.37 to 13.63 keV using a Si(220) monochromator detuned to 50% harmonic rejection. Energy calibration was monitored using a platinum foil and a third ion chamber and was set at 11.564 keV for the Pt L_{III} edge.

Data analysis was performed using the computer program XDAP (XAFS Services, Utrecht). The pre-edge background was subtracted using a Victoreen approximation. The EXAFS oscillations were isolated from the background using a flexible spline approximation. The EXAFS data were normalised by division by the absorption edge. The final χ -data were obtained by averaging the individually processed EXAFS data.

Phase shift and amplitude functions used here were extracted from reference compounds [16]. Regression was performed by multiple shell fitting using a minimisation routine incorporated into the program. Data from the k -range 3–14.4 Å⁻¹ were regressed in R -space 1.5–3.1 Å. The sum of square residuals between the observed and calculated EXAFS χ -data was minimised. The regressions were performed using k^2 -weighted χ -data for the Pt shell and k^1 -weighted χ -data for lower Z shells (C and O). The optimal combination of the co-ordination number and the Debye–Waller factor was determined with the difference file technique, i.e., by optimisation of the individual contributions of the different shells to the k^1 - and k^3 -weighted Fourier transforms [17].

3. Results and discussion

The EXAFS data analysis results are presented in table 1. The quality of the spectra is very high and the statistical error in the spectra is negligible in comparison with the systematic error. A typical Fourier transform of a spectrum and corresponding fit in R -space is shown in figure 4. The accuracies of the results are: Pt co-ordination number (N) 5%, C and O co-ordination number 10%, Debye–Waller factor ($\Delta\sigma^2$) 5%, atomic distance (R) 0.01×10^{-10} m and energy correction (E_{corr}) 10%.

The Pt–Pt co-ordination number 8.4 for completely reduced platinum particles (hydrogen in water) is in good agreement with simulations performed by Kip et al. [18]. According to Kip et al., the Pt–Pt co-ordination number 8.5 corresponds with a spherical 100 atoms particle with diameter 1.9 nm. The Pt–C distance (2.57 Å) is much longer than expected from direct contact between platinum and carbon. This shows the existence of an interfacial layer of hydrogen between the platinum particle and the carbon support, as demonstrated for γ -Al₂O₃-supported platinum particles [9].

Upon exposure to oxygen-saturated water the catalyst showed a large Pt–O co-ordination ($N = 2.1$), while the Pt–C interaction disappeared. The Pt–O interatomic distance of 2.06 Å is typical for platinum oxides. The Pt–Pt interatomic distance remained equal, which indicates that metallic platinum (Pt⁰) is still present. The low remaining Pt–Pt co-ordination suggests that most of the platinum surface has been oxidised towards a platinum oxide. The proposed structure of an oxidised platinum particle is a kernel of metallic platinum, covered by a monolayer of platinum oxide. This proposed structural model also explains the absence of a Pt–C co-ordination.

The Pt–O co-ordination as observed during exposure to nitrogen-saturated cyclohexanol solutions can be attributed to adsorption of cyclohexanol to the platinum surface. The Pt–O interatomic distance (2.09 and 2.10 Å) is longer than

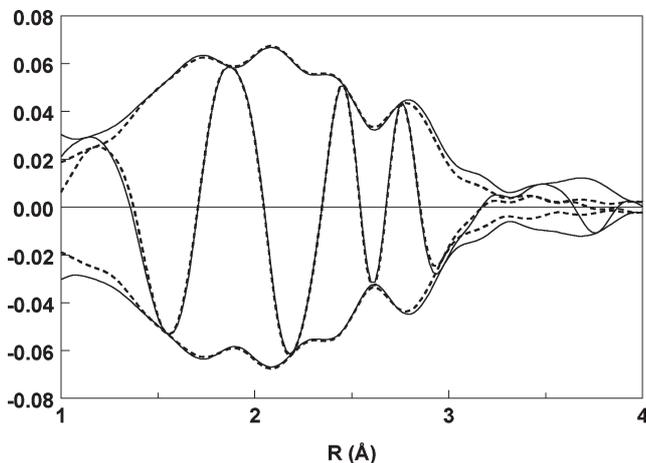


Figure 4. Platinum under oxygen in 0.05 M cyclohexanol after reductive start-up. Fourier transforms, k^1 -weighted, of raw EXAFS data (black lines) and R -space fit (dotted lines).

the typical oxidic distance and is due to an interaction of the surface platinum with an oxygen atom from the cyclohexanol substrate. The Debye–Waller factor $\Delta\sigma^2$ is higher than in the oxidic sample, notably for the lowest cyclohexanol concentration. Also, the lower values for the E_{corr} point to a different type of Pt–O co-ordination. The lower Pt–Pt co-ordination in comparison with the reduced sample (7.6 and 7.8 vs. 8.4 Å) could be explained by a change in particle morphology from spherical to hemi-spherical or flatter platinum particles. The absence of chemisorbed hydrogen (less neighbouring atoms) increases the surface free energy, which can be partly compensated by flattening of the metal particle, thereby increasing the number of neighbouring atoms (i.e., carbon atoms from the support).

The EXAFS spectra recorded during cyclohexanol oxidation reaction (besides cyclohexanol also oxygen present on the surface of the platinum particles) all show a considerable Pt–O co-ordination (between 1.4 and 1.8) at an interatomic distance that is slightly longer than the oxidic distance (between 2.06 and 2.09 Å). Again, the Pt–Pt interatomic distance is typical for metallic platinum (2.75–2.76 Å). The reaction conditions have the most influence on the Pt–Pt co-ordination number N , which varies between 7.5 for the most reductive environment (0.2 M cyclohexanol, reductive start-up) and 5.7 for the least reductive environment (0.01 M cyclohexanol, oxidative start-up). The degree of oxidation is higher after an oxidative start-up than after a reductive start-up. This multiple steady-state behaviour has been demonstrated before in the platinum-catalysed oxidation of aqueous ethanol [19].

The results indicate that during reaction conditions (in the presence of cyclohexanol and oxygen) after a few hours of operation the surface of a deactivated platinum catalyst is partially covered with platinum oxide. Since the oxidation reaction still takes place, both Pt–O bonds due to the reaction with cyclohexanol as well as Pt–O bonds originating from the surface PtO_x will be present. EXAFS will average these two different co-ordinations, and indeed, the detected Pt–O distance lies between a fully oxidic distance (2.05 Å) and a Pt–O distance as found for absorption of cyclohexanol on a platinum metal (2.1 Å). This has been schematically illustrated in figure 5.

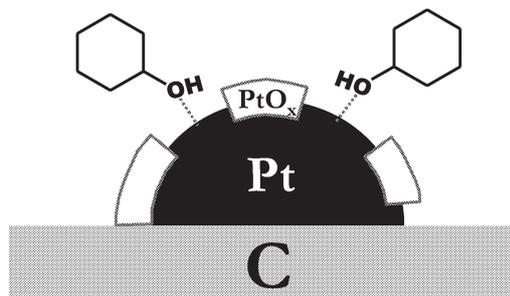


Figure 5. Deactivated platinum catalyst during reaction.

4. Conclusions

EXAFS is very suitable for measurement of the state of platinum catalysts during aqueous-phase reaction. With the described set-up it is possible to measure platinum EXAFS *in situ* under well-defined reaction conditions and without oxygen transfer limitations.

Aqueous hydrogen at room temperature fully reduces carbon-supported platinum particles. Treatment of platinum with water containing oxygen leads to a significantly lower Pt–Pt co-ordination and a high Pt–O co-ordination. This indicates restructuring of the platinum surface, due to surface oxide formation. The oxidised platinum particles consist of a kernel of metallic platinum, covered by a monolayer of platinum oxide. Exposure of platinum to water containing cyclohexanol and nitrogen leads to cyclohexanol chemisorption and a change in particle morphology, i.e., deformation of the platinum particles. This cyclohexanol chemisorption gives rise to a non-oxidic Pt–O co-ordination with typical distance around 2.1 Å.

Under aqueous alcohol oxidation reaction conditions platinum catalyst deactivation takes place. *In situ* EXAFS spectra of deactivated platinum catalysts under steady-state reaction conditions show that the Pt–Pt co-ordination and the Pt–O co-ordination lie between those of reduced and oxidised platinum, which indicates that the platinum surface is partially oxidised. After a reductive start-up as well as after an oxidative start-up the degree of platinum oxidation depends on the cyclohexanol concentration. The lowest degree of platinum oxidation was found after a reductive start-up with the highest cyclohexanol concentration, whereas an oxidative start-up with the lowest reactant concentration resulted in an almost completely oxidised platinum surface.

Due to the long measurement time required in transmission EXAFS only steady-state circumstances could be investigated. More insight into the initial platinum deactivation process is expected from the faster dispersive time-resolved EXAFS techniques. This will be the next step in our research of platinum catalysis in aqueous media.

Notation

d_s^{TEM}	surface area averaged particle diameter (m)
E	photon energy (eV)

E_{corr}	energy correction (eV)
E_0	edge energy (eV)
k	wavenumber (m^{-1})
N	co-ordination number
R	atomic co-ordination distance (m)
$\Delta\sigma^2$	Debye–Waller factor (m^2)
χ	normalised modulation of absorption coefficient

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