Time resolved X-ray absorption spectroscopy applied during ignition of oxidation of carbon monoxide

J Singh, E M C Alayon, M Nachttegaal, and J A van Bokhoven

1 Institute for Chemical and Bioengineering, ETH Zurich, 8093 Zurich, Switzerland
2 Paul Scherrer Institute, General Energy Research Department, Laboratory for Energy and Material Cycles, 5232 Villigen PSI, Switzerland

E-mail: jeroen.vanbokhoven@chem.ethz.ch

Abstract. The structure of supported platinum catalyst (2 wt% Pt/Al₂O₃) has been determined during the sudden change in the activity of the catalyst, referred as “ignition”, during oxidation of carbon monoxide. The catalyst was prepared by incipient wetness impregnation method. The active phase of the catalyst is shown to be a highly disordered platinum oxide. This surface oxide increases with the increase of carbon monoxide conversion during the ignition process, which further increased the conversion, making the process autocatalytic. The QEXAFS spectra collected at Pt L₃ edge with a time resolution of 0.5 sec are compared with the standard EXAFS that are generally collected in transmission mode and are shown to be useful to extract valuable information about the changing structure of the catalyst during the ignition.

1. Introduction
The oxidation of carbon monoxide is a relevant reaction considering its importance in the preferential oxidation of carbon monoxide in hydrogen-rich gas in fuel cells [1] and in the oxidation of carbon monoxide and other hydrocarbons in automobile exhaust systems [2]. Although the oxidation of carbon monoxide seems straightforward, there are still unanswered questions with regard to the reaction mechanism and the catalytically active species. It is common that during the oxidation of carbon monoxide over single crystals [3-8] and supported metal catalysts [3,9-12] self-sustained kinetic oscillations occur. Ertl and co-workers suggested that these oscillations on single-crystal surfaces under low-pressure conditions arise from two different surface reconstructions of the platinum surface after the adsorption of carbon monoxide, forming carbon monoxide-rich and oxygen-rich domains that have different reaction rates [3,4,13]. Over supported catalysts under ambient conditions, the oscillations have been related to alternating oxidation and reduction of the catalyst surface [14], to the blocking of active surface by strong adsorption of products such as carbon [15], and to variation in the size of islands of adsorbed carbon monoxide on the catalyst surface [11].

On single crystal Pt(111) surfaces, two reaction regimes for oxidation of carbon monoxide have been identified: a regime with low activity and one with high activity of the catalyst [16]. There is a sudden transition between these two regimes which is referred as “ignition”. Below the ignition temperature, carbon monoxide is bound atop to the surface, and the reaction rate is low due to poisoning of the active surface by carbon monoxide. Desorption of the carbon monoxide is the rate-limiting step. Similar results have been obtained for supported metal catalysts in the low-activity

1 To whom any correspondence should be addressed.
region [12,17-20]. There is no or very little adsorbed carbon monoxide above the ignition point [21,22]. In the high-activity region the structure of the catalyst for supported platinum catalysts remain unclear and is still debated. In contrast to the single crystals, the high activity state is shown to be characterized by the presence of a surface oxide [20,23]. Determining the structure of the catalyst during the ignition process is important to bridge the gap between structure of catalyst in the low- and the high-activity region. This ignition, which occurs generally in the order of few seconds, is rather a challenging process to characterize as it requires a fast response technique with capabilities of revealing the catalyst structure under in situ conditions. The work presented here is concentrated on determining the structure of the catalyst during the ignition process. We have studied the catalyst structure during this fast ignition process by combining quick extended X-ray absorption spectroscopy (QEXAFS) [24,25] with kinetic measurements. The spectra collected using QEXAFS technique were compared with standard EXAFS spectra to test the validity of this method to track fast structural changes occurring during ignition of oxidation of carbon monoxide.

2. Experimental

2 wt% Pt/Al₂O₃ catalyst, prepared by incipient wetness impregnation, showed a narrow particle size distribution as determined by electron microscopy. The experimental runs were performed on a reactor based on a model [26] which resembles a plug-flow reactor with a diameter of 1.6 mm. The catalyst, (x mg) sieved to 63-125 µm fraction, was pre-reduced in a flow of diluted hydrogen and afterwards exposed to the reaction mixture with an oxygen to carbon monoxide ratio of one. The space velocity was 61,000 h⁻¹. The details of the synthesis of catalyst and kinetic measurements are described elsewhere [27]. QEXAFS experiments were done at superXAS beamline at the Swiss Light Source (SLS), Villigen, Switzerland. A channel cut Si(111) crystal in the QEXAFS monochromator was used to monochromatize the radiation. Spectra were collected in transmission mode using two ionization chambers filled with air. QEXAFS spectra were collected with a time resolution of 0.5 seconds during heating the sample at 2 K/min using oxygen to carbon monoxide ratio of one.

3. Results and discussion

The two reaction regimes – namely low activity regime and high activity regime, have been observed and characterized as far as conversion in CO is concerned [19,20]. To test the potential of the QEXAFS technique, a comparison was made between the spectra collected at the Pt L₃ absorption edge energy by QEXAFS technique with those collected with standard mode EXAFS. Figure 1(a) shows the conventional XAS Pt L₃ edge spectra of supported platinum catalyst in low-activity regime (before ignition) and high-activity regime (after ignition) during oxidation of carbon monoxide in oxygen to carbon monoxide ratio of one. The catalyst in the low-activity regime is characterized by the adsorption carbon monoxide [9,11,13,19,20]. This was confirmed by the spectrum (solid) with lower whiteline intensity and more features in the XANES region after the absorption edge. The reduction of the catalyst by the adsorbed carbon monoxide that poisons the surface [16] resulted in low rate of reaction [19]. Figure 1(a) shows also the spectrum (dash) of platinum in the high-activity regime. Here, the whiteline intensity is much higher and the edge position is shifted slightly to lower energy, showing the oxidic behaviour of the catalyst in this regime [28]. The structure of the oxide was highly defective and platinum was undercoordinated to oxygen [20]. Figure 1(b) shows the two spectra as in Figure 1(a) but acquired using QEXAFS technique with a time resolution of 0.5 second. The spectra collected at this frequency compares very well to the normal XAS spectra taken at Pt L₃ edge energy. All the features after the absorption edges in both the spectra resemble to those in the spectra collected in conventional way.
Figure 1: Pt L₃ edge XANES of 2 wt% Pt/Al₂O₃ recorded in low-activity regime (solid) and high-activity regime (dash) during oxidation of carbon monoxide in (a) standard EXAFS mode and (b) QEXAFS mode.

In Figure 1(a), the spectrum (dash) in the high-activity regime shows higher whiteline intensity in comparison to spectrum (solid) in the low-activity regime as shown in normal XAS. Also, there is a slight shift towards lower energy in the absorption edge of spectrum (dash) of oxidized platinum compared to the spectrum (solid) of reduced platinum with adsorbed carbon monoxide. However, in case of QEXAFS, the shift is not as large as shown in normal XAS. Also, the intensities of the whiteline in case of QEXAFS are lower than whiteline intensities of the normal XAS spectra that could probably be due to reduced energy resolution during fast scanning mode. Nevertheless, overall the comparison shows that QEXAFS is a suitable technique to study the ignition during the oxidation of carbon monoxide. Figure 2 shows the conversion of carbon monoxide as plotted against the temperature during the ignition.

Figure 2: Percentage conversion (■) of carbon monoxide over 2 wt% Pt/Al₂O₃ and corresponding whiteline intensity (●) of Pt L₃ edge XANES taken in QEXAFS mode during ignition.
The whiteline intensities of the spectra collected during the ignition are plotted in Figure 2. The data shown here have been reproduced from the previous work [19]. The whiteline intensity followed the conversion of carbon monoxide during the ignition process. This shows that as the conversion is increasing with temperature, the platinum gets more and more oxidized. We suggest that the increasing temperature facilitated the desorption of carbon monoxide, which in turn resulted in the further oxidation of the surface, thus forming the active platinum oxide species for the reaction. Therefore, the whole process becomes autocatalytic in nature. From these spectra, the Fourier Transforms (FT) were collected, which is a more way of representing the data.

![Figure 3: Fourier Transforms (k1-weighted) of (a) 2 wt% Pt/Al2O3 during ignition, and (b) reference compounds.](image)

Figure 3: Fourier Transforms (k1-weighted) of (a) 2 wt% Pt/Al2O3 during ignition, and (b) reference compounds.

Figure 3(a) shows the magnitude of the Fourier Transformed spectra acquired during the ignition process. The time indicated with each FT is the time after the start of ignition process. The two peaks around R+\(\Delta R\) value of 2.2 Å and 2.7 Å, as seen in the start of ignition is the indication of the reduced state of the catalyst [20]. These peaks are comparable to metallic platinum as shown in Figure 3(b). As the ignition process continued, the peak around 2.7 Å starts decreasing in intensity and shifted to lower R. During the ignition process, a new peak emerges around 1.6 Å which is characteristic of oxidized platinum as compared to platinum oxide shown in Figure 3(b) [20]. Therefore, the ignition process during the oxidation of carbon monoxide could be well characterized by the use of time resolved QEXAFS technique applied here. The technique offers future potentials for measuring in situ changes occurring at high frequencies during various catalytic processes.
4. Conclusions
The fast occurring ignition process during oxidation of carbon monoxide has been characterized using QEXAFS technique. The ignition process is accompanied by increasing amounts of platinum oxide, which autocatalytically increased the conversion of carbon monoxide. The comparison of QEXAFS spectra with the standard XAS spectra shows the high potential of QEXAFS technique for characterizing the fast and sudden changes in real catalysis under real conditions.

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5. References

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