



	Experiment title: Time-resolved in situ XAS/FTIR/MS study on kinetic ignition and extinction phenomena in low temperature oxidation of CO and methane over supported Pt catalysts	Experiment number: SI1799
Beamline: ID24	Date of experiment: from: 090205 to: 090210	Date of report: 090407
Shifts: 15	Local contact(s): Mark A. Newton	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Per-Anders Carlsson*, Elin Becker*, Lisa Kylhammar* and Magnus Skoglundh* Department of Applied Chemistry and Competence Centre for Catalysis, Chalmers University of Technology, 412 96 Gothenburg, Sweden		

Report:

We have carried out time-resolved in situ dispersive XAS measurements of supported Pt catalysts operating at transient conditions. Simultaneously, we monitored the adsorbate composition on the surface of the catalyst and the catalytic activity with, respectively, DRIFT spectroscopy and mass spectrometry (MS) using the impressive set-up developed by the scientists at ID24. The overall goal was to understand the connection between the chemical state of the supported Pt crystallites and the reaction kinetics/mechanisms. At the time of writing, we are working on the detailed evaluation of the XAS/FTIR/MS data. The results will be presented in a series of scientific papers. We thus here only show one example of the type of experiments we performed.

During the laboratory session we focused on detailed studies of ignition- and extinction processes for a few key reaction systems, e.g., CH₄ oxidation, CO oxidation and NO oxidation, through step- and pulse response experiments. The chemical state of the Pt crystallites was studied in the XANES region for the Pt L_{III} absorption and correlated with the adsorbate composition following various specific absorption bands and catalyst activity/selectivity. For evaluation of the XANES data we use a method that is based on analysis of the area under the white-line (WLA). This method has previously been developed for qualitative analysis by our group. The WLA has been found sensitive also to small changes in the absorption spectrum and thus suitable for studies of the mentioned catalytic reactions. During this session we aimed at improving the WLA method so that quantitative results can be obtained.

To facilitate such analysis of spectra we made several measurements on various platinum compounds with different known oxidation state serving as references.

The included figures show the results from an oxygen pulse-response experiment on methane oxidation over a Pt/Al₂O₃ catalyst. The oxygen pulsing induces ignition-extinction events that are carefully monitored by XAS/FTIR/MS. The XAS figure reveals changes in the surface O:Pt ratio, i.e. oxidation state and/or oxygen coverage, of the Pt crystallites as a result of the changes of the oxygen gas phase concentration. This is not surprising, however, interestingly for each switch in oxygen concentration the activity for methane oxidation activity passes through a maximum as reflected by the dip in the m/z 15 signal (MS figure). This suggests that the Pt catalysts used here may exhibit an optimal (intermediate) oxidation state and/or oxygen coverage that leads to highest activity. A more detailed quantification of this state is ongoing. For this particular experiment the FTIR spectroscopy results show no dramatic changes in adsorbate composition, i.e., no obvious poisoning by for example produced CO or other carbonaceous species. Thus the high activity cannot be explained by a favorable adsorbate composition alone. This supports further that the surface O:Pt ratio is crucial for the activity.

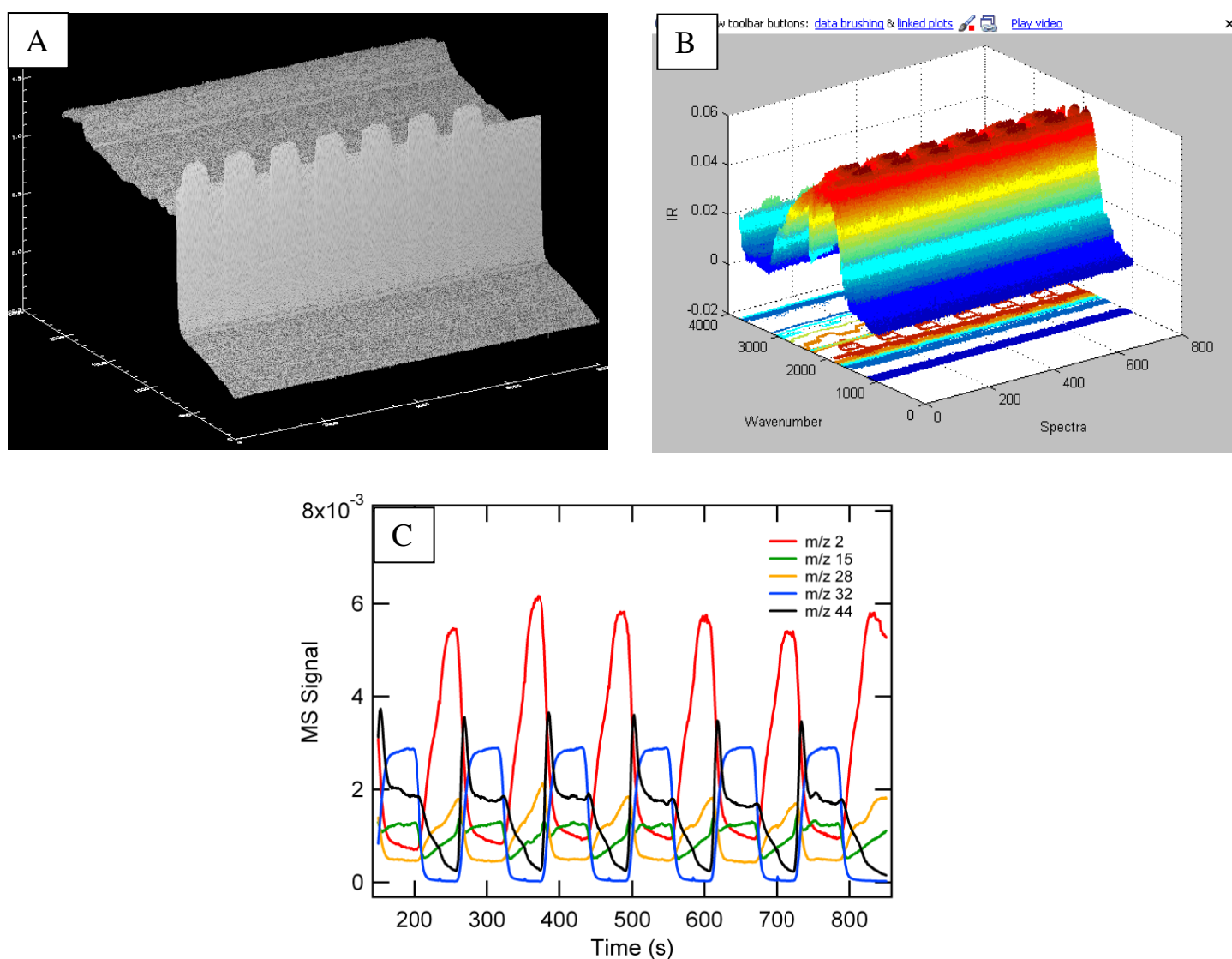


Figure 1. Induced ignition-extinction of CH₄ oxidation over Pt/Al₂O₃ catalyst by oxygen pulsing while simultaneously monitoring the surface O:Pt ratio via the XANES at the Pt L_{III} edge (panel A), gas phase and surface species by DRIFT spectroscopy (panel B) and catalyst activity by mass spectrometry (panel C).