

The Dehydrogenation of Methanol on Pt Electrodes as Revealed by Time-Resolved ATR-SEIRAS

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Abstract: Alcohols and other liquid fuels have the advantage of having a much larger volume energy density than hydrogen as well as easier storage and transport. When produced by hydrogenating CO₂ using green hydrogen, they can be used as a carbon-neutral energy vector. The simplest possible alcohol, methanol, is particularly attractive because its oxidation does not require the rupture of any carbon-carbon bond and such simplicity leads to a higher efficiency. As for many other energy-relevant reactions, Pt and Pt-based electrocatalysts are the most active materials for the oxidation of methanol to CO₂. However, in one of the reaction paths partial oxidation to adsorbed carbon monoxide (CO_{ad}) leads to poisoning of the catalyst. The most common strategy to reduce CO poisoning during methanol oxidation is to design catalysts on which CO oxidation occurs at as low an overpotential as possible. An alternative is to understand the mechanism of methanol dehydrogenation and to use that information to design catalysts on which this reaction is inhibited. For example, our group has shown that on catalysts missing the minimum atomic ensembles required for the formation of CO_{ad} total oxidation to CO₂ is possible in the absence of CO poisoning.¹ We will report on a time-resolved ATR-SEIRAS study of the formation of CO_{ad} on polycrystalline Pt. Our experiments reveal that different sites on the electrode surface are populated successively and have allowed us to identify those sites which are poisoned by CO first. We have also been able to obtain Tafel plots in both sulphuric and perchloric acid solutions, which reveal the role played by specifically adsorbing sulphate.

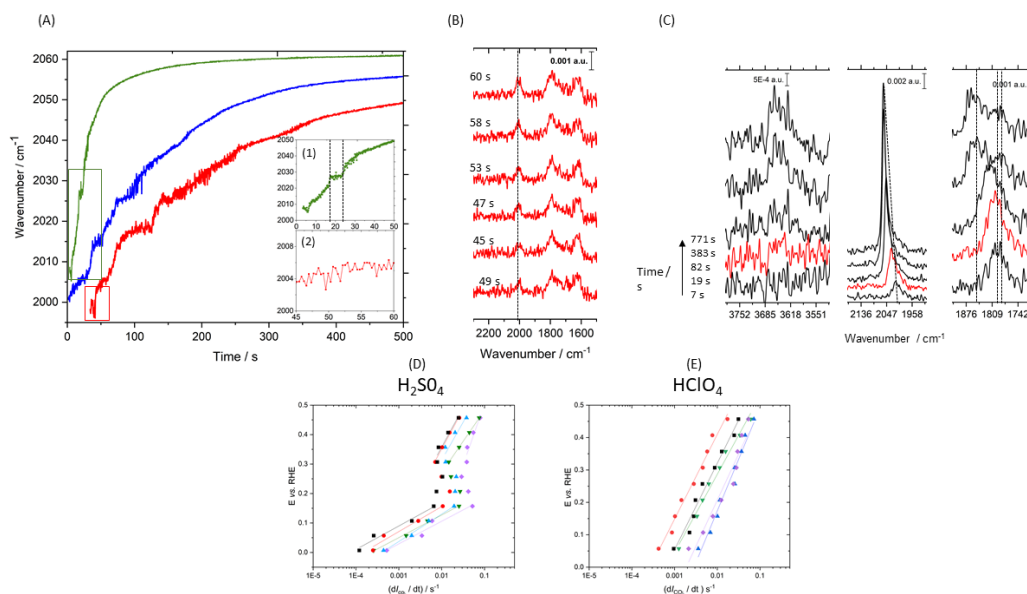


Figure 1. (A) Dependence of the C-O stretching frequency of on-top CO_{ad} on the reaction time at 0.06 V (red), 0.11 V (blue) and 0.21 V (green) vs RHE in 0.1 M H_2SO_4 containing 0.01 M CH_3OH . As shown in (B), in the initial stages of the reaction an increase in CO coverage does not result in an increase of the stretching frequency. (C) Selected spectra at 0.06 V vs. RHE in the regions corresponding to the O-H stretching of water (left), the C-O stretching of on-top CO_{ad} (centre) and the C-O stretching of bridge-bonded CO_{ad} . (D) and (E) are Tafel plots illustrating the dependence of the rate of formation of CO_{ad} on the electrode potential in 0.1 M H_2SO_4 and 0.1 M HClO_4 , respectively.

References:

[1] A. Cuesta, *J. Am. Chem. Soc.* **2006**, *128*, 13332-13333.

Biography: Prof. Angel Cuesta was selected as Provisional Staff Scientist at the Institute of Physical Chemistry “Rocasolano” (CSIC) in Madrid, where he was promoted to Staff Scientist in December 2002. He was promoted to the Senior Scientist scale of CSIC in March 2010 and was appointed as Senior Lecturer at the University of Aberdeen (UK) in July 2013, where he was promoted to Reader in August 2016 and to Personal Chair in August 2018. He was a Visiting Professor at the Catalysis Research Centre of Hokkaido University (Sapporo, Japan) in 2007.

