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“Initial Potential” Effect on the Dissociative Adsorption of Methanol on A Roughened Platinum Electrode in Acidic Solution

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Abstract: *In situ* Raman spectroscopic and voltammetric studies indicate that dissociative adsorption of methanol on the rough platinum electrode occurs in the hydrogen ad/desorption potential range, and the dissociative extent depends on the initial potential of the electrode before contacting methanol, in addition to the contacting time. As the dissociative product, carbon monoxide competes the site of strongly bound hydrogen preferentially, and shifts the ad/desorption potentials of weakly bound hydrogen towards more positive ones gradually with the increase of CO coverage. Whereas, formaldehyde dissociates more easily by far and completely suppresses H-adsorption. The confocal Raman spectroscopy developed on transition metals shows some intriguing advantages in investigating electrocatalytic oxidation of small organic molecules.

Keywords: Methanol, formaldehyde, dissociative adsorption, *in situ* Raman spectroscopy.

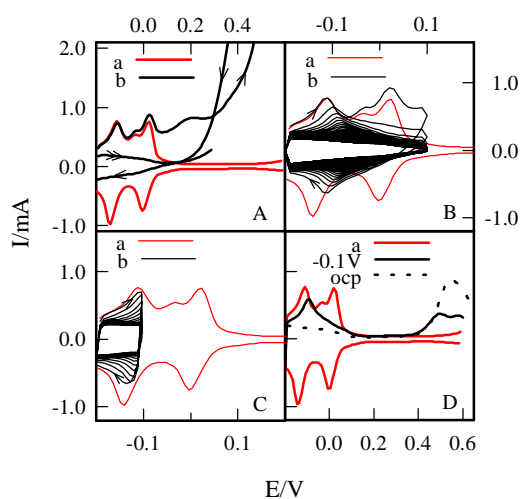
The research of electrocatalytic oxidation of small organic molecules such as methanol, formaldehyde and formic acid has been fascinating electrochemists for more than thirty years, owing to its significance in energy conversion and reaction mechanisms. The surface adsorbed species involved in these electrocatalytic reactions, especially reactive and poisoning intermediates, have been investigated by electrochemical, spectroscopic and other physicochemical methods¹. However, Raman spectroscopy has hardly been used as a technique so far to study the electrocatalytic oxidation processes of these reactants on Pt electrodes mainly due to its low sensitivity for the surface adsorbed species from that electrode². With an appropriate surface roughening procedure for bare Pt electrodes³ to gain the surface-enhanced Raman spectroscopic (SERS) effect and by using a confocal Raman microscope (LabRam I, Dilor, France)⁴, we are able to obtain good quality surface Raman signals of adsorbed CO as the dissociative product of small organic molecules on rough Pt electrodes with a thin-layer of solution as thick as 1 mm, which allows a large Faradaic current without hampering the electrochemical reactions.

In this work, the dissociative adsorption of methanol was studied by *in situ* surface Raman spectroscopy as well as electrochemical cyclic voltammetry. Some interesting results were obtained while different potentials were imposed on the electrode before the reactant was added into the blank solution, 1 mol/L H₂SO₄, which is what we mean by an “initial potential”. A comparative study was performed with formaldehyde.

The roughened electrode³ underwent a potential cycling between $-0.2\sim 1.2$ V *vs.* SCE in the blank solution of 1 mol/L H_2SO_4 till a repeatable cyclic voltammogram appeared (curve a's in **Figure 1**). Then methanol was admitted in while the cell was either on (controlling different initial potentials, -0.2 , -0.1 V) or open, and Raman measurement followed.

Vibrational bands of 490 and 2050 cm^{-1} in Raman spectra of **Figure 2** are from the Pt-C and C≡O of the linearly bound CO respectively, and the ability to obtain both the low frequency and the high frequency vibrations of Pt-C and C≡O bands allows the assignment of surface species unambiguously. The spectra show that the dissociative adsorption of methanol can occur at -0.1 V (**Figure 2b**), as well as at open circuit potential (**Figure 2c**), but doesn't happen at -0.2 V (**Figure 2a**). The open circuit potential (OCP) of the platinum electrode in the blank solution was *ca.* 0.66 V, and it drifted to *ca.* 0.2 V in the methanol-containing solution, a potential value at which methanol dissociates fairly readily.

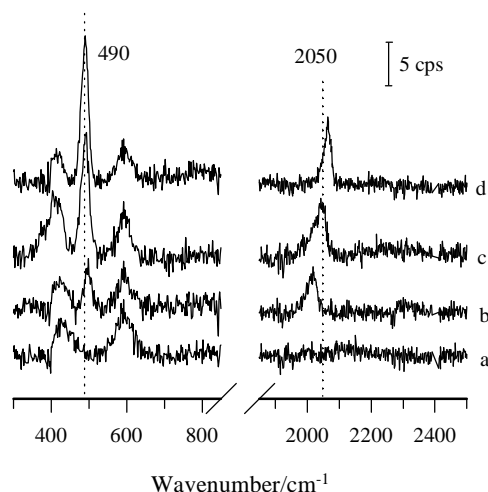
Figure 1 Cyclic voltammograms



On a rough Pt with a roughness factor (see reference 3) about 200 at 100 mV s^{-1} for (a' s) blank solution of 1 mol/L H_2SO_4 , (b' s) 0.5 mol/L CH_3OH admitted in the blank solution while the initial potential was held at -0.2 V, and the upper potential limit was at (A) 0.6 V, (B) 0.1 V and (C) -0.1 V. (D) Oxidative desorption in the blank solution for the adsorbed CO, which came from the dissociative adsorption of methanol with a immersion time of 5 min in the solution of 0.5 mol/L CH_3OH and 1 mol/L H_2SO_4 at an initial potential of -0.1 V or open circuit potential (OCP), and then the electrode was rinsed with Milli-Q water and transferred into the blank solution.

Different dissociative behavior was also observed with the variation of an upper potential limit of the cyclic voltammetry under the same initial potential control of -0.2 V. For example, a new dissociative adsorption peak appeared around 0.2 V (curve b of **Figure 1A**) during the first forward potential scan between $-0.2\sim 0.6$ V, and then the

Figure 2 Surface Raman spectra



On the same Pt electrode of **Figure 1** in 1 mol/L H_2SO_4 with (a-c) 0.5 mol/L CH_3OH , (d) 0.5 mol/L HCHO , while the cell was either (c) open or on with an initial potential control at (a) -0.2 V, (b) -0.1 V, (d) -0.2 V. Excitation line: 632.8 nm.

peaks for hydrogen ad/desorption and the new peak, disappeared during the first backward and second forward (indicated with double arrows) potential scan due to the rapid formation of poisoning CO. The new peak might come from the methanol oxidation on a CO-free surface. Dozens and hundreds of more cycles (*i.e.*, a longer time) were taken to suppress completely the H-adsorption by lowering the upper potential limit to 0.1 V (**Figure 1B**) and -0.1 V (**Figure 1C**), respectively, noticing that the neighbor cycles shown in **Figure 1C** actually have an interval of 50 cycles. It is interesting to note in **Figure 1B** that the strongly bound hydrogen near 0 V is replaced preferentially by CO during the first backward potential scan between $-0.2 \sim 0.1$ V, and the weakly bound hydrogen peak disappears gradually accompanying a potential shift towards positive direction. These phenomena indicate that the adsorption site of CO is selective, and there must be some interaction between the adsorbed CO and the weakly bound hydrogen, and/or between the strongly and weakly bound hydrogen, which need a further study. That the dissociation occurs though more slowly with an upper potential limit of -0.1 V, is consistent with the Raman spectra in **Figure 2b**, where the band intensity is much smaller than that with a more positive potential (*ca.* 0.2 V) as in **Figure 2c**.

Neither hydrogen ad/desorption peaks nor the new peak could be observed while the cell was open before adding the methanol. So a much higher oxidative desorption peak (*i.e.*, a larger area) from the adsorbed CO at *ca.* 0.5 V (**Figure 1D**) was observed, when the electrode was initially at OCP than at -0.1 V, with the same period of contacting time of 5 min in the methanol-containing solution before its transferring into

the blank solution. Their area ratio for the oxidative desorption of the adsorbed CO in **Figure 1D** is basically consistent with that for the vibrational band intensity of C≡O or Pt-C.

Unlike methanol, which does not dissociate on the electrode surface at an initial potential of -0.2 V (**Figure 2a**), formaldehyde dissociates much more easily on the platinum electrode than methanol does, and the hydrogen ad/desorption peaks are completely suppressed by the adsorbed CO even for the first potential cycle (not shown), which is consistent with the Raman spectra in **Figure 2d**, where the band intensity of Pt-C and C≡O vibrations at -0.2 V is comparable with that for methanol at OCP (*ca.* 0.2 V). The difference in dissociative behavior may be due to different dissociative mechanisms as suggested by Parsons⁵.

Through this preliminary study, we have demonstrated that the availability of confocal Raman microscopy offers intriguing opportunities for investigating surface reaction on transition metals in electrochemical environments with at least following advantages: direct vibrational spectra can be obtained on rough electrodes with dark color, under high Faradaic currents, with high sensitivity at low frequency vibrations and low interference from bulk solution. Further investigation is now underway in our groups.

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