

The Investigation of Electro-Oxidation of Methanol on Pt-Ru Electrode Surfaces by in-situ Raman Spectroscopy

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Abstract. Assisted by the highly sensitive confocal microprobe Raman spectrometer and proper surface roughening procedure, the Raman investigation on the adsorption and reaction of methanol was performed on Pt-Ru electrodes with different coverages. A detailed description of the roughening process of the Pt electrodes and the underpotential deposition of the Ru was given. Reasonably good Raman signal reflecting the metal-carbon vibration and CO vibration was detected. The appearance of vibrations of the Ru oxides, together with the existence of Ru-C, Pt-C and CO bands, clearly demonstrates the participation of the bi-functional mechanism during the oxidation process of methanol on Pt-Ru electrodes. The Pt-Ru electrode was found to have a higher catalytic activity over Pt electrodes. This preliminary study shows that electrochemical Raman spectroscopy can be applied to the study of rough electrode surface.

Key words : Platinum, Ruthenium, Methanol, Electro-oxidation, Raman spectroscopy

1. Introduction

Organic molecules have attracted extensive attention in the research and development of fuel cell industry due to their special advantages such as abundant resources, easy storage and transportation, and high energy density. At present, direct methanol fuel cell has become a hot research topic of this field. The research interest of the electro-oxidation of C1 molecules concentrates on the adsorption and reaction mechanism of C1 molecules on the electrode surface. Based on the vast amount of experimental data, two reaction mechanisms have been proposed: parallel reaction mechanism¹⁾ and series reaction mechanism²⁾. During the electrocatalytic oxidation of methanol, methanol can be dissociated into a poisoning intermediate- CO, which can adsorb strongly on the electrode surface. This species will in turn reduce the catalytic activity of the electrode, which leads to the oxidation of methanol at a more positive potential.

In the study of electrocatalytic oxidation of C1 molecules, transition metals have been widely used as the electrode materials. In the acidic electrolytes, compared with other single component metals, Pt possesses the highest catalytic activity and stability upon the oxidation of C1 molecules. Therefore, at present, the most widely used catalysts are still Pt-based materials³⁾. However, due to the high cost of Pt, and the poisoning of Pt by the electro-oxidation intermediates (such as CO), bi- or multi- component materials (which is formed by

Pt with other metals by alloying, adsorbed metal atoms or metal oxides) were used to change metal surface properties to improve the catalytic activity of Pt-based catalyst.

Up to date, the best catalyst to the oxidation of methanol in various bi-metallic catalysts was found to be Pt-Ru. Gas-teriger et al. investigated systematically the reaction activity of different Pt-Ru alloy electrodes of known composition⁴⁻⁶⁾, and it was found that Pt-Ru electrode was less sensitive to the surface poisoning species than the Pt electrode⁵⁾. Furthermore, it was found that the overpotential for the oxidation of methanol was lower than that on Pt electrode⁷⁾, indicating a high catalytic activity of Pt-Ru electrode compared with the pure Pt electrode. In order to explain how the catalytic activity was changed by the different components in different modified or alloying electrode, several mechanisms have been proposed⁸⁻¹¹⁾, such as the electronic effect¹⁰⁾ and the bi-functional model¹¹⁾.

In the past two decades, IR has been widely applied to the investigation of the electro-oxidation of methanol on bi-(multi-) component catalysts¹²⁾. It can obtain very conveniently the vibrational information in the high frequency region (higher than 1000 cm⁻¹) of the adsorbed species on the single crystal surface, smooth electrode surface and the surface of low roughness. It has provided very valuable data for the identification of the adsorbed species on the surface. However, IR spectroscopy has its own limitation. For example, it is very difficult to obtain the information in the low frequency region reflecting the interaction between the substrate and the adsorbates and it can only be applied to the surface of very

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high reflectivity. On the other hand, SERS is complementary to the IR in these aspects. It can be applied not only to the electrode surface of high roughness and low reflectivity which is very close to the practically used materials, but also to detect the vibrations reflecting the interaction between the substrate and adsorbates in the low frequency region. These two unique features make SERS advantageous in the study of electrocatalytic systems. However, the application of SERS is still limited to Ag, Cu and Au surfaces after almost 30 years discovery of SERS phenomenon. Up to date, except our group, there is no other report about the adsorption and reaction of C1 molecules on transition metal surface of bi-(multi-) components using Raman spectroscopy. The purpose of present work is to extend SERS to the investigation of the adsorption and reaction of C1 molecules on bi-component systems and make full use of the advantage of SERS in obtaining the signal in the low frequency region to explore the spectroscopic evidence for the electrocatalytic oxidation mechanism of methanol on the Pt-Ru electrode.

2. Experimental

Electrochemical cyclic voltammograms were recorded on a CHI631A electrochemical workstation. Raman spectra were obtained using a confocal microprobe Raman system (LabRam I, Dilor). The excitation line is 632.8 nm from an internal He-Ne laser. A 50 \times long working-length objective (8 mm) was used in the present experiment. The width of the slit is 200 μ m and the diameter of the pinhole is 800 μ m. A polycrystalline Pt rod with surface area of 0.1 cm² is used as the working electrode, the detailed treatment of which will be described in the following section. The counter and reference electrodes are platinum ring and saturated calomel electrode (SCE), respectively. All solutions were prepared with analytical reagents and Mill-Q water.

3. Results and discussion

3.1. The pretreatment of the Pt-Ru electrode

It is widely accepted that in order to obtain SERS spectra of high quality to enable the detailed investigation at the molecular level, it is necessary to pretreat the surface appropriately. In our group, with several years effort on developing different roughening method to obtain SERS substrates, we have established or modified on some surface pretreatment procedures for various transition metal surfaces, and obtained high quality SERS spectra for a series of transition-metal surfaces¹³⁻¹⁵. In present work, the Pt-Ru electrodes of SERS activity were prepared by electrochemical deposition of Ru of varying coverage on the previously roughened Pt surface.

The mechanically polished Pt electrode was first electrochemically cleaned in a 0.5 M H₂SO₄ solution by cycling in the potential range of 0.25 to 1.25 V at 0.5 V/s to obtain a clean and stable surface. Then, the Pt electrode was immersed in a fresh 0.5 M H₂SO₄ solution with the electrode surface facing up. A square-wave potential with the upper and lower limit of 2.4 and 0.2 V and the frequency of

1.5 kHz was applied on the electrode for the electrochemical roughening. During the roughening process, the surface kept bubbling with high-purity Ar gas and the color of the surface turned slowly to gray-yellow from the rim to the center of the electrode. After about 30 s, the whole surface took on a color of dark brown. This is due to the accumulation of platinum oxides on the surface. After the desired time, the electrode potential was held at 0.2 V for a complete reduction of the surface oxides. Depending on different roughening time, the final surface obtained presented a color from gray to yellow-brown. The roughened surface was then cycled again in 0.5 M H₂SO₄ solution in the potential region of 0.3 to 1.25 V until reproducible cyclic voltammograms (CVs) were obtained. The purpose of this step is to remove surface active or unstable cluster. The Pt surface obtained by this method is very stable, before any electrochemical and Raman experiments, the surface needs only to be cycled in the above solution again to clean the surface until the appearance of reproducible CV curves. Compared with the roughened coinage metal electrodes, the roughened Pt electrode presents better surface uniformity, stability and reversibility, and it can be reused without re-roughening, which makes different experiments highly comparable. Furthermore, by controlling the roughening time, Pt surfaces of different roughness can be easily obtained. The surface roughness of a Pt electrode can be readily obtained by measuring the charge in the hydrogen adsorption/desorption region by the following equation: $R = Q_{rough}/Q_{smooth}$, since the charge passing in this region is right the charge for the formation of a monolayer hydrogen. An ideal value for an extremely smooth polycrystalline Pt electrode surface is about 210 μ C/cm². Therefore, the $R = Q_{rough}/\mu$ C.cm⁻².

Various methods have been developed for the preparation of Pt-Ru electrodes, such as alloying^{16,17}, co-deposition of Pt and Ru^{18,19}, and the electrodeposition of Ru on Pt particles^{9,20}. It has been found out that all these Pt-Ru surfaces prepared by above-mentioned methods can promote the electrocatalytic oxidation of CO and methanol on Pt²¹. In this paper, Pt-Ru electrode was prepared by underpotential deposition of Ru on roughened Pt surfaces.

It should be pointed out that, the coverage of Ru on Pt electrode can not be calculated by the change of the adsorption/desorption charge of hydrogen as it does on Pt electrode, since hydrogen adsorption and desorption also occurs on the Ru surface. Earlier work of Watanabe and Motto used the ratio of the charge of OH adsorption to that of the H adsorption to calculate the coverage of Ru on the Pt surface⁸. On the other hand, the STM and XPS studies of Stimming et al.²² on the underpotential-deposition of Ru on Pt surface revealed that the surface coverages of Ru on both Pt(111) and the smooth polycrystalline Pt electrode obtained at 0.3 and 0.6 V (vs. RHE) were 0.3 and 0.7 in the 5 \times 10⁻³ M RuCl₃ and 0.1 M H₂SO₄, respectively. For the sake of comparison with other groups results, the underpotential deposition condition in the present study was controlled under the same condition as Stimings. Therefore, we assume that the surface coverage of Ru on Pt surface of different roughness is similar to that

of Stimmings, i.e., the surface coverages of Ru are 0.3 and 0.7 at 0.3 and 0.6 V, respectively.

3.2. The electrochemical and Raman spectroscopic study of methanol oxidation on Pt-Ru electrodes.

Figure 1 shows the quasi-static potential-current curve of Pt electrodes with roughness factor of 50, with different Ru coverage on the surface in the 0.1 M methanol and 0.1 M H₂SO₄ solution. It can be found that the Ru covered Pt surface gives lower overpotential compared with that of the pure Pt electrode. The oxidation current of methanol on the Pt-Ru surface is significantly higher than that of the Pt surface. It indicates that, the existence of Ru promotes the oxidation of methanol on Pt surfaces. Furthermore, the catalytic activity of the Pt-Ru ($\theta = 0.7$) electrode is apparently higher than that of the Pt-Ru ($\theta = 0.3$).

Figure 2 shows the potential-dependent surface Raman spectra obtained on the roughened Pt electrode with roughness factor of 50 in the above solution. It can be seen from Figure 2 that, the CO produced by dissociation from methanol shows lower frequency (2045~2053 cm⁻¹) than that (2060~2071 cm⁻¹) of CO obtained from adsorption from solutions saturated with CO¹³. The main reason for the lower frequency is due to the weaker coupling between neighboring CO as a result of the lower surface coverage of CO. Moreover, the CO produced by dissociation from methanol gives a broader full-width-at-half-maximum (FWHM), which is also due to the lower coverage of CO on the surface. There are a large number of kinks, edges and steps on the roughened Pt surface and CO prefers to adsorb on these sites. The vibrational frequency of CO on these sites will be about tens wavenumbers lower than that on the terrace^{23,24}. Therefore, when the surface coverage is low, the adsorption state of CO on the rough surface is highly discrete, leading to a wider FWHM. On the other hand, when the CO coverage is high,

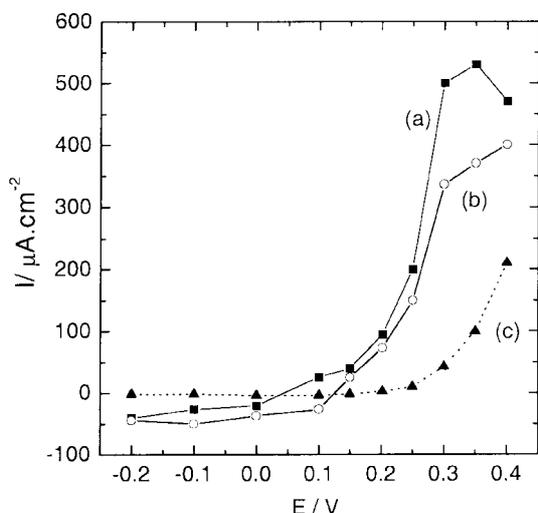


Fig. 1. Current-potential curves of methanol oxidation at a Pt electrode ($R = 50$) with different coverages of UPD-Ru in 0.1 mol/L H₂SO₄ + 0.1 mol/L CH₃OH. The coverage of UPD-Ru: (a) 0.7, (b) 0.3, (c) 0.

CO can still adsorb on these sites. However, the strong coupling between the CO molecules leads to the transfer of the intensity of CO from the lower frequency one to the higher frequency one. Therefore, the vibrational state of CO on the surface will be simpler. As a result, FWHM of CO will be much narrower. After the deposition of Ru on the Pt electrode, the surface coverage of CO further decreases leading to a lower ν_{CO} . It should be noted that, the higher the coverage of Ru is, the lower the frequency of ν_{CO} and the broader the band will be. However, we found that when the surface coverage of Ru was as high as 0.7 (see Fig. 4), a shoulder peak appears on the red side of the 2025 cm⁻¹ peak. This

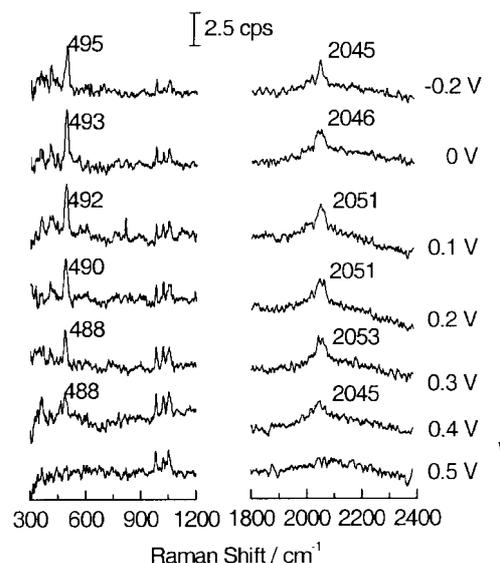


Fig. 2. Surface Raman spectra of CH₃OH at a Pt electrode ($R = 50$) in 0.1 mol/L H₂SO₄ + 0.1 mol/L CH₃OH. Excitation line: 632.8 nm.

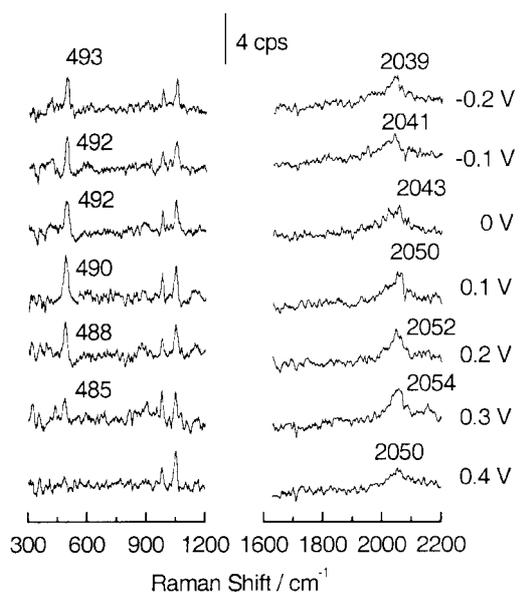


Fig. 3. Surface Raman spectra of CH₃OH at a Pt electrode ($R = 50$) with UPD-Ru $\theta_{Ru} = 0.3$ in 0.1 mol/L H₂SO₄ + 0.1 mol/L CH₃OH. Excitation line: 632.8 nm.

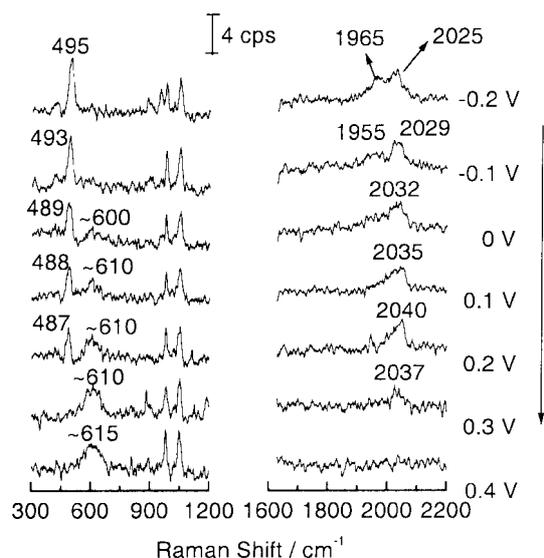
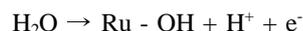
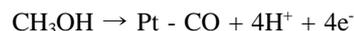


Fig. 4. Surface Raman spectra of CH_3OH at a Pt electrode ($R = 50$) with UPD-Ru ($\theta_{\text{Ru}} = 0.7$) in $0.1 \text{ mol/L H}_2\text{SO}_4 + 0.1 \text{ mol/L CH}_3\text{OH}$. Excitation line: 632.8 nm .

peak can be reasonably assigned to the CO adsorbed onto the Ru surface. The Ru-CO peak is quite obvious in the low frequency region when the electrode potential is more negative than 0.1 V . The low frequency band at 490 cm^{-1} is broader on the Pt-Ru surface than that on the pure Pt surface. However, there is no obvious shift on the vibrational frequency in the $\nu_{\text{Pt-C}}$. On the electrode with $\theta_{\text{Ru}} = 0.3$, no obvious peak from the adsorbed CO on Ru can be detected, which may be due to the lower coverage of Ru on the surface leading to a lower signal intensity of CO.

Among the mechanisms proposed for the promotion of Ru for the oxidation of methanol on the Pt electrode surface, a lot of electrochemistry evidences have proven that the bi-functional mechanism is reasonable. It proposed that different components in the bi-metallic component surface play different roles. For instance, Watanabe and Motoo¹¹⁾ proposed a bi-functional mechanism to interpret the promotion of Ru to the catalytic activity of the Pt electrode on the oxidation of methanol. Since oxygen containing species can adsorb to the Ru surface at a potential about 0.2 to 0.3 V lower than that on the Pt surface, it makes the oxidation of carbon containing species on the Pt surface to CO_2 at a lower potential possible. However, a direct evidence from spectroscopic technique is still lacking. Based on the advantage of Raman spectroscopy that it was able to obtain the information in the low frequency region, an experiment was done to obtain possibly the direct evidence for the bi-functional mechanism, as shown in Fig. 4. At $\theta_{\text{Ru}} = 0.7$, a broad band at 600 cm^{-1} appears at 0 V , which will increase with the positive movement of the electrode potential. Under the same condition, no discernible signal can be detected on the pure Pt electrode. The oxides on the Pt electrode can only be observed when the potential is more positive than 0.7 V . Therefore, it is reasonable to assign the band at 660 cm^{-1} to the adsorbed oxygen-containing species on the Ru surface. Since this band appears

at 0 V , it is in good agreement with the result obtained from the electrochemical study, in which it was found that the adsorbed oxygen species appears at 0 V . Furthermore, with the positive shift of the potential, as shown in Fig. 4, more oxygen-containing species exists on the surface, and as a result the CO band can be more easily oxidized to CO_2 . It provides the direct evidence from spectroscopic technique for the bi-functional effect of electro-oxidation of methanol on Pt-Ru electrode as follows:



The present preliminary study presents the advantage of Raman spectroscopy on the investigation of the roughened Pt or alloying metal surfaces.

4. Conclusion

By underpotential deposition of Ru atom of different coverage over the rough Pt surface, Pt-Ru surface of SERS active were obtained. Based on these kind of surface together with the assistance of the highly sensitive Raman spectrometer, we investigate in-situ the dissociate adsorption and oxidation of methanol on the rough Pt-Ru electrode surface. The Pt-Ru prepared by underpotential deposition presents very good electrocatalytic activity on the oxidation of methanol. The oxidation of CO occurs at a negative potential on the Pt-Ru surface than that on the pure Pt surface. Based on the surface Raman spectra obtained at different potentials, we investigated preliminarily the electrocatalytic oxidation mechanism of methanol on the Pt-Ru electrode surface. At a higher Ru coverage, $\theta_{\text{Ru}} = 0.7$, a broad band from Ru oxides could be observed at ca. 600 cm^{-1} . This band increases in intensity with the decrease of the CO band, indicating that the more oxygen species existing on the surface the easier the CO could be oxidized to be CO_2 . This study provides some spectroscopic evidence for the bi-functional mechanism for the electrocatalytic oxidation of methanol. The preliminary result of present work indicates that electrochemical Raman spectroscopy possess its unique advantage in the study of the rough surface and in the detection of signal in the low frequency region, which may become a very important and versatile technique in electrocatalytic and corrosion study.

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