

Short communication

Adsorbed water and CO on Pt electrode modified with Ru

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Abstract

Highly sensitive ATR-SEIRA spectroscopy was exploited to elucidate water, CO and electrolyte anions adsorbed on the Ru modified Pt film electrode. CO on Ru domains was oxidized below ca. +0.3 V, followed by pronounced water adsorption. Since the oxidation potential of CO on Pt domain was significantly reduced compared to bare Pt, these water molecules on Ru obviously prompt CO oxidation on adjacent Pt surface as consistent with the bifunctional mechanism. Diffusion of adsorbate from Ru to Pt surfaces was indicated in dilute CH₃OH solution by spectral changes with potential. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Pt–Ru alloy [1–3] or Ru modified Pt surfaces [4] are known to be prominently effective catalysts for methanol oxidation. Watanabe and Motoo [5] introduced a ‘bifunctional mechanism’ into electrochemical interfaces in that Ru in Ru–Pt alloy surfaces supplies OH moieties to promote CO oxidation on neighboring Pt surfaces. In this context, it is crucial to elucidate water or hydroxide that are anticipated to adsorb on Ru in the alloy or modified Pt electrode surfaces. Nevertheless, there have been substantial uncertainties on this point because of experimental constraints in vibrational spectroscopy relevant for this purpose, e.g. poor sensitivity or uncompensated interruption by bulk solution species in IRAS (infrared reflection absorption spectroscopy). Watanabe and co-workers recently reported that water molecules were detected on the Ru–Pt alloy surfaces dissimilar to Pt surfaces using ATR-IR spectroscopy [6]. It seems, however, that the surface morphology of their Pt [7] and Pt–Ru alloy films [6] prepared with a sputtering method was not optimized to obtain fairly large enhancement for the IR absorption from adsorbates. Possibly, the enhancement factor of such Pt films was not sufficiently large to detect rather

weak water bands, as absorbance of the O–H stretch is about 1/18 compared to on top CO. In contrast, Pt films prepared by electroless plating give much larger IR absorption for adsorbates by a factor of >10 [8–10]. Concerning the bifunctional mechanism, Friedrich et al. reported on the Ru-modified Pt(1 1 1) surface that (1) the Ru island with 2–5 nm size and monoatomic height is formed by electrochemical deposition, of which coverage is feasibly controlled by the deposition potentials, (2) CO oxidation peak is shifted to more negative potentials by ca. 120–130 mV due to cooperative mechanism between Pt and Ru involving CO surface mobility [11–13]. At this stage, it appears necessary to characterize water and CO adsorbed on various alloy or modified Pt surfaces using ATR-SEIRA spectroscopy to provide information on the role of Ru in their catalytic activity.

2. Experiments

The detailed experimental procedures to prepare the SEIRA-active Pt films are the same as reported earlier [8–10]. Ru island films were electrochemically deposited on the Pt films at +0.2 V (versus Ag/AgCl in saturated KCl solution, which was used as a reference electrode through this paper) in 1 mM RuCl₃ + 0.1 M H₂SO₄ solution [11–13]. It yields a Ru coverage (θ) of ca. 0.5 according to XPS measurement on the Pt(1 1 1) and Pt polycrystal [13]. Prepared Ru–Pt films were fairly stable under the potential region between –0.2 and +1.1 V used here. All the IR

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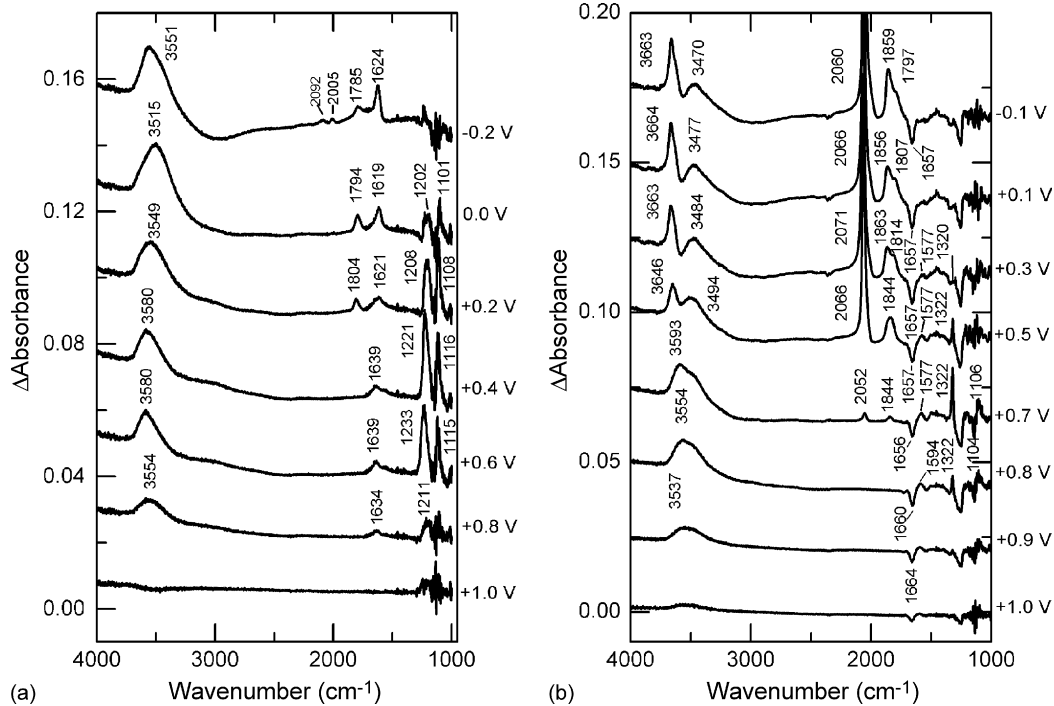


Fig. 3. ATR-IR spectra of adsorbates on bare Pt electrode in 0.1 M H_2SO_4 (a), in 0.1 M H_2SO_4 + 0.5 M CH_3OH aqueous solution (b).

in 0.1 M H_2SO_4 solution with/without CH_3OH , which confirm water bands are observed irrespective of Ru deposition. The O–H stretch bands from water on the Ru–Pt surfaces centered at 3517 (-0.2 V) and 3505 cm^{-1} (0.0 V) in Fig. 1a are about 30–10 cm^{-1} red-shifted from 3551 cm^{-1} (-0.2 V) to 3515 cm^{-1} (0.0 V) on the bare Pt surfaces in Fig. 3a. A diminished frequency jump by +12 cm^{-1} was noted on Ru–Pt compared to 35 cm^{-1} on the

bare Pt surfaces (see also Fig. 3, [9]). This frequency jump is related to desorption of HSO_4^- as shown in Figs. 1a and 3a, which induced prominent structural and/or orientation changes of adsorbed water [9,14]. (Bi)sulfate species on the bare Pt surfaces provided two S–O stretch bands at 1202 and 1101 cm^{-1} (0.0 V, as seen in Figs. 3a and 4a), which was attributed to different orientations of HSO_4^- ions via one or two oxygen atoms

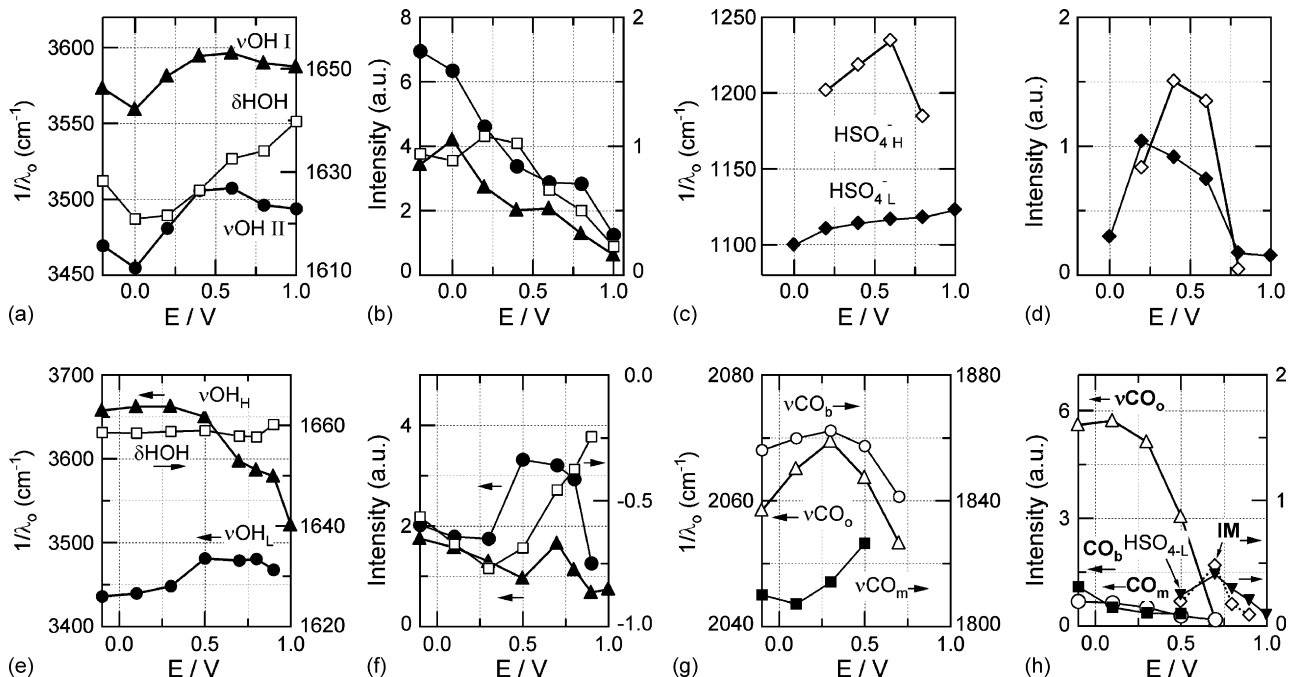


Fig. 4. Potential dependence of the peak wavenumber (a, c, e and g) and integrated intensity (b, d, f and h) in Fig. 3: OH stretch (a and b), HSO_4^- (c and d) in Fig. 3a, OH stretch (e and f) and CO (g and h) in Fig. 3b.

adsorbed on metal surfaces [15], but still controversial [19]. These absorptions presented the maximum intensity at +0.5 V and extinguished below 0.0 V. In contrast, corresponding peaks with slightly higher frequencies at 1221 and 1109 cm^{-1} were detected on the Ru–Pt surfaces even at -0.2 V as shown in Figs. 1a and 2a, probably due to oxiphilic properties of Ru as in UPD-Cu or UPD-Pb on the Pt surfaces [9]. In addition, the second maximum peak appeared at +0.5 to 0.6 V on the Ru–Pt surface in Fig. 2d is assigned to those on Pt surface, as it possesses identical potential dependence on bare Pt electrode (see also Fig. 4d). Accordingly, the (bi)sulfate bands are mostly originated from the Ru domain at $E < +0.2$ to +0.3 V and from the Pt surfaces at $E > \text{ca. } +0.4$ V. The diminished frequency jump is thus rationalized by reduced Pt area, at which (bi)sulfate species completely desorb to yield structural changes of adsorbed water, in contrast to Ru domain. It is in general hard to detect (bi)sulfate species on polycrystalline Ru as reported by Marković et al. [26] probably due to its broader oxidation potential which largely suppresses (bi)sulfate adsorption even at negative potential. Much higher sensitivity in ATR-SEIRA used here by a factor of 10–100 compared to the conventional IRAS method [27] enables us to obtain those bands.

Unfortunately, it is not straightforward to evaluate the electronic interaction between Ru and Pt only from the O–H peak shift on the Pt surface. Since the O–H stretch bands are quite broad, consisting of different peaks from Ru and Pt part with slightly deviated frequencies, the apparent peak position could be diminished even by lower surface coverage of the Pt part. Similarly, CO peak position is shifted with the coverage due to the dipole–dipole interaction.

3.2. Ru–Pt in 0.1 M H_2SO_4 + 0.5 M CH_3OH solution

The OH stretch bands on the Ru–Pt surface consist of a sharp absorption at 3636 cm^{-1} and a broad one centered at

$3451\text{--}3480\text{ cm}^{-1}$ in 0.5 M CH_3OH containing solution as shown in Fig. 1b, which are ca. 30 cm^{-1} lower compared to the bare Pt surface in Fig. 3b. The deviations are consistent with those in 0.1 M H_2SO_4 solution. The higher frequency peak is attributed to water molecules facing to CO on the Ru–Pt surface [8,10,16] according to its extremely high frequency of $>300\text{ cm}^{-1}$ as well as quite narrow width of $50\text{--}60\text{ cm}^{-1}$, intrinsically different from broad bands at $3300\text{--}3250\text{ cm}^{-1}$ of bulk species. In addition, the intensity of the higher frequency peak increases with CO coverage similar to the bare Pt surfaces [17]. An identical O–H stretch was observed at the hydrophobic alkyl end of SAM films prepared on the Au film electrode [14]. Water molecules hydrating to ClO_4^- or Cl^- on Pt surfaces also give the same bands (at $3620\text{--}3600\text{ cm}^{-1}$) at much more positive potentials [8,9]. The Ru–Pt surface provides another broad O–H stretching at $3504\text{--}3451\text{ cm}^{-1}$ as shown in Fig. 1b, fairly lower in frequency compared to the bare Pt. This is ascribed to the O–H bonds facing bulk solution side [8,10,16], and/or directly adsorbed water onto the Ru–Pt surface as schematically drawn in Fig. 5. The latter contribution could not be neglected, as the water molecules adsorb onto the electrode surface from quite positive potentials such as +1.1 V till +0.4 V (with the intensity of ca. 12 for the O–H stretch band), and then partially substituted by CO (to $I = 6.5$ at $E < 0$ V) as shown in Figs. 1 and 2f.

On the Ru–Pt surfaces, on-top CO was seen at $2053\text{--}2014\text{ cm}^{-1}$ (-0.2 to +0.6 V) from the Pt domain and at $1997\text{--}1957\text{ cm}^{-1}$ (-0.2 to +0.2 V) from the Ru domain along with much higher intensity, e.g. integrated intensity (I) of 1.4 on Pt and 5.1 on Ru domain at -0.2 V (Fig. 2h). Similar absorption peaks were observed for CO on the Ru modified Pt(1 1 1) surfaces, while distinct frequencies were evidenced for the Pt(1 1 1) part and Ru domain at 2070 and 2003 cm^{-1} , respectively ($\theta_{\text{Ru}} = 0.45$, at 0.0 V) [11–13]. The other band observed at $1793\text{--}1825\text{ cm}^{-1}$ (-0.2 to +0.4 V) in Fig. 1b is given by CO adsorbed at three-fold sites of Pt domain, because it has equiv-

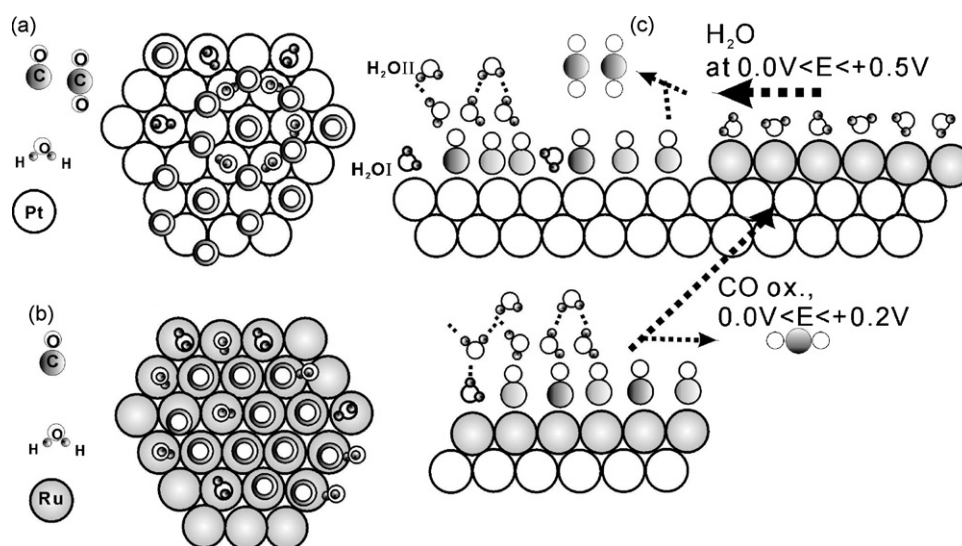


Fig. 5. Schematic adsorbed structure and reaction process of CO on Ru–Pt surface: (a) CO coadsorbed with water on Pt part, (b) Ru domain (at $E < 0.0$ V) and (c) water adsorbed on Ru domain at $E > 0.0$ V and sequential CO oxidation on neighboring Pt surface. Water molecules coadsorbed with CO on Pt give the sharp and high-frequency O–H stretch at ca. 3600 cm^{-1} associating to hydrophobic nature of adjacent CO species, in addition to bulk-like (broad and low-frequency) O–H band at $3450\text{--}3500\text{ cm}^{-1}$ attributed to O–H bond facing to the solution side.

to 1.08 as the potential was raised from -0.2 to 0.0 V, whereas the CO peak at 1936 cm^{-1} on Ru markedly reduced from 1.65 (-0.2 V) to 0.48 (0.0 V). Identical results were observed for multi-fold CO band at $1751\text{--}1813\text{ cm}^{-1}$ on Pt sites. Associating with this, it is known that CO_2 is reduced by adsorbed hydrogen on the Pt electrodes [20,21]. As hydrogen adsorbs on Pt surface below $+0.10$ V (RHE, [28]), the results observed here possibly indicate CO_2 formed on the small Ru patch diffuses/adsorbs on the Pt surfaces as CO below 0.0 V, according to the higher oxidation potential on Pt (Fig. 6c). These results were observed only in quite low CH_3OH concentration that could afford plenty of empty Pt sites. Obviously, local concentration of CO in vicinity of Pt surface could be increased by CO oxidation/desorption at Ru domains. In fact, no drastic intensity variations were seen for the CO bands on the same Ru–Pt surface in $0.5\text{ M CH}_3\text{OH}$ solution (Fig. 1). Further experimental effort is awaited to conclude this. As the potential increased, the higher frequency O–H band at 3600 cm^{-1} becomes unambiguous at ca. 0.0 V, being followed by merging into the lower frequency band at ca. 3486 cm^{-1} until $+0.3$ V as shown in Fig. 6a. Thus, as evidenced by their identical potential dependence of absorption (Fig. 5b and c), the high frequency O–H band (3600 cm^{-1}) is ascribed mainly to water molecules located at CO on the Pt part, i.e. outside the CO layer (see Fig. 5a). The assignment is supported by the diminished intensity of the O–H peak at ca. 3600 cm^{-1} for higher Ru coverage (not shown).

Consequently, it was found using ATR-SEIRA spectroscopy that (1) preferentially adsorbed CO on the Ru surface was oxidized up to ca. $+0.3$ V, (2) it induced marked adsorption of water on empty Ru surface, which could accelerate the following CO oxidation on the adjacent Pt surface, compatible with the bifunctional mechanism, and (3) diffusion of surface species from Ru to Pt was indicated in dilute CH_3OH solution.

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