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Adsorption Behavior of CO at the Ultrathin Rh and Pt Film Electrodes

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Detailed abstract: Pt group metals have been widely used in catalysis such as hydrogenation of organic compounds and the oxidation of carbon monoxide. The information about CO adsorption on the Pt group surfaces and the influence of other surface species, such as hydrogen and CO_2, will be greatly helpful to elucidate the adsorption behavior of CO on Pt-group metal surfaces and get a deeper understanding of catalytic mechanisms of Pt-group metals. Surface-enhanced Raman spectroscopy (SERS) has been becoming an increasingly important means to characterize the electrochemical metal-solution interface over the past two decades. Our laboratory has successfully obtained SERS from neat transition metal surfaces, including Pt[1], Ni[2], Fe[3] and Co. We are able to observe the SERS of CO and the atop adsorbed H on roughened Pt surfaces[1]. However, compared with Ag, Au and Cu which exhibit great surface enhancement, the weak enhancement of the transition metals make it unsuitable for the detailed study for those adsorbates with very small Raman scattering cross sections.

Another method to obtain the SERS signals from Pt group metals has been developed in Weaver's group, which is to electrodeposit ultrathin metal films on SERS active Au surfaces, utilizing the long range effect of the SERS of Au[4,5].. Recently, they obtained the pinhole-free ultrathin (2～5 monolayers, mL) films of Pt-group metals over SERS-active gold, which can produce intense SERS for chemisorbates bound to the overlayer metal.[6] The important advantage of the improved method is that it can avoid the influence from the SERS-active substrate. Further-

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more, the surface enhancement of these metal thin films is higher than that of roughened pure Pt group metals (about 10 to 100 times). Therefore, by using this method, it is possible to obtain good quality Raman signals that enable more detailed information of species with small Raman cross sections to be obtained.

In this study the ultrathin Rh and Pt film electrodes were prepared by electrodeposition over mildly roughened Au surfaces under constant current condition. Since H has been found to have a strong interaction with Rh and Pt surfaces, in order to fully understand the adsorption behavior of CO on Pt and Rh surfaces, we have to consider the possible influence of adsorbed H. Experimentally, this effect can be intensified by comparing the different spectra behavior when CO is introduced to the solution in the potential range more positive or negative than the H adsorption. First from the experiments, we found that CO_2 is easy to be electroreduced on Rh surfaces, and the Raman feature of the reduction product CO shows great difference with that directly adsorbed from the CO saturated solution. Without CO in the solution, to our surprise we could detect a pair of weak bands at 1983 cm^{-1} and 468 cm^{-1} at 0 V, as shown in Fig. 1(a). This pair of bands could be assigned to υ_{CO} and υ_{RhC} of CO according to our previous result of Pt/CO, respectively. This CO species is very possible the reduction product of CO_2 in the solution by Rh. Compared with the

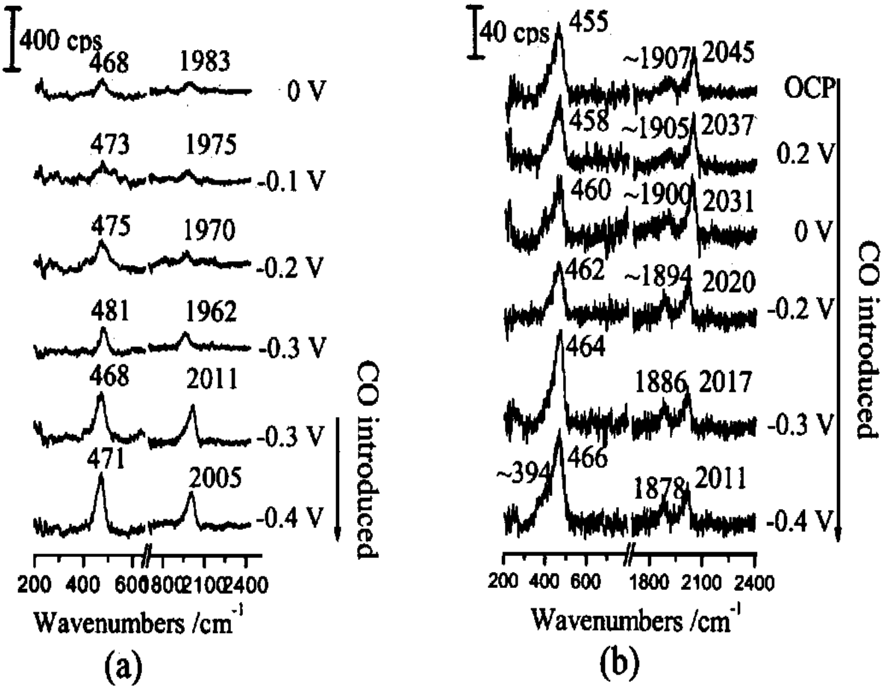

Fig. 1　Potential dependent SERS spectra of CO adsorbed on ultrathin Rh film surfaces in 0.1 mol/L H_2SO_4, with (a) 10 mL thickness and CO introduced at -0.3 V, and (b) 25 mL thickness and CO introduced at OCP

signals of the saturated CO on Rh surfaces, as shown in Fig. 1(b), there is an apparent red-shift of υ_{CO} band. One possible reason for this may be due to the intrinsic low coverage of CO produced in this condition. It has been reported that the CO_2 reduction may involve the participation of one or more surface hydrogens[7] since the reduction potential locates in the H adsorption region. As a result, the formation of CO may require more than one Rh surface atom, thus the CO coverage may be unable to reach a high value. Another possible reason is that, the CO_2 reduction tends to occur at surface defects such as edge, step and kink sites. When CO adsorbs at these sites, the frequency of C ≡O vibration will be lower than that of the CO adsorbed at terrace sites. Apparently, different spectral feature could be found for the reduced CO and the CO adsorbed from the CO saturated solution, as also shown in Fig. 1(a). When CO gas was bubbled into the solution to saturation at - 0.3 V while reduced CO already existed on the Rh surface, an abrupt change on the frequency of the band at 1 962 cm^{-1} occurs. It shifts to 2 011cm^{-1} due to the increase of the CO coverage. In Fig. 1(a), we almost could not detect any band related to the bridge bound CO, which is quite different from the result shown in Fig. 1(b), where both the bands assigned to υ_{CO} of the bridge bound and linear bound CO could be detected when CO was saturatedly adsorbed at the open circuit potential (OCP). No obvious change of the intensity of the bridge-bound CO could be detected when the potential was moved negatively into the hydrogen evolution reaction (HER) region. This gives an indication that the atop adsorbed H will not greatly influence the adsorption of the bridge bound CO. On the other hand, no detectable signal for the bridge bound CO in Fig. 1(a) may indicate that the previously adsorbed H on the Rh hampers the adsorption of bridge bound CO.

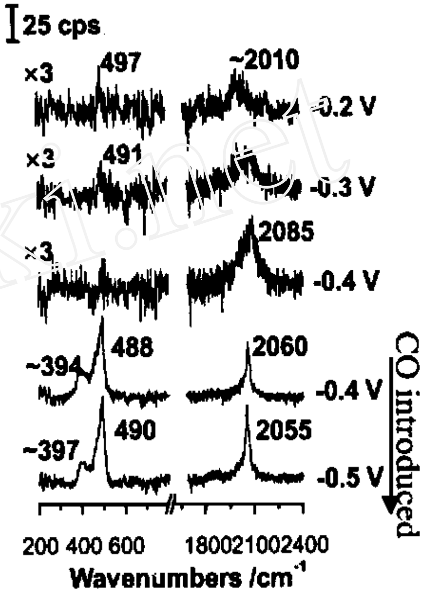

Fig. 2 Potential dependent surface-enhanced Raman spectra of CO adsorbed on ultrathin Pt films (25 mL) in 0.1 mol/L H_2SO_4, and CO was introduced at - 0.4 V

For the Pt surface, different behavior was found as shown in Fig. 2. The spectra were obtained while moving the potential negatively from - 0.2 V. Before purging CO, similar phenomenon to that on ultrathin Rh film surfaces could also be detected. The bands around 2 010 cm^{-1} are also very likely assigned to υ_{CO} of CO, the reduction product of CO_2. This is supported by the relative weak bands of υ_{PtC} detected in the low frequency region. However, on roughened bulk Pt electrodes, we did not detect this pair of bands in the same condition. A possible reason could be the low surface enhancment of the pure Pt electrodes. At - 0.4 V a broad band at 2 085 cm^{-1} with reasonable signal to noise ratio was detected, which is assigned to υ_{PtH} of the on-top ad-

sorbed hydrogen, in agreement with our result on pure Pt electrodes.[1] The difference in the catalytic activity of Pt and Rh in the reduction of CO_2 into CO and their interaction with H could be the possible reason. Thus on Pt surfaces the influence of CO on the H adsorption is weaker than that on Rh surfaces, and we still can detect the signal of H adsorption on Pt surfaces. After the purging of CO, the band at 2 085 cm^{-1} was replaced by a new band at 2 060 cm^{-1} indicating that the adsorpability of CO is stronger than that of the overpotetnial deposited H.

As has been shown above, with the help of the thin film strategy, we are able to detect the signal of the adsorbed H and CO, which allows us to analyze the interaction between the CO molecules and that between the coadsorbed CO and H on various transition metal surfaces. Furthermore, this technique also provides a sensitive way to identify the adsorbed CO formed by different methods, such as directly adsorbed from CO gas or by the reduction of CO_2.

Key words: Ultrathin transition metal layers, Rhodium, Platinum, Hyelrogen, Carbon monoxlde, Carbon dioxide

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Rh 和 Pt 超薄层电极上的 CO 吸附行为

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摘要: 利用沉积在粗糙金电极上的过渡金属超薄层电极技术,我们获得了氢及一氧化碳在 Rh 和 Pt 表面上吸附的拉曼信号,并对两者之间的相互作用进行了分析. 我们还进行了二氧化碳在这两种金属表面的还原行为的初步研究,以及对不同方式获得的一氧化碳吸附拉曼信号的特点进行了分析.

关键词: 过渡金属超薄层电极;铑;铂;氢;一氧化碳;二氧化碳