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induce changes of the Rh electrode surface in acid solution. The potential cycling treatment yielded a surface oxide, the Rh surface clusters may be formed as a transient state when the surface oxide is just reduced. The variation of surface state of Rh electrode was probed using CO adsorption and in situ multi-step FTIRS studies. Two kinds of adsorbed twin CO were detected for the first time on the modified Rh electrode. One is twin CO adsorbed on a surface Rh oxide, yielding two broad bands at 2 166 and 2 112 cm^{-1}, and the other one is twin CO adsorbed on surface clusters of Rh, originating a doublet at 2 102 and 2 032 cm^{-1}. The present results at the solid/liquid electrochemical interface were consistent with those obtained at the solid/gas interface.

Key words　*In situ* multi-step FTIRS, Surface processes, Twin adsorbates, Carbon monoxide, Rhodium electrode

References

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酸性溶液中Rh电极上CO孪生吸附态的FTIRS研究①

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摘要　采用现场多步FTIR光谱技术结合CO吸附分子探针方法，研究了Rh电极表面分子过程。在电化学处理后的光滑Rh电极表面上首次检测到两种CO孪生吸附态及其随电位变化过程。使用电位循环扫描方法改变Rh电极表面状态，在0.05 mol/L H_2SO_4酸性溶液中，选取－0.275至2.4 V电位区间和1.5 V/s扫描速率对Rh电极进行循环扫描处理2 min，处理后的Rh电极表面积累一层氧化物，CO以孪生态吸附于表面Rh氧化物上，在2 166和2 112 cm^{-1}处给出一对宽的IR吸收峰；在负电位下，表面氧化物被还原生成表面Rh原子簇，CO仍以孪生态吸附于表面Rh原子簇上，在2 102和2 032 cm^{-1}处给出一对尖的IR吸收峰；表面Rh原子簇不稳定，随着电位正移分解和扩散形成平滑的Rh表面，此时CO则以线式和桥式吸附于平滑的Rh表面，分别在2 048和1 919 cm^{-1}处给出两个IR吸收峰。

关键词　现场多步FTIR光谱，表面过程，孪生吸附态，一氧化碳，铑电极

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FTIRS Observation of Twin Adsorbates of CO on Rh Electrode in Acid Solution①

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Because of its great importance both in electrocatalysis and C_1 chemistry applications, the adsorption of CO on metallic electrodes such as Pt, Pd, Au, Ag, Rh[1~2], etc. has been extensively studied by *in situ* infrared spectroscopy since 1981. In all these studies only three types of CO adsorbates, i.e., linear (2 090~2 000 cm^{-1}), bridged (2 000~1 900 cm^{-1}) or multi-bonded (1 900 ~ 1 800 cm^{-1}) species, were identified. A different adsorbate, twin CO on rhodium ((Rh $(CO)_2$), does exist on the solid/gas interface of highly dispersed Rh or Rh_n clusters[3~4] on supports, this species originating a doublet at 2 100 and 2 030 cm^{-1} for its symmetrical and asymmetrical stretch modes, respectively. To our knowledge, this doublet has not been reported yet for the Rh/electrolyte interface.

It is well known that in electrocatalysis the surface state of an electrode determines its reactivity, which is especially important in fuel cell applications where highly dispersed electro-catalysts are employed. Here we have used potential cycling to induce changes in the Rh electrode surface, and *in situ* Fourier Transform IR Spectroscopy (FTIRS) to investigate CO adsorption on the modified Rh electrode in 0.05 mol/L H_2SO_4 electrolyte. Two types of adsorbed twin CO have been observed for the first time at the electrochemically modified Rh electrode.

In order to investigate the electrochemically modified Rh electrode, which is not stable, we used the programme for *in situ* FTIRS experiments represented in Figure 1. The potential was changed in steps, a spectrum being recorded at each

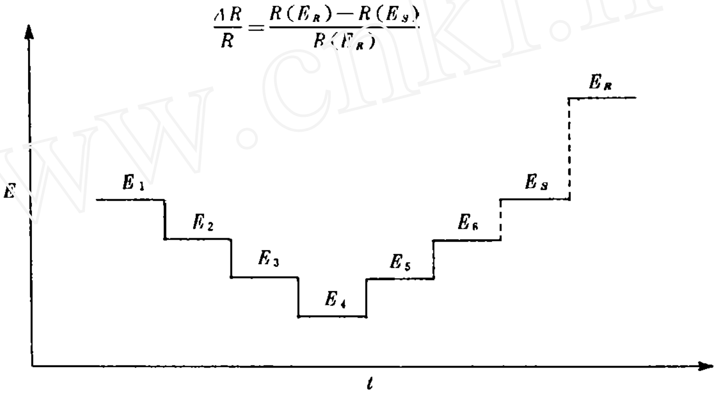

Fig. 1 Potential programme followed in the multi-step FTIR spectroscopy measurements

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step E_S. Finally a reference spectrum was recorded at a potential E_R higher than 0. 4 V vs. SCE, at which all adsorbed CO is removed quickly by oxidation. Normalized differential reflection spectra were calculated by means of the equation:

$$\Delta R/R=[R(E_R)-R(E_S)]/R(E_R) \qquad (1)$$

where $R(E_S)$ and $R(E_R)$ are single beam spectra recorded at E_S and E_R, respectively. With this definition species that adsorb at E_S yield upward going bands.

The surface state of Rh electrode was modified electrochemically by potential cycling for 2 minutes between −0. 275 V and 2. 4 V, at 1. 5 V · s^{-1}, in 0. 05 mol/L H_2SO_4. The adsorbates of CO on the potential cycled Rh electrode gave interesting FTIR spectra displayed in Figure 2.

The measurement started at 0. 10 V (the potential of open circuit, $E_{o.c.}$), at which a doublet at around 2 166 and 2 112 cm^{-1} appeared. This doublet may be ascribed to CO adsorption in twin form on a surface oxide or hydroxide of Rh formed in the potential cycling treatment, because the position of this doublet is too high to assign it to CO adsorption on metallic Rh clusters[3~4]. The broad doublet may imply an energetically heterogeneous surface oxide.

When the potential was shifted negatively to reduce the Rh oxides, the intensity of the doublet decreased progressively until it disappeared at −0. 20 V, a new doublet at 2 103 and 2 033 cm^{-1} appearing at potentials more negative than −0. 05 V and increasing with decreasing potential, reaching a maximum at −0. 20 V. This new doublet can be assigned to twin CO on metallic Rh clusters[3~4], which were formed when the surface oxide was just reduced and kept in contact with CO. Therefore, the changes in the IR spectrum would indicate that at −0. 20 V all surface Rh oxide was reduced to form surface clusters of Rh.

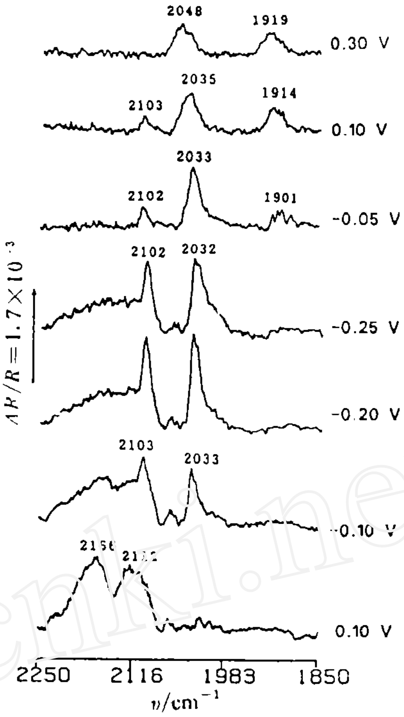

Fig. 2　Multi-step FTIR spectra of CO adsorbed on an electrochemically modified Rh electrode in 0. 05 mol/L H_2SO_4 saturated with CO. The sample potentials E_S were indicated in the spectra, the reference potential was 0. 45 V

The stability of the Rh clusters at −0. 25 V was followed by recording spectra every 5 minutes. The intensity of the band near 2 102 cm^{-1} decreased progressively, whilst that of the band at around 2 032 cm^{-1} remained, although slightly broadened. This result demonstrates that the twin CO on the Rh clusters is unstable already at −0. 25 V.

Finally the potential was increased from -0.25 V to 0.30 V. The band near 2 102 cm^{-1} characteristic of IR absorption by the twin CO on Rh clusters decreased progressively and disappeared at 0.25 V. At the same time only a slight decrease of the intensity of the band at 2 032 cm^{-1} was observed, the band became broader, and shifted to 2 048 cm^{-1} at potentials above 0.20 V. The broadening and the positive shift of the band center demonstrated the evolution of the CO adsorbate, from twin CO to a mixture of twin and linear CO (whose IR absorption bands overlap), and finally to a majority of linearly bonded CO. It was also observed that at potentials higher than -0.10 V, a broad band at around 1 900 cm^{-1} assigned to bridged CO appeared, and its intensity increased continuously and shifted to 1 919 cm^{-1} at 0.30 V.

The change of CO adsorbate species with the change of potential, from twin CO on Rh oxide to twin CO on Rh clusters and finally to linear and bridged CO on smooth Rh surface, implies an evolution of the surface of Rh which may be described by the model in Figure 3. The potential cycling between -0.275 and 2.40 V at 1.5 $V \cdot s^{-1}$, forms a oxide or hydroxide of Rh on the Rh electrode surface, characterized by two CO broad bands at 2 166 and 2 112 cm^{-1}. The reduction of the oxide and hydroxide produces metallic Rh clusters at negative potentials, as evidenced by the CO doublet at 2 102 and 2 032 cm^{-1}. At positive potentials these Rh clusters are not stable because of the diffusion of Rh surface atoms, and consequently the surface of Rh electrode returned to its initial smooth state, as shown by the IR bands of linear and bridged CO adsorbates at 2 048 and 1 919 cm^{-1}, respectively.

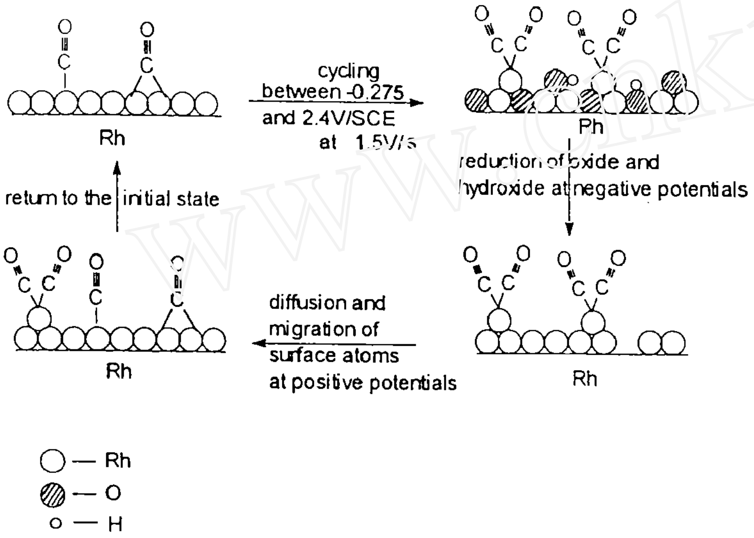

Fig. 3 Proposed model for surface processes of a Rh electrode during processes of electrochemical modifying and the variation of electrode potential in 0.05 mol/L H_2SO_4 saturated with CO

In conclusion, we have used potential cycling at 1.5 $V \cdot s^{-1}$ between -0.275 and 2.4 V to

induce changes of the Rh electrode surface in acid solution. The potential cycling treatment yielded a surface oxide, the Rh surface clusters may be formed as a transient state when the surface oxide is just reduced. The variation of surface state of Rh electrode was probed using CO adsorption and in situ multi-step FTIRS studies. Two kinds of adsorbed twin CO were detected for the first time on the modified Rh electrode. One is twin CO adsorbed on a surface Rh oxide, yielding two broad bands at 2 166 and 2 112 cm^{-1}, and the other one is twin CO adsorbed on surface clusters of Rh, originating a doublet at 2 102 and 2 032 cm^{-1}. The present results at the solid/liquid electrochemical interface were consistent with those obtained at the solid/gas interface.

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摘要　采用现场多步FTIR 光谱技术结合CO 吸附分子探针方法,研究了Rh 电极表面分子过程。在电化学处理后的光滑Rh 电极表面上首次检测到两种CO 孪生吸附态及其随电位变化过程。使用电位循环扫描方法改变Rh 电极表面状态,在0.05 mol/L H_2SO_4 酸性溶液中,选取－0.275 至2.4 V 电位区间和1.5 V/s 扫描速率对Rh 电极进行循环扫描处理2 min,处理后的Rh 电极表面积累一层氧化物,CO 以孪生态吸附于表面Rh 氧化物上,在2 166 和2 112 cm^{-1}处给出一对宽的IR 吸收峰;在负电位下,表面氧化物被还原生成表面Rh 原子簇,CO 仍以孪生态吸附于表面Rh 原子簇上,在2 102 和2 032 cm^{-1}处给出一对尖的IR 吸收峰;表面Rh 原子簇不稳定,随着电位正移分解和扩散形成平滑的Rh 表面,此时CO 则以线式和桥式吸附于平滑的Rh 表面,分别在2 048 和1 919 cm^{-1}处给出两个IR 吸收峰。

关键词　现场多步FTIR 光谱,表面过程,孪生吸附态,一氧化碳,铑电极

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