Effect of SnO₂ Deposition Sequence in SnO₂-Modified PtRu/C Catalyst Preparation on Catalytic Activity for Methanol Electro-Oxidation

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SnO₂-modified PtRu/C catalysts were prepared in a polyl process to investigate the effect of a SnO₂ deposition sequence on the catalytic activity for methanol electro-oxidation. The structure, morphology, and chemical state of the prepared catalysts were characterized by X-ray diffraction, scanning transmission electron microscopy, and X-ray photoelectron spectroscopy. The electrochemical activities were evaluated by cyclic voltammetry, linear sweep voltammetry, and chronoamperometry measurements in combination with in situ IR reflection-absorption spectroscopy (IRRAS). Compared with those in the PtRu/C catalyst, a simultaneous deposition of PtRu and SnO₂ particles or a deposition of SnO₂ prior to PtRu improved the metal dispersion and decreased the alloyed Ru fraction. The deposition sequence of SnO₂ did not alter the chemical-state distribution of Pt and Ru but resulted in a different surface atomic ratio of Pt, Ru, and SnO₂. Electrochemical and in situ IRRAS measurements indicated that the SnO₂-modified PtRu/C catalyst prepared by the deposition of PtRu prior to SnO₂ gave the best catalytic activity for COads and methanol electro-oxidation among the PtRu/C and SnO₂-modified PtRu/C catalysts. The roles of SnO₂ deposited with different sequences in the SnO₂-modified PtRu/C catalysts were proposed.

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The electro-oxidation of methanol has attracted considerable interest due to its importance for direct methanol fuel cells (DMFCs), and the PtRu/C catalyst has been recognized as the most active binary catalyst. The enhanced performance on the PtRu/C catalyst is usually explained by a bifunctional mechanism, where methanol is adsorbed and dehydrogenated to produce COads on Pt active sites, Ru is more active than Pt to provide OHads at low potentials by a water-discharge reaction, and COads on Pt active sites reacts with the neighboring OHads to yield CO₂. A PtRu alloy is also thought to weaken CO adsorption on Pt active sites by the electronic effect. However, the slow kinetics of methanol electro-oxidation at low temperatures is still an obstacle for further development of DMFCs. To improve the catalytic activity for methanol electro-oxidation, several PtRu-based ternary catalysts, such as PtRuIr, PtRuSn, PtRuFe, and PtRuPd, were investigated.

In this work, SnO₂-modified PtRu/C catalysts with three kinds of SnO₂ deposition sequences were prepared in a polyl process, and the effect of the SnO₂ deposition sequence was investigated by evaluating the catalytic activity for methanol electro-oxidation. The prepared catalysts were characterized by X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), and X-ray photoelectron spectroscopy (XPS). CO stripping voltammetry was conducted to evaluate the COads electro-oxidation activity on the catalysts as well as the electrochemical surface area of the catalysts. Conventional electrochemical techniques, in combination with in situ IR reflection-absorption spectroscopy (IRRAS), were applied to compare the electrochemical performance of the SnO₂-modified PtRu/C catalysts for methanol electro-oxidation.

Experimental

Catalyst preparation.—PtRu and SnO₂ colloids were prepared separately in a polyl process under air atmosphere as described below.

(i) PtRu colloid: Calculated amounts of H₂PtCl₆·6H₂O (Wako Pure Chemical Industries, Ltd.) and RuCl₃·H₂O (Nakarai Chemicals, Ltd.) were dissolved in ethylene glycol (Wako Pure Chemical Industries, Ltd.) in a three-necked flask to form a brown solution with a 2 mg (Pt + Ru) mL⁻¹ solvent. Then the pH value of the solution was increased to about 13 with a 1 M NaOH (Wako Pure Chemical Industries, Ltd.) solution. The solution was heated to 170°C at a rate of 10°C min⁻¹ and kept at that temperature for 4 h, and then the PtRu colloid solution was cooled to 90°C. (ii) SnO₂ colloid: A calculated amount of SnCl₂·2H₂O was added to ethylene glycol to form a clear solution with a concentration of about 0.5 mg Sn²⁺ mL⁻¹ solvent, and the solution was heated to 190°C at a rate of 10°C min⁻¹, kept at that temperature for 0.5 h, and then cooled to 90°C.

Three SnO₂-modified PtRu/C catalysts were prepared by varying the deposition sequences of SnO₂: (i) PtRu and SnO₂ colloids were mixed for 2 h and then codeposited onto Vulcan XC-72 carbon
1.2 V at a scan rate of 10 mV s\(^{-1}\). The calculated peak charge bubbled for 30 min to remove the CO dissolved in the electrolyte.

The angle was extended from 10 to 85° at a step of 10°. The tube current was 40 mA with a tube voltage of 40 kV. The XRD patterns of \(\text{SnO}_2\) were prepared in the polyol process. A Pt-wire electrode (Hokuto Denko Corp.) and a saturated calomel electrode (Hokuto Denko Corp.) were used as an electrode substrate for \(\text{SnO}_2\) and PtRu/C catalysts, respectively. The potential of the working electrode was controlled by an Iviumstat Electrochemical Interface System HR200, and the counter electrode was polished with alumina (0.5 \(\mu\)m) and rinsed with Milli-Q water. The catalyst layers were deposited on the gold electrode surface, which is inert to methanol electro-oxidation, with the same method as that described for the CO stripping experiments. The electrode was pushed onto the window with the thin-layer geometry of the catalysts. XPS measurements were carried out using a JEOL JPS-9010MC spectrometer with a Mg K\(\alpha\) radiation source. The Pt 4f and Ru 3p signals were collected and analyzed by the deconvolution of the spectra using the free software XPSPeak.

The broad peak at around 26° is associated with the (002) reflection of the Pt face-centered cubic structure was fitted to a Gaussian line shape so that the position of the peak maximum (26\(\theta\)) could be obtained precisely for the alloying degree calculation. Catalyst morphology was investigated by using an STEM (Hitachi HD-2000) at 200 kV and 30 \(\mu\)A, and more than 200 particles were calculated to obtain the average particle size and particle-size distribution of the catalysts. XPS measurements were carried out using a JEOL JPS-9010MC spectrometer with a Mg K\(\alpha\) radiation source. The Pt 4f and Ru 3p signals were collected and analyzed by the deconvolution of the spectra using the free software XPSPeak.

The alloying degree of the PtRu/C catalyst is defined as the Ru atomic fraction (\(x_{\text{Ru}}\)) in the PtRu alloy, which is related to the lattice parameter \(a\) by the following equation proposed by Antolini and Cardellini:

\[
a = \frac{\sqrt{3}a_0}{\sin \theta_{\text{max}}}
\]

where \(a_0 = 0.39155\) nm is the lattice parameter of carbon-supported platinum. The PtRu/C alloy catalyst with an atomic ratio of 1:1, the theoretical value of \(X_{\text{Ru}}\) is 0.5. The alloying degree of the PtRu/C catalyst was calculated to be 0.17, which is similar to the reported result. Although the PtRu colloid was prepared by co-reduction of Pt and Ru precursors in the polyol process, the majority of the PtRu nanoparticles still existed as separate Pt and Ru phases in the colloid solution. After decreasing the pH value to about 2, the stability of the PtRu colloid was destroyed; consequently, the Pt and Ru particles were deposited onto the carbon support. The Pt and Ru particles on the carbon support are thought to be in close contact with each other due to the homogeneous mixing in the PtRu colloid solution. The alloying degree of the \(\text{SnO}_2\)-modified PtRu/C catalysts changes with the \(\text{SnO}_2\) deposition sequence. The PtRuSnO\(\text{2}/\text{C}\) catalyst has the lowest alloying degree of 0.05, and this result suggested that PtRu alloy formation was affected by the codeposition of PtRu and \(\text{SnO}_2\) particles. When the PtRu and \(\text{SnO}_2\) colloids were mixed homogeneously and then codeposited onto the carbon support, the addition of \(\text{SnO}_2\) lowered the contact between Pt and Ru particles and resulted in a poor PtRu alloy formation. The alloying degree of the PtRu/SnO\(\text{2}/\text{C}\) catalyst is also poorer than that of the PtRu/C catalyst, suggesting that prior deposition of the \(\text{SnO}_2\) particles onto the carbon support still had a negative effect on the PtRu alloy formation. For the SnO\(\text{2}/\text{PtRu/C}\) catalyst, \(\text{SnO}_2\) deposition did not affect the intimate contact of Pt and Ru particles, and the alloying...
degree of the SnO2/PtRu/C catalyst is slightly greater than that of the PtRu/C catalyst, which is probably due to a greater PtRu deposition density on the carbon support prior to SnO2 deposition.

The mean crystallite size of the catalysts was also calculated from the COads stripping charge. On the basis of the average particle size from the STEM image.

Table I. Physical characteristics and surface areas of PtRu/C and different SnO2-modified PtRu catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lattice parameter (Å)</th>
<th>Xmax</th>
<th>Mean particle size</th>
<th>PtRu utilization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>XRD (nm)</td>
<td>STEM (nm)</td>
</tr>
<tr>
<td>PtRu/C</td>
<td>3.8939</td>
<td>0.17</td>
<td>1.9</td>
<td>2.5</td>
</tr>
<tr>
<td>PtRuSnO2/C</td>
<td>3.9093</td>
<td>0.05</td>
<td>1.7</td>
<td>2.2</td>
</tr>
<tr>
<td>PtRu/SnO2/C</td>
<td>3.9029</td>
<td>0.10</td>
<td>1.7</td>
<td>2.2</td>
</tr>
<tr>
<td>SnO2/PtRu/C</td>
<td>3.8919</td>
<td>0.19</td>
<td>2.0</td>
<td>2.7</td>
</tr>
</tbody>
</table>

\( a \) On the basis of the average particle size from the STEM image.

\( b \) Calculated from the COads stripping charge.

CO stripping voltammetry measurement.—Figure 3 shows the CO stripping voltammograms of PtRu/C and different SnO2-modified PtRu/C catalysts. For the PtRu/C catalyst, COads is electro-oxidized in a relatively sharp stripping peak centered at 0.502 V. On the PtRuSnO2/C and PtRu/SnO2/C catalysts, COads is electro-oxidized over a broad potential region with a peak at 0.497 and 0.494 V, respectively, while the SnO2/PtRu/C catalyst exhibits a similarly sharp stripping peak with a negative shift of 0.024 V in peak potential. This result indicated that the COads electro-oxidation activity was improved by the interaction between PtRu and SnO2 particles via the bifunctional mechanism. It is obvious that the SnO2/PtRu/C catalyst showed the most pronounced promotional effect on COads electro-oxidation among the three SnO2-modified PtRu/C catalysts.

The PtRu utilization is defined as the ratio between the electrochemical surface area (\( S_E \)) determined by CO stripping voltammetry and the geometrical surface area (\( S_G \)) determined by the average particle size from the STEM image, as listed in Table I. The PtRu utilization can be regarded as a measure of the fraction of the PtRu metal utilization and alloying degree, indicating that the addition of SnO2 in the PtRuSnO2/C catalyst lowered the contact between Pt and Ru particles in the manner of SnO2 particles covering Pt or Ru particles. The PtRu utilization in the SnO2/PtRu/C catalyst was much greater than that in the PtRuSnO2/C catalyst and slightly lower than that in the PtRu/C catalyst. Considering that the SnO2/PtRu/C catalyst showed the most negative shift in peak potential for COads electro-oxidation, SnO2 particles in the SnO2/PtRu/C catalyst were thought to be in contact with PtRu particles, rather than cover a large fraction of PtRu particles.
Electrochemical measurement of methanol electro-oxidation.— The catalytic activities for methanol electro-oxidation of the catalysts were characterized by CV, LSV, and chronoamperometry in a solution of 0.5 M HClO₄ + 0.5 M CH₃OH at 25°C. Figure 4 shows the sixth circle of CVs. Compared with the PtRu/C catalyst, the PtRuSnO₂/C catalyst showed a positive shift of 0.041 V in peak potential, which also suggested that Pt and Ru particles covered by SnO₂ particles in the PtRuSnO₂/C catalyst were not beneficial for methanol adsorption and electro-oxidation. The PtRu/SnO₂/C and SnO₂/PtRu/C catalysts showed a similar peak potential with the PtRu/C catalyst, and the current density of methanol electro-oxidation on the PtRu/SnO₂/C and SnO₂/PtRu/C catalysts was obviously greater than that on the PtRu/C catalyst.

To validate the onset potential of methanol electro-oxidation on
PtRu/C and different SnO2-modified PtRu/C catalysts, LSV curves with a slow scan rate of 1 mV s\(^{-1}\) were recorded and are presented in Fig. 5. The PtRuSnO2/C catalyst showed a higher onset potential of methanol electro-oxidation than the PtRu/C catalyst, shifting positively by about 0.069 V, and the current density on the PtRuSnO2/C catalyst was also poorer than that on the PtRu/C catalyst. Due to the lowest metal utilization in the PtRuSnO2/C catalyst, a large fraction of Pt active sites was thought to be blocked by SnO2, which inhibited methanol adsorption and electro-oxidation.\(^{10}\) The PtRuSnO2/C and SnO2/PtRu/C catalysts exhibited a slightly lower onset potential and a superior activity compared with the PtRu/C catalyst. At an anode potential of 0.55 V, the current densities for methanol electro-oxidation on the PtRuSnO2/C and SnO2/PtRu/C catalysts were 20 and 36% greater than those on the PtRu/C catalyst, respectively, while the current density on the PtRuSnO2/C catalyst was 30% poorer than that on the PtRu/C catalyst.

The chronoamperometry measurement provided further information on the stability of the catalysts for methanol electro-oxidation. Figure 6 shows the current–time curves at 0.55 V. Similar to the LSV results, the current densities of the chronoamperometry measurement decreased in the sequence of SnO2/PtRu/C > PtRuSnO2/C > PtRu/C > PtRuSnO2/C, in agreement with the CV and LSV results.

XPS characterization.—As described before, the PtRuSnO2/C catalyst exhibits a negative effect of the addition of SnO2, while the PtRu/SnO2/C and SnO2/PtRu/C catalysts show a positive effect of the addition of SnO2, highlighting the importance of the SnO2 deposition sequence in the SnO2-modified PtRu/C catalyst preparation. XPS was performed to investigate whether the deposition sequence of SnO2 affected the chemical state of Pt and Ru and the surface.
composition in the SnO$_2$-modified PtRu/C catalysts. Figure 7 shows the Pt 4f and Ru 3p spectra of the PtRu/C and different SnO$_2$-modified PtRu/C catalysts. The less intense Ru 3p region was analyzed instead of the main Ru 5d spectra, as the latter was overlaid with the C 1s region. The results obtained by deconvoluting the XPS spectra are summarized in Table II. The Pt 4f$_{7/2}$ XPS line is fitted with a convolution of three peaks corresponding to three different Pt chemical states, as displayed in Fig. 7. The first peak (71.2 eV) is assigned to the reduced Pt (0) species, whereas the second peak (72.3 eV) is associated with oxidized Pt atoms from PtO species. The third peak (74.1 eV) is assigned to PtO$_2$ species. The Ru 3p$_{3/2}$ spectra could be deconvoluted into two components for Ru and RuO$_2$. The XPS analysis result indicated that the deposition sequence of SnO$_2$ did not alter the chemical-state distribution of Pt and Ru but resulted in a different surface atomic ratio of Pt, Ru, and SnO$_2$ in the PtRu/C and SnO$_2$-modified PtRu/C catalysts, as listed in Table III. The ratio of Pt:Ru in the PtRu/C catalyst is 0.76:0.24, indicating that the polyol-synthesized PtRu/C catalyst was Pt rich in the catalyst surface because the surface tension of Pt is lower than that of Ru. For all of the SnO$_2$-modified PtRu/C catalysts, the ratio of Pt:Ru was similar and greater than that of the PtRu/C catalyst regardless of the SnO$_2$ deposition sequence. The SnO$_2$ deposition sequence had a remarkable effect on the surface ratio of Sn despite the same nominal ratio, and the ratio of Sn decreased in the sequence of SnO$_2$/PtRu/C > PtRuSnO$_2$/C > PtRu/SnO$_2$/C. This agrees with the fact that the ratio of metals that were supported at the last step showed a relatively larger surface atomic ratio. The ratios of Sn in all the SnO$_2$-modified PtRu/C catalysts were larger than the nominal ratio, which coincided with previously reported results. Although the SnO$_2$/PtRu/C catalyst has the largest surface ratio of Sn, the metal utilization, as listed in Table I, is still greater than that of the PtRuSnO$_2$/C and PtRu/SnO$_2$/C catalysts, also suggesting that the majority of SnO$_2$ particles in the SnO$_2$/PtRu/C catalyst were just in contact with PtRu particles.

In situ IRRAS measurement.— The PtRuSnO$_2$/C and SnO$_2$/PtRu/C catalysts exhibited the poorest and the greatest catalytic activity among the PtRu/C and SnO$_2$-modified PtRu/C catalysts; in situ IRRAS measurement was carried out to understand the molecular structures on the surface of PtRu/C, PtRuSnO$_2$/C, and SnO$_2$/PtRu/C catalysts.

![Figure 7. Pt 4f and Ru 3p signals in the XPS spectra of PtRu/C and different SnO$_2$-modified PtRu/C catalysts.](image-url)
SnO₂/PtRu/C catalysts during the electrocatalytic reaction. Figure 8 shows in situ IR spectra obtained in the 0.5 M HClO₄ + 0.5 M CH₃OH solution at (i) PtRu/C, (ii) PtRuSnO₂/C, and (iii) SnO₂/PtRu/C, deposited on the gold substrate surface, in the potential region between 0.1 and 0.9 V. In the present work, the electrode potential was controlled at 0.05 V as soon as the electrolyte solution was introduced into the cell. As shown in Fig. 8a, almost no IR peak can be observed at 0.1 V, indicating that the oxidative decomposition rate of CH₃OH on the catalyst surface is very slow in the low potential region. A peak at 2040 cm⁻¹ with a small shoulder at 1964 cm⁻¹ is clearly observed at 0.2 V, and a broad band can also be identified at 1824 cm⁻¹. The peaks at 2040 and 1824 cm⁻¹ are assigned to linearly adsorbed CO(CO₂) and bridge adsorbed CO(CO₂) on the Pt sites. The small shoulder around 1964 cm⁻¹ can be attributed to CO adsorbed on Ru sites (CO(Ru)). It is known that only one CO adsorption band is observed on the PtRu alloy surface, indicating that separated Pt and Ru phases should exist in the present PtRu/C catalyst, which coincides with the low alloying degree of Ru in the PtRu/C catalyst, as listed in Table I. The CO₂ intensity increases slightly with potential, while its peak position shifts to a higher frequency region, which can be attributed to the electron back-donation from the Pt to CO antibonding orbit. The band intensity and the position of the CORu do not change much with potential. At 0.45 V, a peak appears at 2343 cm⁻¹, which can be assigned to the C–O stretching mode of CO₂, i.e., the final product for the CH₃OH electro-oxidation. The onset potential for the CO₂ formation is lower than that of the pure Pt electrode, suggesting that Ru works to oxidize CO from the OH_ads species through the bifunctional mechanism. It is also interesting to note that the amount of the adsorbed CO is almost the same even when the CO₂ formation does not interfere with the OH_ads formation on SnO₂ sites. In the PtRuSnO₂ catalyst (Fig. 8b), the spectral features are generally similar to that of the PtRu/C catalyst except for the absence of CORu, suggesting that these Ru sites may be blocked by SnO₂. This result agrees with the lowest PtRu metal utilization in the PtRuSnO₂/C catalyst as described above. In addition to CO adsorption bands on Pt sites, the SnO₂/PtRu/C catalyst (Fig. 8c) also shows COH_ads. The IR peak positions for these CO species on the SnO₂/PtRu/C catalyst surface are quite similar to those of the PtRu/C catalyst. These results suggest that separated Pt and Ru phases are present on the catalyst surface, and this state is not affected by the later deposition of SnO₂ in the SnO₂/PtRu/C catalyst preparation. The onset potential for the CO₂ formation on the SnO₂/PtRu/C catalyst is ca. 0.4 V, lower than that on the PtRu/C and PtRuSnO₂/C catalysts. Figure 9 shows integrated IR intensities for CO₂ generated as a function of electrode potential for the three catalysts. More CO₂ is formed on the SnO₂/PtRu/C catalyst surface, indicative of the greatest catalytic activity for methanol electro-oxidation among these catalysts. This result agrees with those shown in Figs. 4–6 in the same solution.

**Proposed roles of SnO₂ in SnO₂-modified PtRu/C catalysts**—CO does not adsorb on the surface of SnO₂ particles, so the COH_ads formation does not interfere with the OH_ads formation on SnO₂ sites in contrast to the situation on Pt and Ru sites. In the CO stripping voltammetry, COH_ads poisoned the Pt and Ru sites, and OH_ads was formed on SnO₂ sites by a water-discharge reaction at a low potential, where OH_ads could not be formed on Pt and Ru sites. The
removal of CO\textsubscript{ads} on Pt or Ru sites proceeded via its reaction with OH\textsubscript{ads} on SnO\textsubscript{2} sites, so the onset potential of CO\textsubscript{ads} electro-oxidation on all the SnO\textsubscript{2}-modified PtRu/C catalysts was lower than that on the PtRu/C catalyst. Once CO\textsubscript{ads} on Ru sites was electro-oxidized, OH\textsubscript{ads} was produced on Ru sites at a faster rate than on SnO\textsubscript{2} sites. After the onset potential, CO\textsubscript{ads} electro-oxidation on the SnO\textsubscript{2}-modified PtRu/C catalyst could be maintained at a faster rate than that on the PtSnO\textsubscript{2}/C catalyst with further increase in potential, so the peak potential of the CO\textsubscript{ads} electro-oxidation on all the SnO\textsubscript{2}-modified PtRu/C catalysts shifted negatively.

For methanol electro-oxidation, methanol was first adsorbed on Pt sites and then dehydrogenated step by step to produce CO\textsubscript{ads}.\textsuperscript{10} A large fraction of Pt sites covered by SnO\textsubscript{2} particles in the PtSnRuSnO\textsubscript{2}/C catalyst were not facile for methanol adsorption and stepwise dehydrogenation, so both the onset and peak potentials of methanol electro-oxidation shifted positively compared with those on the PtRu/C catalyst, and the PtSnRuSnO\textsubscript{2}/C catalyst showed a poorer catalytic activity for methanol electro-oxidation than the PtRu/C catalyst. During the methanol electro-oxidation, CO\textsubscript{ads} also could migrate from Pt sites to Ru sites,\textsuperscript{42} which competed with OH\textsubscript{ads} formation on Ru sites, and the addition of SnO\textsubscript{2} into PtRu therefore provided an additional route for OH\textsubscript{ads} formation, favoring methanol electro-oxidation. Because SnO\textsubscript{2} deposition did not affect the intimate contact of Pt and Ru particles on the carbon support and the alloyed Ru fraction, the SnO\textsubscript{2}/PtRu/C catalyst showed the most pronounced promotional effect for methanol electro-oxidation among the three SnO\textsubscript{2}-modified PtRu/C catalysts.

Conclusions

SnO\textsubscript{2}-modified PtRu/C catalysts with different SnO\textsubscript{2} deposition sequences were prepared by the polyol process. XRD and STEM results indicated that the SnO\textsubscript{2} deposition sequence affected the particle size and alloyed Ru fraction of the SnO\textsubscript{2}-modified PtRu/C catalysts. A simultaneous deposition of SnO\textsubscript{2} and PtRu or a prior deposition of SnO\textsubscript{2} onto the carbon support improved the metal dispersion and, at the same time, decreased the alloyed Ru fraction. The XPS result suggested that the deposition sequence of SnO\textsubscript{2} did not alter the chemical-state distribution of Pt and Ru but resulted in a different surface atomic ratio of Pt, Ru, and SnO\textsubscript{2}. CO stripping voltammetry verified that the addition of SnO\textsubscript{2} into PtRu promoted CO\textsubscript{ads} electro-oxidation in all the SnO\textsubscript{2}-modified PtRu/C catalysts. Electrochemical measurements of methanol electro-oxidation exhibited that the catalytic activity decreased in the sequence of SnO\textsubscript{2}/PtRu/C > PtRuSnO\textsubscript{2}/C > PtRuC > PtRuSnO\textsubscript{2}/C. In situ IRRAS results validated that the SnO\textsubscript{2}/PtRu/C catalyst possessed the best catalytic activity for methanol electro-oxidation among these catalysts, exhibiting the lowest onset potential for CO\textsubscript{2} formation and the highest CO\textsubscript{2} band intensity. The same spectral features of CO adsorbed on the PtRu/C and SnO\textsubscript{2}/PtRu/C catalysts suggested that the addition of SnO\textsubscript{2} did not affect the intimate contact of Pt and Ru particles in the SnO\textsubscript{2}/PtRu/C catalyst preparation, which is crucial for obtaining a superior catalytic activity for methanol electro-oxidation.

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