The Effect of Ruthenium on the Binding of CO, H$_2$, and H$_2$O on Pt(110)
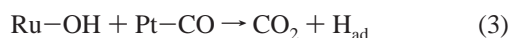
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Ruthenium is known to improve the CO tolerance of platinum based fuel cell catalysts, but the mechanism is unclear. Some investigators believe that the main role of ruthenium is to dissociate water, and thereby provide a faster route for the oxidation of CO. Other investigators believe that ruthenium changes the electronic structure of platinum, in a way that lowers the binding energy of the CO and thereby promotes easy reaction. In this study, we have used TPD to measure the magnitude of the two effects in UHV. When we deposit 0.25 monolayers of ruthenium on Pt(110), we find that the adsorption properties of the surface change substantially. The surface only adsorbs about half as much CO and H$_2$. The sticking probability of water is also reduced. The β_2 hydrogen peak disappears, whereas the α_1 CO peak is attenuated by a factor of 2. The binding energy of the α_1 CO decreases from 31 to 29 kcal/mol when ruthenium is added to the surface, whereas the binding energy of the α_2 CO decreases from 25 to 23 kcal/mol. The exchange of ^{18}O into H$_2$^{16}O is substantially enhanced showing that the activation barrier for OH recombination is reduced from 12 kcal/mol to between 7 and 9 kcal/mol. Together these effects would be expected to produce between a 170 and 260 meV reduction in the activation barrier for CO removal from the surface. This is in close agreement with the 200 meV reduction in the potential for CO removal measured electrochemically by previous workers. Quantification of our results shows that only about 40meV of the total reduction is associated with the ligand effect, whereas the remaining portion is associated with the bifunctional mechanism. These results show that ruthenium on platinum has very different properties than ruthenium metal. It slightly weakens the CO binding, and has a more substantial effect on activating water. There also is a site blocking effect that needs to be explained.

Introduction

The purpose of this paper is to try to understand the role of ruthenium in improving the CO tolerance of fuel cell catalysts. Recall that many previous workers[1,2] have found that ruthenium additions improve the CO tolerance of platinum based fuel cell catalysts. There are two proposed mechanisms, the so-called "bifunctional" mechanism[3−6] and the "ligand" mechanism.[7,8] According to the bifunctional mechanism, the ruthenium in a Pt/Ru catalyst dissociates water into OH and H on the surface of the catalyst. The OH's can then react with CO to yield CO$_2$ and H. i.e.,

$$CO + Pt \rightarrow Pt-CO \qquad (1)$$

$$H_2O + Ru \rightarrow Ru-OH + H_{ad} \qquad (2)$$

$$Ru-OH + Pt-CO \rightarrow CO_2 + H_{ad} \qquad (3)$$

According to the ligand mechanism, the presence of ruthenium changes the electronic structure of platinum in a way that weakens Pt−CO bond. The weakening of the CO binding is assumed to promote easy CO removal.

So far, the experimental confirmation of these mechanisms has been indirect. There are no direct measurements on the influence of ruthenium on the binding energy of CO on platinum. Nor is there any direct measurements showing that water is activated on a Pt−Ru surface.

In this study, we have examined the influence of submonolayer ruthenium additions on the temperature-programmed desorption (TPD) spectrum of various gases on Pt(110) in UHV. Previous workers have found that Pt(110) is a good model for the sites on a supported platinum particle in a fuel cell electrode.[14] In experiments with methanol or CO electro-oxidation, submonolayer amounts of ruthenium were found to provide the same type of enhancements in CO removal as is seen in bulk Pt−Ru alloys.[5,9] A platinum crystal in UHV is not quite the same as a platinum electrode in solution, so one might not expect to observe identical effects. Still, the UHV measurements can provide a useful basis for understanding the chemistry in fuel cells. In this paper, we will use temperature-programmed desorption to probe the influence of ruthenium on fuel cell chemistry.

Experimental Section

The apparatus and procedures have been described elsewhere.[10−13] The TPD experiments were performed in a UHV chamber having a base pressure of 1×10^{-10} Torr. The chamber was pumped by a turbomolecular pump and was equipped with a PHI 4−161 sputter gun system, a PHI 10−155 Auger electron spectroscopy (AES) system, a Princeton reverse-view LEED, and a UTI-100C quadrupole mass spectrometer. Prior to the experiments reported here, the sample was repolished with diamond paste and was oxidized in flowing oxygen and washed in dilute HF to remove residual calcium and silicon. The sample was then mounted in a tantalum wire and placed in the vacuum system. The sample was cleaned by heating it in oxygen at 800 C and sputtering it with argon ions until no impurities could be
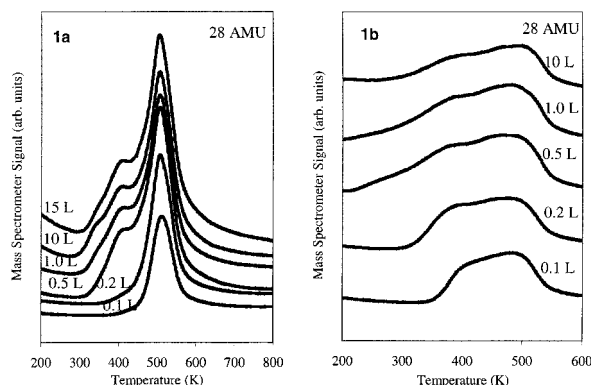
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Figure 1. A series of 28 amu TPD spectra taken by exposing either a clean 110K (2×1)Pt(110) sample (a) or a ruthenium-covered (2×1)Pt(110) sample (b) to various amounts of CO and then heating at 15 K/s.

Figure 2. A series of 2 amu TPD spectra taken by exposing either a clean 110K (2×1)Pt(110) sample (a) or a ruthenium-covered (2×1)Pt(110) sample (b) to various amounts of H_2 and then heating at 15 K/s.

Figure 3. A series of 18 amu TPD spectra taken by exposing either a clean 110K (2×1)Pt(110) sample (a) or a ruthenium-covered (2×1)Pt(110) sample (b) to various amounts of H_2O and then heating at 15 K/s.

detected in AES. The sample was then annealed for 3 min at 1000 C to repair sputtering damage, and put into a (2×1) reconstruction. The sample showed a sharp (2×1) LEED pattern at this stage. We also checked the reconstruction using H_2 TPD; H_2 TPD is very sensitive to defects in the Pt(110) surface. We observe the α state characteristic of a defect-free sample.[18]

Ruthenium deposition was done by exposing a clean, 220 C Pt(110) crystal to 5×10^{-8} Torr of $Ru_3(CO)_{12}$ vapor for about 10 min and letting the $Ru_3(CO)_{12}$ decompose on the surface of the sample. Ruthenium and carbon are deposited onto the sample during the $Ru_3(CO)_{12}$ decomposition process. The carbon was burned away by heating the sample at 300 C in 2×10^{-7} Torr of oxygen for 30 min. No residual carbon could be detected by AES at that point,[1] and TPD in oxygen did not show evidence of CO production. ([1]The carbon and ruthenium AES peaks overlap, so we used peak shape analysis to infer carbon and ruthenium coverages.) The sample was then cooled to 100 K, and 5 L of hydrogen was added to reduce the surface oxide. Finally, the sample was flashed to 600 K to remove any residual hydrogen. At the end of this procedure, AES showed that the surface was oxygen free, and that there was about 0.25×10^{15} atoms of ruthenium on the surface.

In other work, we have varied the ruthenium coverage, but here, we will concentrate on the results with 0.25 monolayers of ruthenium because surfaces with Ru coverages of 0.25 have nearly the maximum CO tolerance.[14]

In a TPD experiment the sample was cleaned as described above. The sample was cooled to 110 K and dosed with hydrogen, oxygen, CO, or water by backfilling the chamber. Exposures were calculated using uncorrected ion gauge readings. The TPD heating rate was 15 K/s. Subsequent runs were made by cleaning the surface in oxygen to remove residual carbon, reducing the surface with hydrogen and then flashing to 600 K to remove residual hydrogen.

Results

Figure 1 compares the TPD spectrum of carbon monoxide on a clean Pt(110) sample to one from a Pt(110) sample covered by 0.25 monolayers of ruthenium. At low coverage, CO desorbs from the clean surface in a single peak at about 515 K in good agreement with previous reports.[15-17] That peak shifts to about 510 K with increasing coverage. In addition, a shoulder grows into the spectrum at about 415 K.

Two peaks are seen on the ruthenium-covered surface, one peak around 480 K, and another peak around 400 K. The 480
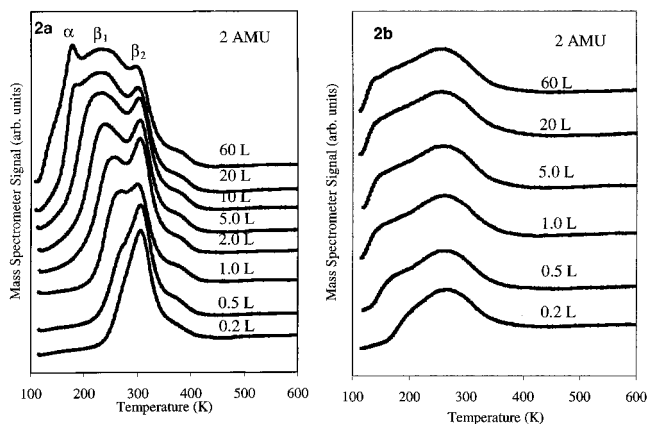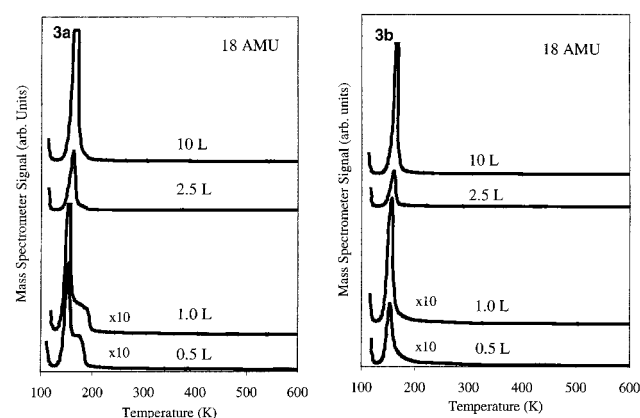
K peak shifts down to 470 and then back to 490 K with increasing coverage, while the 400 K shifts down to 380 K.

Integration of the TPD peak areas shows that the initial sticking probability of CO is similar on the clean surface and on the ruthenium-covered one. However, at saturation a clean (2×1)Pt(110) sample adsorbs about a factor of 2 more CO than a ruthenium-covered sample.

Figure 2 compares the TPD spectrum of hydrogen on a clean Pt(110) sample to one from a Pt(110) sample covered by 0.25 monolayers of ruthenium. At low coverage, H_2 desorbs from the clean surface in a single peak at about 310 K. That peak shifts to about 300 K with increasing coverage. In addition, new peaks grow into the spectrum at about 250 and 180 K. Following the literature,[18-20] we will call the 300 K peak the "β_2 peak", the 250 K peak the "β_1 peak" and the 180 K peak the "α peak". Notice that the β_2 peak disappears when we adsorb ruthenium onto the surface while the β_1 peak shifts to slightly higher temperatures and the α peak shifts to lower temperatures. Integration of the TPD peak areas shows that the initial sticking probability of H_2 is similar on the clean surface and the ruthenium-covered one. However, at saturation the ruthenium-covered surface adsorbs about a factor of 2.5 less hydrogen than a clean sample.

Figure 3 compares the TPD spectrum of water on a clean Pt(110) sample to one from a Pt(110) sample covered by 0.25 monolayers of ruthenium. In this case, we observe a single peak at about 160 K on both samples. There is also a small shoulder
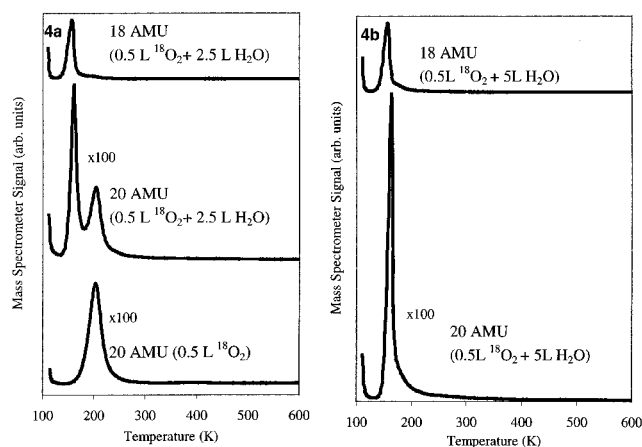
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Figure 4. A comparison of the 18 and 20 amu TPD spectra taken by adsorbing about 0.5×10^{15} molecules/cm² of ^{18}O onto either a clean 110K (2×1)Pt(110) sample (a) or a ruthenium-covered (2×1)Pt-(110) sample (b) adding about 1×10^{15} molecules/cm² of $H_2^{16}O$, and flashing in a background containing 1×10^{-10} Torr of hydrogen.

at around 180−190 K on the clean surface; this peak is absent on the ruthenium-covered surface. Integration of the TPD peaks indicates that at submonolayer coverages, the sticking probability of water on the clean surface is about twice that on the ruthenium-covered surface. However, at high coverages the differences between the two surfaces decrease.

Figure 4 shows the results of a more complex experiment. We adsorbed a small amount of ^{18}O onto a Pt(110) sample, added $H_2^{16}O$ and flashed the sample in a background containing about 1×10^{-10} Torr of hydrogen. If we adsorb oxygen alone, with no water, we observe a single peak in the water TPD at 200 K. This peak has been observed previously,[21] and seems to be associated with recombination of isolated OH moieties. When we add water, the 200 K peak shrinks, and we see a new peak at 160 K, due to exchange of ^{18}O into the water. Previous workers[22−24] have found that this reaction occurs via

$$^{18}O + H_2O \rightarrow {}^{18}OH + OH \qquad (4)$$

$$^{18}OH + OH \rightarrow H_2^{18}O + O \qquad (5)$$
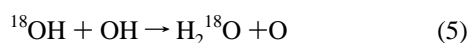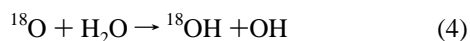
When we add ruthenium, the 200 K peak disappears entirely, whereas the 160 K peak is substantially enhanced. The implication of Figure 4 is that ruthenium activates the exchange of ^{18}O via reactions 4 and 5.

Discussion

The results here show that the addition of 0.25 monolayers of ruthenium on platinum have substantial effects on the binding of species on platinum surfaces. The initial sticking probabilities of H₂, and CO are similar to those on a clean surface but the saturation coverages of H₂ and CO are approximately halved. The β_2 hydrogen peak is completely suppressed. The α_2 CO peak is reduced by a factor of 3. Interestingly, we observe substantial changes in the TPD peak intensities, but only small changes in the peak positions. Therefore, to a first approximation, the main role of ruthenium is to block the adsorption of gases and modify the chemistry of OH. The variation in the binding energies of the adsorbed species seems to be a smaller effect.

The changes in Figures 1, 2, and 4 closely mimic the effects seen in electrochemical experiments. We observe a factor of 2 reduction in the saturation coverage of CO when ruthenium is

added to the surface. The same factor of 2 reduction is observed electrochemically during CO adsorption on a ruthenium modified Pt(111) sample using radioactive labeled carbon.[25] We observe a factor of 2.5 reduction in the saturation coverage of hydrogen when ruthenium is added to the surface. The same kind of reduction is observed electrochemically.[26] We observe the disappearance of the most strongly bound hydrogen state when ruthenium is added to the surface. The disappearance of the high potential dehydrogenation peak is also observed electrochemically when there is a moderate ruthenium coverage on Pt(110).[26,27] Overall, our data show many of the same trends as are seen in previous electrochemical experiments, which suggests that ruthenium has similar effects in UHV as in an electrochemical cell.

The advantage of the UHV experiments is that it is possible to quantify the effects of ruthenium. For example, it is possible to quantify the change in binding energy of CO using an initial slope analysis (i.e., making an Arrhenius plot of the initial part of the TPD curve). The result shows that the binding energy of the α_1 CO decreases from 31 to 29 kcal/mol when ruthenium is added to the surface, whereas the binding energy of the α_2 CO decreases from 25 to 23 kcal/mol. Thus, although there is a clear ligand effect, the ligand effect only makes a 2 kcal/mol change in the binding energy of CO.

According to Polanyi's relationship,[28] a 2 kcal/mol change in the binding energy of CO due to the ligand effect should produce about a 1 kcal/mol (∼40 meV) decrease in the activation energy for reaction 3.

One issue that we need to consider is whether we are measuring the properties of the CO that is in close proximity to the ruthenium. Recall that submonolayers of ruthenium form islands on Pt(111).[29] One can imagine a situation where the ruthenium is changing the properties of the platinum atoms in the first several layers around the ruthenium, but the CO far away from the ruthenium is unaffected. In such a case, one would not observe a substantial change in the binding of CO with TPD.

The data in Figure 2 though, are not consistent with there being a substantial amount of platinum that is not in close proximity to the ruthenium. Notice that the formation of β_2 hydrogen is completely suppressed when 0.25 monolayers of ruthenium are added to the surface. β_2 hydrogen is seen on clean platinum, so if some of the platinum were not being affected by ruthenium, one should still observe β_2 hydrogen desorption. The fact that no β_2 hydrogen is observed is strong evidence that essentially all of the exposed platinum is being strongly affected by the ruthenium i.e., there is a strong ligand effect. It is just that the ligand effect only changes the binding energy of CO by about 2 kcal/mol.

The data also show evidence for a bifunctional mechanism where the reactivity of OH's are enhanced by ruthenium. Notice that the 200 K peak in Figure 4 due to slow recombination of hydroxyls is completely suppressed when ruthenium is added to the surface. In its place we observe a peak at 160 K. The fact that the 200 K peak is suppressed while the 160 K peak is enhanced implies that the OH's are being activated on the ruthenium-covered surface. Thus, there is a strong bifunctional mechanism.

One can quantify the effects by comparing the activation barrier for OH recombination on a clean surface to that on a ruthenium-covered one. If we assume a preexponential of 10^{13}/s and substitute into Redhead's equation[30] we calculate an activation barrier of 12 kcal/mol for OH recombination on the clean surface. It is harder to get an accurate value on a

ruthenium-covered surface. The OH recombination peak is at 160 K on the ruthenium-covered surface. Water itself desorbs at 160 K so the 160 K peak must be desorption-limited not reaction-limited. Therefore, one cannot use the TPD to accurately measure the activation barrier for OH recombination on the ruthenium-covered surface. Still, the barrier for OH recombination on the ruthenium-covered surface must be less than the activation barrier for desorption of water, 9 kcal/mol, because water desorption is rate-determining. The barrier for OH recombination on the ruthenium-covered surface must be at least 7 kcal/mol or we would observe water formation during dosing at 100 K. Thus, the presence of ruthenium has reduced the barrier for OH recombination from 12 kcal/mol to 7−9 kcal/mol. This result shows that the bifunctional mechanism is active on the ruthenium-covered platinum surface producing a 3−5 kcal/mol reduction in the activation barrier for hydroxyl recombination.

There is additional evidence for a bifunctional mechanism in the data in Figure 4. Notice that Figure 4 shows that there is a substantial increase in the rate of ^{18}O exchange into water when ruthenium is added to the surface. Thus, it seems that reactions 4 and 5 are being substantially enhanced when ruthenium is added to the Pt(110) surface. Such a result is as expected if the bifunctional mechanism is active.

The conclusion from our study, then, is that both the bifunctional and the ligand mechanism are active on our sample but the bifunctional effect has a larger effect on CO removal than the ligand effect. Notice that the binding energy of CO only changes by 2 kcal/mol when ruthenium is added to the surface, which only produces a 1 kcal/mol change in the activation barrier of reaction 3. In contrast, there is a 3−5 kcal/mol change in the activation barrier for recombination of OH. Such a change should produce the same amount of change in the activation barrier to reaction 3. Therefore, although both the "ligand model" and the "bifunctional mechanism" seem to be active on our sample, the bifunctional effects seem to be larger than the ligand effects.

In a more quantitative basis, according to our data, the activation barrier for CO removal via reaction 3 should change by a total of between 4 and 6 kcal/mol ($\sim$170 and $\sim$260 meV/molecule) when ruthenium is added to the surface. The 170 to 260 meV compares well to the 200 meV decrease in the potential for CO removal measured electrochemically by previous investigators.[8,31] According to our data of the 4−6 kcal/mol (170−260 meV) reduction in the potential for CO removal, only about 1 kcal/mol (40 meV) is associated with the ligand effect, whereas 3−5 kcal/mol (130 to 200 meV) are associated with the bifunctional mechanism. Thus, the effect of the bifunctional mechanism is about 4 times larger than the ligand effect.

Our data shows that there is another effect in our data that has not been considered previously: the ruthenium seems to reduce the saturation coverage of CO and H_2. The details are not very clear, but the saturation coverage of CO on the ruthenium-covered surface is about 50% of that on a clean Pt-(110) surface, whereas the saturation coverage of H_2 is about 40% of that on the clean surface. CO and hydrogen adsorb readily on bulk ruthenium crystals. However, unlike bulk ruthenium, submonolayer amounts of ruthenium on platinum do not seem to strongly bind CO or H_2.

In previous work, Buatier de Mongeot et al.[32] found that when submonolayers of platinum were deposited onto a ruthenium surface, the platinum reduced the amount of CO and H_2 that

adsorbed onto the ruthenium. Such observations are consistent with the measurements here.

We can speculate why ruthenium on platinum behaves so differently than bulk ruthenium. In previous work, Pallassana et al.[33] used DFT calculations to examine the binding of hydrogen on rhenium overlayers on Pd(111). They find that there is a significant charge transfer from the palladium to the rhenium so hydrogen only binds weakly on rhenium overlayers. We speculate that a similar process occurs when ruthenium adsorbs on platinum. Evidently, there is a significant charge transfer when ruthenium adsorbs on platinum, so the ruthenium is no longer able to adsorb CO and H_2.

Conclusions

In summary then, the results of our study show that the adsorption properties of Pt(110) change substantially when 0.25 monolayers of ruthenium are deposited onto the surface. The surface only adsorbs about half as much CO and H_2. The sticking probability of water is also reduced. The β_2 hydrogen peak disappears, while the α_1 CO peak is attenuated by a factor of 2. The exchange of ^{18}O into $H_2^{16}O$ is substantially enhanced showing a strong bifunctional mechanism. There is also a smaller ligand effect. Together the two effects should reduce the activation barrier for CO removal by a total of between 4 and 6 kcal/mol ($\sim$170 and $\sim$260 meV/molecule) in good agreement with the 200 meV decrease in the potential for CO removal measured electrochemically by previous investigators.[8,31] According to our data, of the 4−6 kcal/mol (170−260 meV) reduction in the potential for CO removal, only about 1 kcal/mol (40 meV) is associated with the ligand effect, whereas 3−5 kcal/mol (130 to 220 meV) is associated with the bifunctional mechanism showing that the bifunctional effect is larger than the ligand effect.

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