

Dependence of CH₃OH Oxidation Activity for a Wide Range of PtRu Alloys

Detailed Analysis and New Views

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Unsupported PtRu alloy powders of a wide range of compositions were prepared at low temperatures by carefully adjusting the preparation procedure. PtRu alloys of essentially the same surface, nominal and bulk composition, were formed up to *ca.* 46 atom % Ru content. Adsorbed CO stripping voltammetry and CH₃OH oxidation characteristics, namely, i-V curves and pseudo-steady-state current density values recorded at constant potentials, were the same as reported for corresponding bulk alloys, suggesting that the electrocatalytic activities of the powders can be compared to bulk alloys. CH₃OH oxidation activities obtained for PtRu alloy, Pt, and Ru powders showed the PtRu alloy of 70:30 atom % Pt:Ru composition to exhibit the highest activity independent of the temperature and potential tested (0.3 and 0.4 V *vs.* a reversible hydrogen electrode). The experimental pseudo-steady-state current density values for the CH₃OH oxidation reaction were found to show the same dependence on Ru content as theoretical values calculated assuming that an assembly of three neighboring Pt and one Ru site are involved in the oxidation of a CH₃OH molecule.

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Pt-Ru catalysts are of major interest as anode materials for lowtemperature fuel cells such as the direct methanol fuel cell. Platinum catalyzes the methanol adsorption and dehydrogenation reactions, shown in Eq. 1 + 2. As a result, an intermediate "CO"-type species is formed that can be oxidized to CO₂ with the assistance of -OH type groups that are formed by the partial oxidation of H₂O on neighboring surface sites (M), Eq. 3 + 4

$$Pt + CH_3OH = Pt - (CH_3OH)_{ads}$$
[1]

$$Pt-(CH_3OH)_{ads} = Pt-(CO)_{ads} + 4H^+ + 4e^-$$
 [2]

$$M + H_2O \rightarrow M-OH + H^+ + 1e^-$$
[3]

$$Pt-(CO)_{ads} + M - OH \rightarrow Pt + M + CO_2 + H^+ + 1e^-$$
 [4]

The -OH formation needs to take place at low potentials in order for a fuel cell to generate high power outputs. Until now, bimetallic Pt-Ru catalysts have exhibited some of the best catalytic activities toward the electrochemical CH₃OH oxidation reaction, likely due to the ability of Ru to form active oxygen species at low potentials.^{1,2} Equation 4 suggests that the Pt and Ru site distribution at the atomic level influences the CH₃OH oxidation activity, as discussed in a number of studies.^{3,4} Gasteiger et al.³ studied the CH₃OH oxidation reaction using well-characterized bulk PtRu alloys prepared by arcmelting. Based on data collected for three different Pt:Ru ratios, they concluded that a Pt:Ru composition of close to 90:10 atom % shows the highest activity for the CH₃OH oxidation reaction at room temperature. Furthermore, the general view exists that an increase in temperature results in a change of the optimal Pt:Ru ratio (toward higher, namely, 50 atom % Ru, contents).^{3,5} This change in the optimal PtRu ratio has been based on an apparent activity of Ru to dehydrogenate CH₃OH at higher temperatures (>60°C), while Ru does not show such an activity at room temperature.³ These conclusions have been questioned by Iwasita et al.5 and Kabbabi et al.4 The latter suggested an optimal Ru content of 10-15 atom % independent of the temperature; however, they reported experimental current density data for the oxidation of CH₃OH that were more than one order of magnitude too high, thus casting some doubt on the validity of their data. Iwasita et al. found very similar CH₃OH oxidation activities at room temperature for Pt:Ru ratios between 90:10 and 70:30 atom %. As pointed out by Iwasita et al.,⁵ they

mainly used PtRu catalyst systems that consisted of Ru particles/ islands deposited onto Pt surfaces prepared using a variety of methods, *i.e.*, they used catalysts for which the distribution of Ru and Pt sites is less random than for true alloy catalysts. This may explain the independence of the CH₃OH oxidation activity on the Pt:Ru ratio for 10-30 atom % Ru contents. Other studies that involve different Pt:Ru ratios exist.^{2,6} Often these studies compare the CH₃OH oxidation activities per catalysts weight or geometrical electrode area and not the true catalytic activity and/or use catalysts for which the bulk and surface composition varies. However, for fundamental and mechanistic studies, the use of catalysts of known and preferably random site distribution, *i.e.*, true alloys, is essential. Indeed, it is difficult to prepare well-defined PtRu alloys for which the bulk and surface composition is known and the same. Typically, this involves expensive methods such as sputter deposition, arc-melting followed by surface polishing that leads to bulk metal alloys.^{3,4,7,5}

In this work, the preparation and properties of a range of PtRu alloy powders is discussed for Pt:Ru atomic ratios of up to *ca.* 45 atom % Ru. PtRu alloy powders that show essentially the same bulk and surface compositions are used to obtain the CH₃OH oxidation activities as a function of the Pt:Ru atomic ratio for a broad potential range. This includes the low-potential region which is relevant to real fuel cell applications and where the -OH formation is believed to be rate determining.⁹ The use of PtRu powders allows facile preparation of electrodes of easily adjustable and sufficiently high surface areas that permit reliable CH₃OH oxidation current measurements to be made, even at low potentials. The influence of temperature on the optimal Pt:Ru atom % for the CH₃OH oxidation reaction is also discussed.

Experimental

Catalyst powder preparation.—A range of Pt, Ru, and PtRu alloy powders were synthesized using a simple chemical reduction method. The nominal atomic Pt to Ru ratio for the PtRu alloy powders was varied between 91 and 54 atom % Pt, *i.e.*, between 9 and 46 atom % Ru. All powders were prepared at room temperature using NaBH₄ (Anachemia) as reducing agent. RuCl₃ (99.99% purity, Alfa Aesar) and PtCl₄ (99.9% purity, Alfa Aesar) were used as precursor salts. Table I summarizes the amounts of Pt and Ru precursor salts used for the synthesis of the catalyst powders. In all cases, the precursor salts were dissolved in 150 mL H₂O and stirred for 30 min. 75 mL of 0.2 M NaBH₄ was added dropwise (within less than 5 min) to the well-stirred solution for the catalyst powders of less than 30 atom % Ru. For the catalysts made of more Ru, 75 mL

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Table I. Amounts of precursor salts used for the powder synthesis and Pt:Ru nominal and surface ratios.				
PtCl ₄ (g)	RuCl ₃ (g)	Nominal Pt:Ru ratio (atom %) ^a	Surface Pt:Ru ratio (atom %) ^b	
1.06	-	100:0	100:0	
1.06	0.073	91:9	91:9	
1.06	0.115	85:15	84:16	
1.06	0.163	80:20	82:18	
1.06	0.217	75:25	77:23	
1.06	0.28	70:30	70:30	
1.06	0.351	65:35	68:32	
1.06	0.435	60:40	60:40	
1.06	0.555	54:46	55:45	
-	1.6	0:100	0:100	

^a Nominal Pt:Ru atom % ratio calculated from the Pt and Ru precursor salts used for the powder preparation.

^b Surface Pt:Ru atom % ratio determined from XPS measurements.

of 0.4 M NaBH₄ was added within less than 1 min to the precursor salt solution (unless otherwise stated). Solid catalyst powder particles were formed immediately and the precursor salts were transformed completely into solid catalyst powders. The formed Pt, PtRu, and Ru catalyst powders were filtered and excessively washed with H₂O and subsequently dried in an air oven at 80°C for 30 min unless otherwise stated. The precursor salts were dried in air at 135°C prior to their use. Pt, Ru, and PtRu alloy powders were prepared using different glassware. All glassware involved in the powder preparation was cleaned using aqua regia prior to its use.

Working electrode preparation.—The catalyst powders were formed into electrodes by sonicating 13 mg of a particular powder dispersed in solutions consisting of 300 μ L Nafion solution (5 wt % Nafion dissolved in lower alcohols, Fluka) and 2 mL H₂O for 30 min. Appropriate amounts (1-20 μ L) were pipetted onto *ca.* 0.25 cm² Au foil electrodes (99.9% Au, 0.1 mm thick, Goodfellow) forming thin catalyst layers. The electrodes were dried in air at room temperature, cold-pressed for *ca.* 30 s applying 1 ton, and subsequently washed excessively with H₂O. The Au foils were firmly attached to Au wire electrodes, and Au not covered with the catalyst powder was carefully wrapped with Teflon tape.

Cells and electrodes.—Three-compartment cells, in which the reference electrode was separated from the working and counter electrode compartment by a Luggin capillary, were employed for the electrochemical studies. The cells were equipped with water jackets and condensers that allowed electrochemical studies under temperature control between 20 and 60°C. All potentials reported in this paper are *vs.* the reversible hydrogen electrode (RHE) unless otherwise stated. However, mercury sulfate electrodes (MSE, -0.68 V *vs.* RHE¹⁰) were used as reference electrodes in the experiments. Large-surface-area Pt gauzes served as counter electrodes.

Techniques and instrumentation.—Electrochemical experiments were performed using a Solartron SI 1287 electrochemical interface (Solartron Group, Ltd.) driven by Corrware software (Scribner Assoc.). A Scintag XDS2000 system was employed using a Cu Ka source to obtain X-ray diffraction (XRD) spectra for the as-prepared catalyst powders. The scanning angle extended from 2θ of 20 to 120°. The software program Topas 2 (DIFFRAC^{PLUS} Topas, Bruker Axis, Inc.) was employed to extract lattice parameter constants from the experimental XRD spectra. The entire XRD spectra (20-120°) were employed to analyze the data. Si powder (typically 1-20 µm, 99.9985% purity, Alfa Aesar) was used as the internal standard for the XRD analyses. The powders were analyzed using a Si(510) plate (GEM Dugout). X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Kratos Axis Ultra spectrometer equipped with a monochromatized Al K α source. The as-prepared catalyst powders were attached to sticky Cu tape (3M copper tape, Soquelec,



Figure 1. Typical XRD spectra for Pt, PtRu 70:30 atom %, and PtRu 54:46 atom % powders. An approximate amount of Si powder was homogeneously mixed into the powders as an internal standard. The XRD spectra were collected using a step size of 0.06° and an accusation time of 20 s. The spectra were collected between 20's of 20 and 120°; however, a zoomed-in window of 25-85° is shown in Fig. 1.

Montreal) for the XPS analyses. For each catalyst, a survey spectrum was collected before high-resolution spectra of the C 1s, O 1s, Pt 4f, Ru 3p, and Ru 3d core level regions were collected. Deconvolutions of the XPS spectra were performed using a CasaXPS version 2.1.34 (Neal Fairley). A Shimadzu UV-1201 S UV-visible spectrophotometer was also used.

CO adsorbed (CO_{ads}) stripping voltammetry.—CO was adsorbed onto the Pt-based powder electrodes at 0.15 V by bubbling CO gas (Matheson purity, Matheson gas) through the 0.5 M H₂SO₄ solution for 20 min. Solution CO was subsequently removed by argon gas bubbling (air products) for 40 min, maintaining the potential at 0.15 V. The potential was then cycled at 10 mV s⁻¹ starting at 0.15 V for two complete oxidation/reduction cycles.

Solutions.—All CH₃OH oxidation studies were carried out using 0.5 M CH₃OH + 0.5 M H₂SO₄ solutions. Prior to the electrochemical studies, the solutions were deoxygenated using high-purity argon gas. A.C.S. grade chemicals and high resistivity 18 M Ω water were used.

Results and Discussion

Characterization of the catalyst powders XRD characterization.-XRD spectra were obtained for the as-prepared catalyst powders as well as for the catalyst powders mixed homogeneously with Si powder that served as internal standard. Figure 1 shows typical XRD spectra for Pt, PtRu 70:30 atom %, and PtRu 54:56 atom % catalyst powders that were homogeneously mixed with Si. The main peak of the hexagonal Si is clearly seen at 28.44(29)°.11 The peak position for Pt is seen to shift to more positive 2θ values with increasing Ru content. This indicates a decrease in the lattice parameter of the face centered (fcc) Pt lattice, and hence, an incorporation of Ru into the Pt lattice. Diffraction peaks for Ru, such as Ru metal or RuO₂ phases, were not recognizable in the raw XRD spectra. Figure 2 shows the dependence of the lattice parameter for fcc Pt (a_{Pt}) determined using the Topas 2 program as a function of the nominal atom % of Ru. Microstrain was taken into consideration and the entire XRD spectra were used for the data-fitting procedure. Particle size and microstrain values estimated using the Topas software program are shown in Table II. Figure 2 shows that the lattice parameter values obtained from the raw XRD data for the catalyst powders prepared in this work decrease in a linear manner as the atom % of Ru increases, in agreement with Vegard's law.¹² Lattice parameter values reported for bulk PtRu alloys⁷ and values obtained



Figure 2. Pt lattice parameter (a_{Pl}) dependence on the nominal atom % of Ru for fcc Pt. (\blacklozenge) The data obtained from fitting the experimental XRD spectra for the Pt-based powders prepared in this work. A Si standard was homogeneously dispersed between the powders for the analysis, and the entire slow-scan spectra (20 between 20 and 120°) were used to calculate the lattice parameter values using the Topas software program. The vertical lines represent the errors of the lattice parameter in the *y* direction, while the bars are only used to better locate the error lines. The solid line represents the lattice parameter dependence obtained from *ab initio* calculations, ¹³ while the crosses represent the same, but for previously reported data obtained from experimental XRD spectra for bulk PtRu alloys.⁷

from ab initio calculations¹³ are also shown in Fig. 2. Ab initio cell and structure optimizations were performed with VASP¹³ on the known structure of Pt as well as on hypothetical cubic models for the stoichiometric compositions Pt107Ru, Pt31Ru, Pt26Ru, Pt15Ru, Pt₇Ru, Pt₃Ru, and PtRu with resulting symmetries Fm3m, Im3m, or Pm3m. The cell edge for a hypothetical Fm3m model of Ru was also optimized. Results of the *ab initio* computed cell edge (a_{Pt}) vs. the atom % Ru content are seen (Fig. 2) to plot on a straight line with a slope of -0.000133 nm, indicating that these cubic PtRu alloys have a cell edge which follows Vegard's law. We did not attempt to establish the maximum Ru content of such alloys, but this limit is experimentally known to be about 80 atom %. Hard-sphere considerations based on experimental cell volumes for fcc Pt and hexagonal close packed (hcp) Ru, and assuming a Vegard law type of behavior of a_{Pt} vs. the atom % of Ru, actually give a slope of -0.000137 nm, a result which is in excellent agreement with the quantum results. Ab initio calculations for Pt-Ru systems have been

Table II.	Parameters	derived	from	raw	XRD	data ^a	for	the	as-
prepared	Pt-based cat	alysts.							

Nominal Pt:Ru ratio (atom %)	Particle size (nm)	Microstrain (%)
100:0	27.5 ± 3.4	1.1 ± 0.063
91:9	13 ± 1.2	2.6 ± 0.15
85:15	13.4 ± 1.4	1.7 ± 0.17
80:20	12.2 ± 1.2	1.1 ± 0.063
75:25	11.2 ± 1.5	1.8 ± 0.08
70:30	11.6 ± 1.7	2.6 ± 0.26
65:35	5.4 ± 0.7	2.7 ± 0.5
60:40	7.9 ± 0.6	2.5 ± 0.5
54:46	4.6 ± 2.1	2.5 ± 0.5

 a Complete slow-scan XRD spectra collected between 20s of 20 and 75° were used for the data fitting.

carried out previously, focusing on the CO and -OH adsorption on Pt and Ru sites,¹⁴ as well as calculating the lattice parameters as a function of the Ru content for PtRu alloys.¹⁵

It is seen that the lattice parameter values for the powders prepared in this work are close to the bulk alloy and ab initio calculation data. This indicates that the Ru content of the alloy is similar to the nominal content for the catalysts prepared in this work. The fitting of the XRD data of the higher Ru atomic composition (>35 atom %) required the addition of a hexagonal Ru phase. The Ru amount in this phase was, however, very small compared to the alloy, thus suggesting that the majority of the Ru is incorporated into the fcc Pt lattice. Particle sizes estimated from the raw XRD data suggests particle sizes of less than 25 nm (Table II). The particle size is seen to decrease with increasing Ru content, consistent with previously reported results.¹⁶ It is clear, however, that these unsupported and unstabilized catalyst powders consist of larger, agglomerated particles of ca. 150-200 nm size, as indicated by transmission electron microscopy (TEM) measurements. Microstrain analyses suggest stress to be considerable (in the percentage range) for all powders. This is expected for these rapidly synthesized powders.

XPS characterization.-The Pt-based powders were analyzed by XPS to obtain the Pt to Ru atomic ratios as well as to identify the oxidation states of the Pt and Ru surface components. The Pt:Ru atomic ratios determined from the Pt 4f and Ru 3p spectra are shown in Table I. The less intensive Ru 3p region was used instead of the main Ru 3d region. The latter overlays with the C 1s peak, thus complicating the deconvolution and interpretation of the Ru 3d spectra. It is seen that for all catalyst powders, the surface atomic ratio is close to the nominal value, thus suggesting that the surface and bulk concentrations of these catalysts are essentially the same. Figures 3a and b show deconvoluted XPS spectra for the Pt 4f and Ru 3p region, respectively, for the PtRu 54:46 atom % catalyst. The position of the C 1s peak, i.e., 284.6 eV, was used to correct the XPS spectra for charging effects that were in the range of ± 0.1 eV. The deconvolution of the Pt spectra indicates that a significant fraction (54%) of the Pt is present as Pt metal, indicated by Pt $4f_{7/2}$ and $5f_{5/2}$ peaks at 71.4 and 74.7 eV, respectively, and full widths at half maximum (fwhm) of 1.05 eV of each peak.¹⁷ 39% of the Pt is suggested to be present as PtO, indicated by Pt $4f_{7/2}$ and $5f_{5/2}$ peaks at 72.1 and 75.4 eV, respectively, and fwhm of 2.1 eV.¹⁷ A small fraction (*ca.* 6%) of the Pt is suggested to be present as Pt chlorides, indicated by the Pt $4f_{7/2}$ and $5f_{5/2}$ peaks at 75 and 78.3 eV, respectively, and fwhm of 2.3 eV. 18 The presence of a small amount of Cl $^-$ (that is introduced into the catalyst systems by use of chloride-based precursor salts) was confirmed in the XPS survey spectra. The deconvolution of the Ru 3p spectra suggest 70% of the Ru to be present as Ru metal (Ru $3p_{1/2}$ and $3p_{3/2}$ peaks at 462 and 484 eV, respectively, fwhm of 2.6 eV^{18,19}) and 30% of the Ru between the metallic and +IV state, *i.e.*, as lower, reducible Ru oxides (Ru $3p_{1/2}$ and $3p_{3/2}$) peaks at 464.1 and 486.1 eV, respectively, fwhm of $3.5 \text{ eV}^{18,19}$). It is noteworthy that the XPS spectra shown in Fig. 4a and b are qualitatively representative for the PtRu powders of Pt:Ru atom % ratio of 91:9 to 65:35 atom %, i.e., the catalyst particle surfaces are suggested to mainly consist of Pt and Ru metals as well as lower, reducible oxides. Similarly, the XPS data for the Ru powder showed the surface to consist of mainly Ru metal and lower Ru oxides.

 CO_{ads} stripping voltammetry.—CO_{ads} stripping voltammetry is a technique that can be used to obtain *in situ* information of catalyst surfaces under electrochemical conditions.^{7,20} CO adsorbs on metallic Pt sites at sufficiently negative potentials and the adsorbed CO (*ca.* 0.8-1 monolayer) can be anodically stripped from the Pt surface to form CO₂.⁷ In the case of Pt-only catalysts, the CO_{ads} stripping charge (Q_{COads}) can be used to obtain the electroactive Pt surface area.^{7,21} For example, a charge-to-Pt area conversion factor of 420 μ C cm⁻² is used for the case of the adsorption of one CO molecule per Pt surface site. Figure 4a shows a CO_{ads} stripping voltammogram for a Pt powder catalyst electrode. The current axis is normal-



Figure 3. XPS spectra for the as-prepared PtRu alloy catalyst of Pt:Ru ratio of 54:46 atom %: (a) the spectra for the Pt 4f core region and (b) the Ru 3p core region, (\Box) the experimental data, (\longrightarrow) convoluted peaks, and (\longrightarrow) the sum of the deconvoluted peaks.

ized by the Q_{COads} value determined for this particular electrode. The first cycle (thick line) represents the CO stripping curve, while the second cycle (thin line) is equivalent to the background CV for this catalyst in 0.5 M H₂SO₄. For polycrystalline Pt, typical hydrogen adsorption/desorption peaks are observed in the background cyclic voltammetry (CV). The experimentally observed Q_{COads} values were found to be 80% of two times the H desorption charge ($Q_{\rm Hdes}$) for Pt powder electrodes. This suggests that under the conditions used in this work 0.8 of a CO monolayer is adsorbed on the Pt surface sites, i.e., the correct $Q_{\rm COads}$ to Pt surface area conversion factor is 336 μ C cm⁻² (=0.8 × 420 μ C cm⁻²). The conversion of the Q_{COads} values to Pt surface areas in the presence of Ru is more complicated unless the number of CO molecules that adsorb per Ru and Pt sites is known. In recent work in our laboratory,²¹ it has been shown that activation-controlled (COOH)₂ oxidation currents can be used to obtain electroactive Pt areas even for multicomponent catalysts such as PtRu powders. It has also been shown that the combination of the (COOH)₂ technique and CO_{ads} stripping voltammetry can be used to estimate the number of CO molecules that adsorb on Ru and Pt sites. 21 The $Q_{\rm COads}$ value and the Pt surface area (A_{Pt}) estimated using the (COOH)₂ oxidation currents are related using an experimentally determined conversion factor (f_{APt}) , as follows

$$A_{\rm Pt} = \frac{Q_{\rm COads}}{420\mu \rm Ccm^{-2}} * f_{\rm APt}$$
[5]

As discussed in previous work, the value of the $f_{\rm APt}$ factor depends on the catalyst powder; it is unity for Pt-only powders and less than unity if CO adsorbs on other, *e.g.*, Ru, catalyst sites.²¹ In the case of PtRu alloys, the same ratio of CO molecules per Pt and Ru sites are suggested to adsorb, and the experimentally determined $f_{\rm APt}$ factor is equivalent to the atomic fraction of Pt surface sites. For example, for a Pt:Ru surface ratio of 70:30 atom %, the $f_{\rm APt}$ factor is 0.85; for a Pt:Ru surface ratio of 70:30 atom %, the $f_{\rm APt}$ factor is 0.7,²¹ etc. These $f_{\rm APt}$ factors and Eq. 5 will be used in this work to obtain the real catalytic activities for the PtRu catalysts toward the CH₃OH oxidation reaction, *i.e.*, to obtain CH₃OH oxidation currents per Pt surface area.

Fig. 4a-d shows typical CO_{ads} stripping voltamograms for Pt powder and PtRu powders of 70:30 and 54:46 atom % composition, respectively. The current scales in these CVs are normalized using the corresponding, experimental Q_{COads} values to better compare the data. As discussed in previous work,²¹ the CO_{ads} oxidation potential can be linked to the PtRu surface concentration for the case of alloys. With an increase in atomic Ru content (up to ca. 46%), the CO_{ads} stripping potential is shifted to more negative values in the same manner as also seen in our data. The CO_{ads} stripping voltammograms observed in this work also show that they can be used to gain some insight into the PtRu alloy catalyst surface within a certain error range mainly due to variations in the potential measurements $(\pm 10 \text{ mV})$]. The shape and characteristics of the entire CO_{ads} voltammograms observed in this work for a catalyst powder of a particular composition are in good agreement with literature data for bulk alloys of the corresponding Pt:Ru surface ratio.^{7,20} Therefore, the CO_{ads} stripping data suggest that the surface composition of these catalyst powders prepared in this work are the same as the bulk and nominal composition, as also suggested by the XRD and XPS results. Furthermore, the good agreement between the CO_{ads} stripping characteristics of the powder and bulk alloys validates the use of these powders to obtain mechanistic CH₃OH oxidation information. It is also seen that for the Ru powder (e.g., Fig. 4b Ru powder), very positive potentials are required to strip the adsorbed CO completely from the catalyst surface and the CO_{ads} stripping peaks become broad.

In this work, CO_{ads} stripping voltammograms were also recorded for the catalysts before and after CH_3OH oxidation studies. The CO_{ads} stripping voltamograms were used to calculate Pt surface areas and to ensure that the catalyst surfaces are not altered as a result of the CH_3OH oxidation experiments.

Catalyst preparation parameters and resulting catalyst properties.—Influence of the NaBH₄ addition rate on the degree of PtRu alloy formation.—In this work, the rapid addition of high concentrations of NaBH₄ solutions to the Pt and Ru precursor solutions was found essential to incorporate the Ru into the Pt fcc lattice. The influence of the rate and amount of NaBH₄ addition is more pronounced for the synthesis of the catalyst powders made of higher Ru (>30 atom %) ratio. The influence of the NaBH₄ addition rate is

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Figure 4. CO_{ads} stripping voltammograms recorded at 10 mV s⁻¹ in 0.5 M H₂SO₄ solutions for (a) Pt powder, (b) Ru powder, (c) PtRu 70:30 atom % alloy, and (d) PtRu 54:46 atom % alloy. (—) The first oxidation cycle, *i.e.*, the anodic stripping of the CO_{ads} , and (—) the second complete oxidation/reduction cycle, which is equivalent to the background CV of the catalyst powder electrode in 0.5 M H₂SO₄.

discussed in this section using Pt:Ru precursor ratios of 54:46 atom %. The slow addition of NaBH₄ (*i.e.*, the dropwise addition of 75 mL of 0.2 M NaBH₄ over a period of 30 min) was found to not entirely reduce the Ru(+III)-chloride precursor salt, while UV-visible (UV-vis) spectroscopy did not show detectable amounts of dissolved Pt. These differences can be assigned to different reduction rates of the Ru and Pt precursor salts, *i.e.*, to a faster reduction rate of PtCl₄ than RuCl₃.

Values of a_{Pt} estimated using raw XRD data recorded for powders 1 (slow addition rate, 30 min for the addition of 75 mL of 0.2 M NaBH₄) and 2 (more rapid addition rate, 5 min for the addition of 75 mL of 0.2 M NaBH₄) showed that PtRu alloys of less than 46 atom % Ru were formed. $a_{\rm Pt}$ values of 0.387192 \pm 3 \times 10⁻⁵ and 0.387102 \pm 8 \times 10^{-5} nm and corresponding Pt:Ru alloy ratios of ca. 62:38 and 61:39 atom % for powders 1 and 2, respectively, were estimated. These a_{Pt} values also suggest lower Pt:Ru alloy ratios than for the rapidly synthesized powder 3. XPS analyses were also carried out for these PtRu catalyst powders of nominal 54:46 atom % ratio. The XPS data suggest Pt:Ru atom % ratios of 12:88 for powder 1, 28:72 for powder 2, and 55:45 for powder 3 (rapid addition rate and increased NaBH4 amount, less than 1 min for the addition of 75 mL of 0.4 M NaBH₄). These data indicate that Ru is preferentially located on the catalyst surface for the powders prepared using a smaller amount and slower addition rate of the NaBH₄ reducing agent, and hence, the catalyst particle composition (surface



Figure 5. Typical XRD spectra for PtRu 54:46 atom % catalyst powders subjected to heat-treatments for 1 h in an air oven at (a) 600, (b) 450, (c) 350, (d) 250, and (e) 100°C. The spectra are corrected using the position of the internal Si powder standard at 28.44°. The XRD spectra were collected using a step size of 0.06° and 40 s accusation time. The spectra were collected between 20's of 20 and 60°; however, a zoomed-in window of 30-45° is shown in Fig. 5.



Figure 6. Dependence of the lattice parameter of (+) fcc Pt on the temperature used to treat a 54:46 atom % PtRu powder catalyst in air for 1 h. (\bigcirc) The dependence of atom % Ru in the fcc Pt phase on the temperature. The atom % Ru values were calculated using the lattice parameter values and the theoretical Vegard's law relationship shown in Fig. 2.

vs. bulk) of the "more slowly" synthesized PtRu powders 1 and 2 is not uniform. XPS analysis for powders of nonuniform conditions such as powders 1 and 2 likely yields only an estimate of the Pt:Ru surface ratio.

Heat-treatment of the prepared catalyst powders.—In this work, care was taken to avoid the exposure of the PtRu catalysts to high temperatures. Treatment at high temperatures of PtRu alloys typically results in Pt segregation on the catalyst surface.²² In this section, the influence of heat-treatment on the prepared catalyst powders is discussed to ensure that suitable catalyst preparation conditions are used. PtRu alloy catalysts of 54:46 atom % composition were heated in air for 1 h at either (a) 600, (b) 450, (c) 350, (d) 250, or (e) 100°C. Figure 5 shows an enlarged region of the XRD spectra recorded for the heat-treated catalyst powders. The XRD spectra clearly indicate the formation of a RuO₂ phase for the catalysts treated at 600°C. The Pt(111) peak is seen to become narrower with increasing temperature, indicating (an expected) increase



Figure 7. CO_{ads} stripping voltammograms for PtRu 54:46 atom % catalyst powders subjected to different heat-treatments. The first anodic cycle (after CO adsorption at 0.15 V) is shown. The CVs were recorded at 10 mV s⁻¹ in 0.5 M H₂SO₄ solutions. (——) The CO_{ads} stripping voltammogram for the catalyst powder heated at 100°C, (—) the same for the catalyst powder heated at 250°C, and (—) the stripping voltammogram for the catalyst powder heated at 600°C. The currents were normalized by the CO_{ads} charge to better compare the data.

in catalyst particle size. This was confirmed from particle size calculations for the full XRD spectra using the Topas software. The 20 position of the Pt(111) peak is seen to shift to smaller values, indicating that the amount of Ru in the fcc Pt lattice is smaller, *i.e.*, the Pt:Ru alloy ratio decreases with increasing temperature. This is reflected more quantitatively in the lattice parameter values estimated for the full spectra shown in Fig. 6. Figure 6 also shows the dependence of the atom % of Ru in the fcc Pt phase, calculated from the $a_{\rm Pt}$ lattice parameter and using the theoretical Vegard's law relationship shown in Fig. 2, showing a clear depletion of Ru in the PtRu alloy with increasing temperature. Best fits of the XRD spectra for the powders heat-treated at 350°C and higher temperatures were only obtained using Pt, Ru, and RuO₂ phases.

Changes in the surface properties of the PtRu catalyst induced



Figure 8. CVs (5th cycle) in 0.5 M CH₃OH + 0.5 M H_2SO_4 recorded at 10 mV s⁻¹ between 0.09 and 0.8 V for Pt powder, PtRu alloy (54:46 atom %), and 1 day old Ru powder. The background CV for the Ru powder electrode recorded in the 0.5 M H_2SO_4 (CH₃OH-free) solution is also shown. (a, left) The CVs recorded at 20°C, and (b, right) the CVs recorded at 60°C. The current scales were normalized for the Pt + Ru area.



Figure 9. Arrhenius plots, *i.e.*, $\ln j vs. 1000/T$ graphs for the CH₃OH oxidation reaction using PtRu alloys of (\Box) 70:30 atom %, (\triangle) 54:46 atom %, and (\diamond) 1 day old Ru powder. The current density data were extracted at 0.68 V *vs.* RHE from slow-sweep CV data (see Fig. 8).

by the heat-treatment were also observed by CO_{ads} voltammetry. Figure 7 shows the CO_{ads} stripping voltammograms (normalized for the corresponding $\mathrm{CO}_{\mathrm{ads}}$ charge values) for the PtRu 54:46 atom % catalysts heated at 100, 250, and 600°C. The $\rm CO_{ads}$ stripping voltammograms for the catalysts heated at 100°C is essentially the same as for the same catalysts but dried at 80°C (Fig. 4c), as well as room temperature, indicating that the catalyst surface is not affected by the 100°C heat-treatment. However, differences in the CO_{ads} stripping voltammograms are seen for the catalyst powders heated at 250 and 600°C. Both the $\mathrm{CO}_{\mathrm{ads}}$ oxidation peak and oxidation onset potential are shifted more positive with increasing temperature. This indicates that the catalyst surface properties are altered by the heattreatment, resulting in conditions that are less favorable for the CO_{ads} oxidation reaction. It is most likely that the Pt: Ru site distribution of the heat-treated catalysts (250°C and higher) is less random than for the 100°C and lower temperature-treated catalysts, as suggested by the XRD data that show a decrease in the amount of Ru dissolved in the Pt fcc lattice with increasing temperature.

Activation enthalpies and CH₃OH oxidation activities: PtRu alloys vs. Ru powder electrodes.-In this section the CH₃OH oxidation activities as a function of temperature for the PtRu alloys (of 54:46 and 70:30 atom %) and the freshly synthesized Ru metal powder electrodes were obtained using cyclic voltammetry (CV). Figures 8a and b show typical CVs for the CH₃OH oxidation reaction for Pt powder, PtRu alloys 54:46 atom %, and Ru powder catalyst electrodes. In all cases, five cycles were sufficient to reach current density-voltage (i-V) characteristics that were independent of subsequent potential cycling. Therefore, the 5th CV cycles are shown in Fig. 8a and b. All currents were normalized for the Pt + Ru surface area estimated using CO_{ads} stripping voltammetry, as discussed previously. Figure 8a shows the CH₃OH oxidation characteristics for 20°C, while Fig. 8b shows the situation for 60°C. A background CV for the Ru powder catalyst in 0.5 M H₂SO₄ is also shown in the two figures for comparison. It is seen that the freshly prepared Ru powder shows a recognizable activity toward the CH₃OH oxidation reaction at both 20 and 60°C. However, its activity is clearly smaller than for the PtRu 54:46 atom % alloy powder. The activity of the Ru powder toward the oxidation of CH₃OH appears high when compared to literature data.³ However, a freshly synthesized (1 day old) Ru catalyst powder was used for the CV data shown in Fig. 8a and b. The activity of the Ru powder toward CH₃OH oxidation reaction was observed to decrease with time, e.g., a 2 week old powder exhibited only ca. 20% of CH₃OH oxidation activity of the 1 day old powder, while a 6 month old Ru powder showed no activity for the CO_{ads} and CH₃OH oxidation reactions. This decay in activity may be due to the oxidation of the Ru surface in air. The mechanism and final product(s) of the CH₃OH oxidation using Ru is not known and may be different than for the Pt and PtRu alloy electrodes.

Figure 9 shows Arrhenius plots, *i.e.*, plots of the logarithm of the CH₃OH current density $[\ln(j)]$ *vs.* the inverse of the temperature (1/T) for two PtRu alloys, *i.e.*, 54:46 (Δ) and 70:30 (\Box) atom %, as well as for 1 day old Ru powders (\diamond). The CH₃OH current density values were extracted from steady-state (5th) CV data at 0.68 V, *i.e.*, from CV data as shown in Fig. 8a and b. The experimentally observed CH₃OH oxidation current is seen to increase with increasing temperature, as expected.³ For all tested temperature and potential ranges, the PtRu 70:30 atom % alloy catalyst shows the highest CH₃OH oxidation activity, *i.e.*, higher than the PtRu 54:46 atom %



Figure 10. CH₃OH oxidation activity dependence on atom % Ru at (a, left) 0.3 and (b, right) 0.4 V vs. RHE. (\times) The current density values obtained from i-t transients after 5 min in 0.5 M CH₃OH and 0.5 M H₂SO₄ at 20°C. The current values are normalized by the Pt + Ru surface area, as described in the text. (\blacksquare) The theoretical current density values per Pt + Ru surface area calculated assuming that CH₃OH to CO₂ oxidation requires three Pt and one adjunct Ru sites, as discussed in the text and using Eq. 8.

alloy and the Ru powder. These data suggest that the optimal Pt:Ru ratio for the CH₃OH oxidation reaction is independent of temperature (between 20 and 60°C), consistent with Kabbabi *et al.*'s conclusions⁴ and the raw data in Gasteiger *et al.*'s work.³ Activation enthalpy values ($\Delta \bar{H}^{o\#}$) were also extracted from the slope of these Arrhenius plots at a particular potential (*E*) employing Eq. 6²³

$$slope = \left(\frac{\partial \ln j}{\partial \frac{1}{T}}\right)_{E} = \frac{-\Delta \bar{H}^{o\#}}{R}$$
[6]

(Note that in the case of measurements in aqueous solutions, the terms activation enthalpy and energy can be used interchangeably.²³ In Eq. 6, T is temperature and \vec{R} the gas constant (8.314 J K⁻¹ mol^{-1} ²⁴). In this work, activation enthalpy values of 30, 33, and $28 \pm 5 \text{ kJ mol}^{-1}$ were obtained at 0.68 V for the 54:46 atom % alloy, the 70:30 atom % alloy, and the Ru powders, respectively. The activation enthalpy values for the two PtRu alloys are lower than previously reported for similar catalysts that were estimated, however, at lower overpotentials.³ In fact, activation enthalpies similar to literature values of *ca*. 60 kJ mol⁻¹ were estimated in this work for the 70:30 and 54:46 atom % PtRu alloys at 0.5 V. The CH₃OH oxidation activity for the Ru powder was too small at lower potentials to allow the extraction of the activation enthalpy value. The activation enthalpy values estimated at 0.68 V are similar for the three powders. These data suggest that the activity for the CH₃OH oxidation reaction of the Ru does not increase more strongly with

the cathodic current was found to result in the complete recovery of the catalyst activity for the CH₃OH oxidation reaction.

Figures 10a and b shows the CH₃OH oxidation activities at 20°C as a function of the atom % of Ru at 0.3 and 0.4 V, respectively. The crosses show the experimentally observed CH₃OH oxidation currents divided by the Pt + Ru surface area, while the squares show theoretical curves obtained as described below. The experimental CH₃OH current density values for the 65:35 and 54:46 atom % alloy are similar to previously reported values for bulk metal alloys of similar composition and comparable experimental conditions.³ This agreement shows that these unsupported catalyst powders can be used for fundamental and reaction mechanistic studies. It is seen that for both potentials the 70:30 atom % composition yields the highest CH₃OH oxidation activity. The 70:30 atom % maximum and the shape of the curves can possibly be explained by considering a simple statistical model that views the alloys as fcc lattice made up of randomly distributed Pt and Ru sites. The CH₃OH oxidation reaction is assumed to involve three neighboring Pt sites and one Ru site, while all other sites are assumed not to be notably involved in the CH₃OH oxidation reaction. Electrostatic interactions between adsorbed CH₃OH molecules that may lead to a decrease in CH₃OH adsorption and possible alloying effects such as electronic influences of Ru on the Pt sites are ignored in this model. Using this simple model the number of catalyst sites involved in the CH₃OH oxidation reaction per total surface sites, *i.e.*, the theoretical catalyst site utilization percentage (csu %) can be calculated as a function of the Pt:Ru atom % ratio. The csu % is defined as follows

$$csu \% = \frac{no. of catalyst sites actively utilized in the CH3 OH oxidation reaction no. of total catalyst surface sites$$

increasing temperature than for the PtRu alloy electrodes. A significant contribution of Ru sites toward the CH_3OH dehydrogenation and oxidation reaction in PtRu alloys appears further questionable, as current density values for Ru are clearly lower than for PtRu alloys even at elevated temperatures. It should also be noted that contrary to the case of the Pt and the PtRu alloys, the relationship between the number of CO molecules that adsorb on Ru-only powders and its real Ru surface area is not known and the true Ru surface area may actually be higher. This would result in smaller CH_3OH oxidation current density values on the Ru-only powders than reported here.

CH₃OH oxidation currents as a function of Pt:Ru atomic concentration.-In this section, the influence of the Pt:Ru atomic ratio on the CH₃OH oxidation activity is investigated using a wide range of catalyst compositions. CH₃OH oxidation activities were estimated from current-time (i-t) transients recorded at 0.3 and 0.4 V after 5 min, i.e., when pseudo-steady-state conditions were achieved. The amount of catalyst powders used for the measurements was adjusted depending on the potential range and the PtRu ratio studied. Pt + Ru areas of 2-100 cm^2 were generally used for measurements at 0.3 V, while Pt + Ru areas of less than 10 cm² were used for the measurements at 0.4 V. The use of the higher surface area electrodes at the lower potential allowed for sufficiently high current measurements to achieve good quality data, while use of the lower surface area electrodes at more positive potentials avoided the production of large amounts of H2 at the counter electrode. The latter is particularly important as an undivided cell is used in this work. Between the recordings of the individual i-t transients, a cathodic current of 5×10^{-5} A was applied until the monitored electrode potential reached a value of 0.025 V. The application of

In Eq. 7, Pt + Ru, Pt, and Ru sites are used to calculate Pt + Ru, Pt, and Ru csu % numbers, respectively, shown in Table III as a function of the PtRu alloy composition. It is seen that the 70:30 atom % alloy yields the maximum utilization of Pt + Ru catalyst sites (of 92%) consistent with the experimental data. The Pt + Ru csu % numbers shown in Table III were further used to calculate theoretical CH₃OH oxidation currents ($J_{CH_3OH(theoretical)}$) as a function of the Pt:Ru atom % to better compare the catalyst site utilization and the experimental CH₃OH oxidation data, as shown in Eq. 8

[7]

Table III.	Theoretical	catalyst	utilization	percentage	(csu %)
numbers a	s a function	of the Pt	Ru atomic	ratio ^a	

atom % Ru	$Pt + Ru csu \%^b$	Pt csu % ^c	Ru csu % ^d
9	43	43	100
15	56	56	100
20	78	78	100
25	83	83	83
30	92	94	82
35	84	86	83
40	70	83	50
45	57	79	30

^a csu % numbers are calculated assuming that an assembly of 3 Pt and 1 adjunct Ru site are the prerequisite for the CH_3OH to CO_2 oxidation reaction, as discussed in the text.

^b Pt + Ru csu % is the percentage of Pt + Ru sites utilized per total Pt + Ru surface sites.

^c Pt csu % is the percentage of Pt sites utilized per Pt surface sites.

^d Ru csu % is the percentage of Ru sites utilized per Ru surface sites.

Table IV. Average CH ₃ OH	oxidation current densities at 20 and
60°C estimated at 0.4 V vs.	RHE. ^a

Pt:Ru ratio atom %	$J_{\rm CH_3OH}$ at 20°C (A cm ⁻²) ^b	J_{CH_3OH} at 60°C (A cm ⁻²) ^b	Ratio: $\frac{J_{\rm CH_3OH} (60^{\circ}{\rm C})}{J_{\rm CH_3OH} (20^{\circ}{\rm C})}$
70:30	6.4×10^{-6}	5.8×10^{-5}	9
54:46	3×10^{-6}	2.6×10^{-5}	8.7

^a The CH₃OH activities are estimated from pseudo-steady state i-t transients recorded in $0.5 \text{ M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$ solution, as described in the text;

^b Current density values are normalized for total Pt + Ru surface area.

$$J_{\rm CH_3OH(theoretical)} = \frac{J_{\rm CH_3OH(exp.70.30 atom \%)}}{92\%} * Pt + Ru \ csu \%$$
[8]

Equation 8 uses the experimental CH₃OH oxidation current for the 70:30 atom % alloy ($J_{CH_3OH(exp.70:30 atom \%)}$), namely, 4 \times 10⁻⁷ and 6.5 \times 10⁻⁶ A per cm⁻² Pt + Ru area, at 0.3 and 0.4 V, respectively, and the theoretical Pt + Ru csu % value of 92% for the 70:30 atom % PtRu alloy to calculate the theoretical CH₃OH current densities shown as squares in Fig. 10a and b. It is seen that the theoretical and experimental CH₃OH oxidation current densities per total Pt + Ru surface area are essentially the same (with a few exceptions that may be due to experimental factors), thus supporting the rather simple model used here. These results also suggest that CH₃OH oxidation current arises mainly from CH₃OH molecules that are adsorbed and oxidized on assemblies consisting of three neighboring Pt and one Ru site, and that one Ru and three Pt sites are involved in the oxidation of a CH₃OH molecule within the potential range studied here. Table III also shows the calculated Pt and Ru csu % numbers, i.e., the percentage of Pt sites utilized per Pt sites on the catalyst surface and the percentage of Ru sites utilized per Ru sites on the catalyst surface, respectively. The data suggest that a significant number of Pt surface sites is not involved in the CH₃OH to CO₂ oxidation reaction for the PtRu alloys of lower Ru composition (<20 atom % Ru), while the Ru sites are entirely utilized. For the PtRu alloys of 30 atom % and higher values, the utilization of both the Pt and Ru sites decreases with increasing Ru content. However, all the theoretical CH₃OH current density and csu % values calculated in this work reflect trends and the true values may be different, as only a simple model has been used that ignores a number of possibly relevant factors, as mentioned previously

Table IV shows CH₃OH oxidation currents obtained at 20 and 60°C for PtRu alloys of 70:30 and 54:46 atom % PtRu alloy powders. It is seen that the CH₃OH oxidation activity is higher for the 70:30 atom % than for the 54:46 atom % alloy independent of temperature. In fact, the CH₃OH oxidation current increases for both catalysts by a factor of *ca*. 9 with an increase in temperature from 20 to 60°C. This increase is consistent with literature data³ and the activation enthalpy values reported in this work.

Conclusions

A wide range of PtRu powders of Pt:Ru ratio up to 54:46 atom % have been synthesized using a simple chemical reduction method involving low temperatures. Pt and Ru powder catalysts were also synthesized using the same method. Lattice parameter estimation for the fcc Pt shows a linear decrease in the lattice parameter value with increasing Ru content. This is in agreement with Vegard's law and indicates the formation of PtRu alloys. The relationship of the fcc Pt lattice parameter on the nominal atom % of Ru was found to be essentially the same as predicted by *ab initio* calculations¹³ and previously reported data for bulk PtRu alloys.³ XPS studies

suggest the Pt:Ru surface ratio to be the same as the nominal Pt:Ru ratio, thus suggesting that PtRu particles of uniform compositions were formed. Furthermore, in situ electrochemical CO_{ads} stripping voltammograms recorded for the various Pt, Ru, and PtRu alloy powders were consistent with previously reported voltammograms for bulk PtRu alloys of corresponding Pt:Ru surface ratio, indicating that catalyst powders of similar nominal, bulk, and surface ratios were made. XPS data also suggest the Pt and Ru surface components to mainly consist of Pt and Ru metal as well as lower, reducible Pt and Ru oxides. It is noteworthy that chemical reduction route synthesis provides a simple and less expensive method for the preparation of PtRu catalysts as compared to arc-melting and chemical vapor deposition techniques. Furthermore, the method described in this work allows the preparation of catalyst powders at low temperatures, thus minimizing undesirable segregation of Pt on the catalyst surface. Many powders of a wide range of Pt:Ru atomic ratios can be easily prepared at "low" cost and used for detailed studies. Also, catalyst powder electrodes of variable surface areas can be prepared, thus allowing the study of the CH₃OH oxidation activity over a broad potential range, and most importantly, including lower potential ranges that are of interest to real fuel-cell applications.

Activation enthalpy values for the CH₃OH oxidation reaction were extracted for PtRu alloys and Ru powder electrodes over a temperature range of 20-60°C. It was found that freshly prepared Ru powders also exhibit an activity for the CH₃OH oxidation reaction even at low temperatures such as 20°C. However, the CH₃OH oxidation activity for the Ru powder is clearly smaller than for PtRu alloys and decays with the age of the Ru powder, eventually becoming completely inactive. The activation enthalpy values extracted at 0.68 V were essentially the same for the Ru and the PtRu alloy powders. This indicates that the optimal PtRu alloy composition for the CH₃OH oxidation does not change with temperature. This conclusion is further supported by CH₃OH oxidation activities obtained from current-time transients at 20 and 60°C for PtRu alloys of 70:30 and 54:46 atom % ratio and is consistent with actual raw data reported in the literature.³

CH₃OH oxidation activities were also obtained as a function of Ru content for the PtRu alloy powders using many PtRu alloy powders of different Pt:Ru ratios at 0.3 and 0.4 V. For all tested potentials, the 70:30 atom % PtRu alloy was found to yield the highest CH₃OH oxidation activity. Theoretical CH₃OH oxidation activities were calculated as a function of the Pt:Ru ratio using a simple model that assumes that the CH₃OH to CO₂ oxidation reaction requires three Pt sites and one neighboring Ru site. The theoretical and experimental data were found to show the same behavior, thus supporting the model.

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