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Citation for published version (APA):

Frelink, T., Visscher, W., & Veen, van, J. A. R. (1995). On the role of Ru and Sn as promoters of methanol electro-oxidation over Pt. *Surface Science*, 335, 353-360. [https://doi.org/10.1016/0039-6028\(95\)00412-2](https://doi.org/10.1016/0039-6028(95)00412-2)

DOI:

[10.1016/0039-6028\(95\)00412-2](https://doi.org/10.1016/0039-6028(95)00412-2)

Document status and date:

Published: 01/01/1995

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Surface Science 335 (1995) 353–360

surface science

On the role of Ru and Sn as promoters of methanol electro-oxidation over Pt

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Received 12 September 1994; accepted for publication 18 November 1994

Abstract

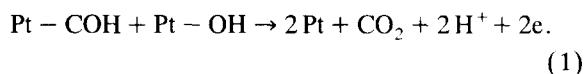
The role of Ru and Sn on the methanol oxidation over Pt was investigated for three different systems viz. Pt covered with adatom layers of Ru and Sn, electro-codeposited Pt–Ru and carbon supported Pt–Ru. By following the oxide growth on the Pt–promoter metal electrodes with ellipsometry it was found that in the presence of methanol the surface oxides of the promoter metal are no longer present on the surface. This supports the bifunctional model of the promoter action. DEMS measurements at Pt with submonolayer coverage of Ru or Sn revealed that the current efficiency of the methanol oxidation to CO₂ is increased in the presence of Ru or Sn and that the onset potential of the oxidation keeps lowering with increasing amounts of the promoting metal. On electrodeposited Pt–Ru systems the adsorption of methanol already takes place at potentials in the hydrogen range. These results seem to point to an electronic (ligand) effect. This is further corroborated by activity measurements at carbon supported Pt–Ru with very small particles, which show a tenfold higher activity compared with the Ru-free system.

It is concluded that the promoting action of Ru and Sn may involve both a bifunctional and an electronic (ligand) effect.

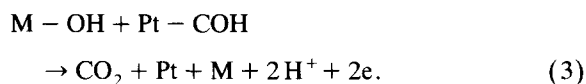
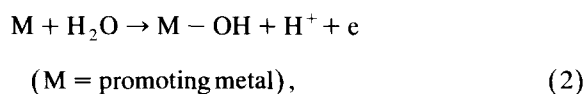
1. Introduction

Although it is quite well known that Sn and Ru can promote the electrochemical oxidation of methanol over Pt electrodes, it is still less well known by what mechanism they actually act. The electro-oxidation of methanol over Pt proceeds via an adsorbed methanolic species, for example Pt–COH [1] or Pt–CO [2] at high methanol concentra-

tions, which is oxidized by an adsorbed oxygenated species or activated water:



At present the most popular view is that the promoters act by supplying the oxygen atom:



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The formation of an oxygenated species on Pt is reputedly difficult, as Pt–OH groups are only formed, in substantial quantities, above ca. +0.7 V versus RHE. The idea is that both Ru and Sn are more easily oxidised than Pt and thus are able to oxidise the methanol adsorbate at a lower potential. The promoters act via a so-called bi-functional mechanism, as was suggested for both Sn [3] and Ru [4]. An alternative explanation however, is that the Pt properties themselves are modified by Sn [5] and Ru [6,7] (the so-called ligand or electronic effect). Such an effect was for example observed in gas-phase adsorption of CO on Sn/Pt(111) [8], where the Pt–CO bond strength was found to weaken in the presence of Sn.

Taking into account that ensembles of Pt surface atoms are required for the adsorption of methanol on Pt [9] and that methanol does not adsorb on Sn or Ru [10], it follows that the promotor atoms should be present in low amounts, although this is not yet the general opinion. The optimal ratio M/Pt is still not definitely established, but it was confirmed by several authors [9,11,12] that a Pt–Ru electrode with a low Ru content (ca. 10%) has the highest activity for the methanol electro-oxidation. This was also found for Sn [5]. The activity of Ru for the methanol adsorption appears to be strongly temperature dependent. In a recent article Gasteiger et al. [13] showed that at 60°C the optimum Ru composition is about 30%.

We have tried to obtain further evidence for either a bifunctional or a ligand effect through ellipsometry, differential electrochemical mass spectroscopy (DEMS) and activity measurements. Three different systems were used for these measurements; (i) smooth Pt with adatom coverage of Sn and Ru, (ii) electro-codeposited Pt–Ru and (iii) carbon supported Pt–Ru systems.

2. Experimental

2.1. Electrode preparation

Platinum electrodes with submonolayer coverage of Sn or Ru were prepared by potential cycling between –0.65 and +0.6 V versus MSE in 0.5M H₂SO₄ containing small (< 1.10^{–3}M) amounts of

SnSO₄ (Aldrich) or Ru(NO)(NO₃)₃ (Johnson and Matthey), respectively.

Electro-codeposited Pt–Ru electrodes were prepared from a solution containing 2.4 × 10^{–3}M H₂PtCl₆ and 1.2 × 10^{–3}M Ru(NO)(NO₃)₃ using different deposition times and currents. The Ru/Pt atom ratio, measured with SEM/EDX, increases with higher deposition current.

Carbon supported Pt–Ru catalysts were prepared by depositing a Pt–Ru colloid on Vulcan XC-72 carbon support. The colloid was prepared via the Turkevich method [14]. The catalyst was mixed with PTFE suspension and the mixture was pressed on a Pt current collector. After drying at 125°C, the electrode was sintered at 325°C for two hours under argon atmosphere. The final Teflon content was 17%.

2.2. Measurements

Ellipsometry experiments were carried out using an automated ellipsometer Rudolph RR 2200 with tungsten iodine light source and monochromatic filter resulting in light with a wavelength of 546.1 nm. The optical cell is cylindrical and supplied with windows arranged for an angle of incidence of 70° at the substrate. The optical measurements were performed during potential scanning at disk electrodes of Pt (area 0.5 cm²) and of Ru (area 0.79 cm²) covered with electrodeposited Pt–Ru. The potential scan was supplied by a Wenking potentiostat POS 73 with Philips PM 8043 recorder. The activity for the methanol oxidation was determined from voltammetry measurements at low sweep rate (2 mV s^{–1}). Combined voltammetric and DEMS experiments were performed at a platinized platinum gauze electrode (specific area 60 cm²) using a computer controlled AutoLab potentiostat (Eco Chemie) suitable for simultaneous recording of current and mass response. The experimental setup of the mass-spectrometer system (Leybold) is similar to that of Vielstich and co-workers [15].

In all electrochemical cells the counter electrode is a Pt foil; the reference electrode is a Hg/Hg₂SO₄ electrode (MSE); *E* = +0.68 V versus RHE. The measurements were performed in 0.5M H₂SO₄. The methanol concentration was either 0.1M or 0.33M. (Merck). All chemicals are p.a. grade. The solutions

were prepared with Ecostat water (18.2M Ω). Argon (99.99%) was used to provide oxygen-free electrolyte.

3. Results and discussion

3.1. Ellipsometry

Fig. 1A shows the change in the ellipsometric parameter Δ during a potential scan at Pt in 0.5M H_2SO_4 . The growth of the oxide layer during the anodic scan and its subsequent reduction during the cathodic scan is observed as a decrease respectively increase of Δ . Upon addition of methanol the curve is virtually the same (cf. dashed line in Fig. 1A) hence no change in the Pt-oxide formation occurs in the presence of methanol.

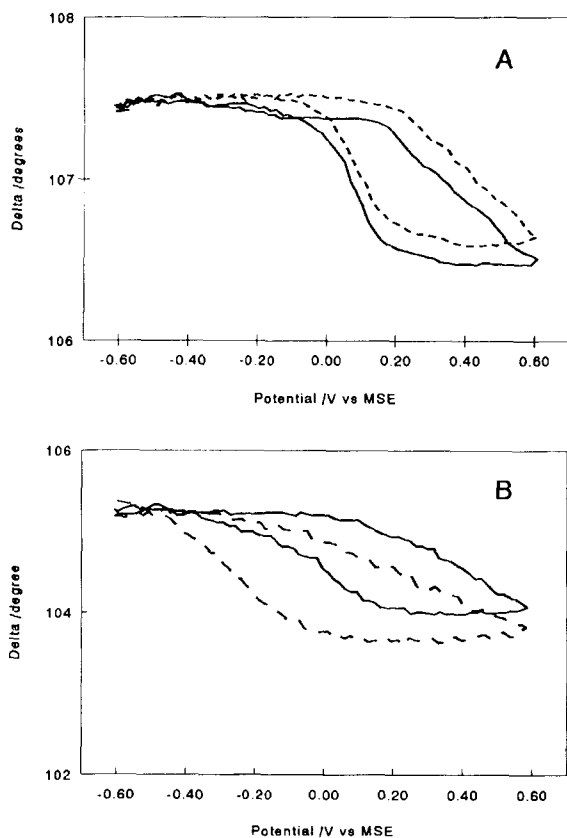


Fig. 1. Ellipsometric $\Delta - E$ curves for Pt (A) and Pt-Ru (B); scan rate 10 mV/s. (—) 0.5M H_2SO_4 ; (---) 0.5M H_2SO_4 / 0.33M CH_3OH .

Fig. 1B (drawn line) gives the optical change observed at an electro-codeposited Pt-Ru electrode (30% Ru, estimated bulk content) in 0.5M H_2SO_4 . Here the change in Δ reflects the oxide film growth on Pt-Ru. It is seen that the surface is oxidised more easily in the presence of Ru (it is known that oxidation of Ru begins at -0.3 V versus MSE [16]) and that the oxide is reduced over a larger potential range compared with Pt. This behaviour is in agreement with the results found for bulk $Pt_{0.5}Ru_{0.5}$ alloy [17]. The optical response alters in the presence of methanol (0.33M) as shown by the dashed curve of Fig. 1B. The curve is shifted to higher Δ values and the total Δ change is smaller. In the anodic scan the decrease of Δ begins at a higher potential; in the cathodic scan the Δ increase begins at higher potential than without methanol. Apparently in the presence of methanol less Ru-oxide film is "seen" on the surface, which implies that it is removed by reaction with methanol. For Pt partially covered with Ru adatoms or with upd Sn we found a similar effect [18]; in both systems the adatom-oxide features diminish or are completely absent. The disappearance of the metal-oxide layer in the presence of methanol supports the bifunctional mechanism in which the promoting metal transfers oxygen to Pt-COH, cf. Eqs. (2) and (3); the rate of reaction (3) is apparently much higher than that of reaction (2).

3.2. DEMS at Pt with submonolayer coverage of Sn and Ru

With DEMS the methanol oxidation was measured on Pt in the presence of different amounts of $SnSO_4$ and $Ru(NO)(NO_3)_3$ in the electrolyte. The results are given in Fig. 2 for the Pt-Ru system. It can be concluded that Ru indeed enhances the CO_2 production in the potential region up to 0 V versus MSE and also that the onset potential for CO_2 production (and thus CH_3OH oxidation) decreases with increasing amount of the promotor metal. For Pt-Sn similar results were obtained. In Table 1 the onset potentials for the Pt-Ru and Pt-Sn systems are summarized, these data were evaluated from the mass-potential curves, as the currents at the onset of the methanol oxidation are extremely small. The lowering of the onset potential is quite remarkable; however this must be distinguished from the overall

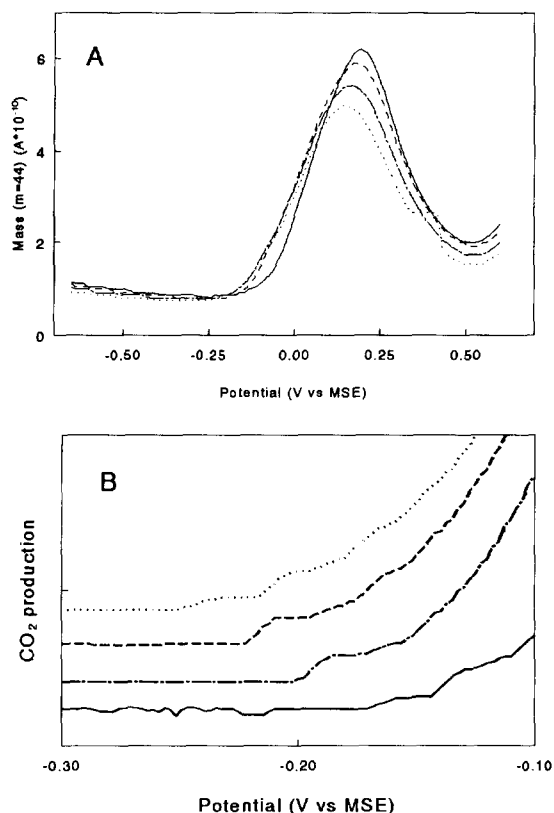


Fig. 2. CO_2 production during methanol oxidation on Pt in 0.5M H_2SO_4 /0.33M CH_3OH in the presence of Ru; scan rate 2 mV/s. (A) full potential region; (B) enlarged potential section (-0.3 to -0.1 V). (—) 0M; (---) 5×10^{-5} M; (-·-) 1×10^{-4} M; (···) 1.5×10^{-4} M $\text{Ru}(\text{NO})(\text{NO}_3)_3$.

activity. At higher potentials the methanol oxidation current decreases with increasing amount of promotor metal, due to blocking of the Pt surface. It is furthermore striking that the peak potential of the

Table 1

Change of the onset potential for CO_2 production during methanol oxidation on Pt in the presence of Sn and Ru

Concentration	Onset-potential of CO_2 production (V)
0M Sn	-0.135
1×10^{-4} M Sn	-0.197
2×10^{-4} M Sn	-0.282
0M Ru	-0.135
1×10^{-4} M Ru	-0.222
2×10^{-4} M Ru	-0.276

Table 2

Ratio between current (I) and mass current (M) for the electro-oxidation of methanol on Pt in the presence of Sn or Ru; The ratios were determined from the second scan of a cyclic voltammogram; The ratios without promotor metals were set to 1

I/M ratio	$E = -0.1$ V	$E = 0$ V	$E = +0.1$ V
0M Sn	1	1	1
1×10^{-4} M Sn	0.46	0.72	0.93
2×10^{-4} M Sn	0.45	0.67	0.93
0M Ru	1	1	1
1×10^{-4} M Ru	0.80	0.74	0.84
2×10^{-4} M Ru	0.67	0.70	0.76

methanol oxidation decreases in the presence of Ru, but does not change in the presence of Sn.

Determination of the ratio between the current (I) and the mass current (M) – which is directly related to amount of CO_2 molecules [19] – showed that for the dynamic measurements the ratio becomes smaller in the presence of Sn or Ru. The I/M ratio values, calculated at three different potentials, are presented in Table 2; the ratio without promoting metal is set at 1. A decrease of the I/M ratio means an increase of the current efficiency for CO_2 . Shibata and Motoo [20] also reported a higher current efficiency in the presence of Ru, however they found a lower current efficiency in the presence of Sn.

Although a change in current efficiency can be explained on the basis of the bifunctional model where the role of the promotor is solely to donate an oxygen species, it is difficult to see how the continuous lowering of the onset potential with increasing promotor metal fits in this model. This phenomenon may therefore indicate that the promotor metals also evoke a ligand effect, i.e. the strength of the Pt-adsorbate bond is weakened by increasing amounts of promotor metal which results in a lowering of the oxidation potential of the adsorbate.

3.3. Codeposited Pt-Ru electrodes

Fig. 3 gives the cyclic voltammograms for codeposited Pt-Ru electrodes with different Ru contents. For all electrodes only one oxide reduction peak is observed, implying that only one type of oxide is formed. Platinum and ruthenium therefore may be assumed to be present as one phase. The position of the oxide reduction peak shifts to lower potentials

for electrodes deposited with higher current, i.e. with higher Ru content. This agrees well with the results of McNicol and co-workers [21,22] who found that the oxide reduction peak of Pt–Ru alloys shifts to lower potentials with an increase in Ru content of the alloys. At electrodes with a bulk Ru content of 28% the oxide reduction can no longer be distinguished from the hydrogen reduction as was also observed by Entina and Petrii [23].

The voltammetric scan during methanol oxidation changes with the Pt–Ru composition; with increas-

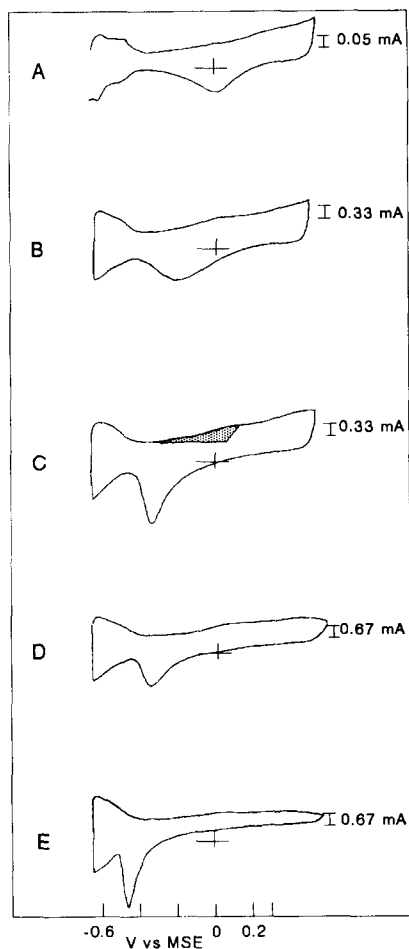


Fig. 3. Cyclic voltammograms of Pt–Ru codeposits in 0.5M H_2SO_4 ; scan rate 10 mV/s. (A) Pt–Ru (13%); (B) Pt–Ru (18%); (C) Pt–Ru (25%); (D) Pt–Ru (27%); (E) Pt–Ru (28%). Deposition time: 10 min; deposition current: (A) 0.5 mA/cm²; (B) 1.0 mA/cm²; (C) 1.7 mA/cm²; (D) 2.0 mA/cm²; (E) 2.4 mA/cm². In (C) the area for Ru-oxidation is indicated.

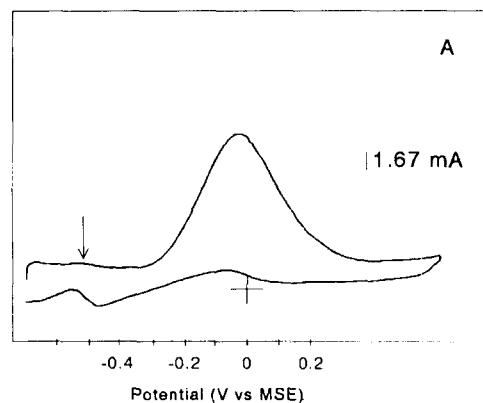
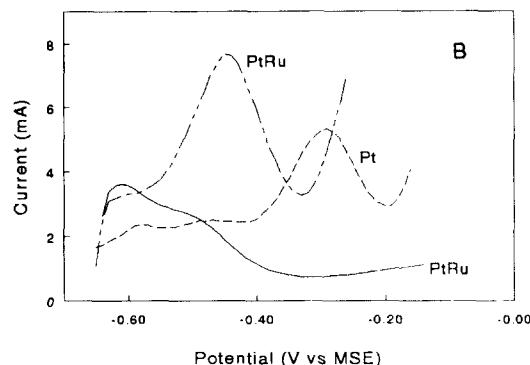


Fig. 4. (A) Voltammogram of electro-codeposited Pt–Ru (27%) in 0.5M H_2SO_4 /0.1M CH_3OH ; scan rate 5 mV/s. Arrow indicates methanol adsorption peak, cf. curve (– · – ·) in (B). (B) Voltammograms of electro-codeposited Pt–Ru (27%) and Pt in 0.5M H_2SO_4 /0.1M CH_3OH ; scan rate 5 mV/s. (– · – ·) methanol adsorption peak on Pt–Ru (27%); (– – –) methanol adsorption peak on Pt–Pt; (—) hydrogen desorption at Pt–Ru in 0.5M H_2SO_4 .

ing Ru content the methanol oxidation peak in the cathodic scan decreases and disappears completely at high Ru contents. In Fig. 4A the methanol oxidation is shown for Pt–Ru(27%). It is noted that an oxide reduction peak appears at the same potential as without methanol. Also a new (small) peak emerges in the anodic scan at -0.5 V versus MSE; this is more clearly seen in the enlargement in Fig. 4B, in which part of a cyclic voltammogram is shown for an electrode with a different geometric surface area than in 4A, but with the same Ru content (27%). A peak at this potential was also reported by Gasteiger et al. [9] for Pt–Ru (10%) and by Caram and Gutierrez [24] for Pt. With DEMS we established that no CO_2 was produced during this peak. If the potential

scan is reversed immediately after this peak, we found that the hydrogen coverage had diminished; this indicates that the -0.5 V peak is due to oxidative adsorption of methanol on the surface. Fig. 4B shows also the methanol adsorption at Pt–Pt at the same methanol concentration; here the peak is observed at a higher potential. It thus appears that while methanol is adsorbed on Pt after virtually all adsorbed hydrogen has been removed from the surface, the methanol adsorption on Pt–Ru can already occur at potentials in the hydrogen region (cf. full line in Fig. 4B). This could point to the formation of another adsorbate and might indicate that Ru does not solely act via the bifunctional mechanism.

In order to compare the activities of the different electrodes for the methanol oxidation, it is necessary to know the amount of Ru present on the surface and the specific surface area. The SEM/EDX data present bulk values and may differ from the surface values due to surface segregation. For adatom Ru–Pt systems Watanabe et al. [4] measured the charge necessary to oxidise Ru and calculated the Ru coverage by assuming that this charge corresponds with the formation of RuOH. We performed electrochemical quartz crystal microbalance experiments, in which the mass change of a Pt electrode was monitored during Ru deposition and oxidation [25]. It was concluded from these measurements that the Ru-oxide is Ru(OH)₂. Furthermore a linear correlation was observed between the mass change of the electrode and the shift of the oxide reduction peak. The coverage, obtained by measuring the electrode-mass change during Ru deposition ($\theta = 0.20$), was found to be fairly close to the coverage established from

the decrease in the amount of adsorbed hydrogen ($\theta = 0.23$), although it is recognized that this measurement of the surface content gives only an upper limit of the amount of Ru, because Ru adsorbs hydrogen itself [16]. The Ru surface content of the codeposited electrodes was calculated from the charge corresponding with the Ru oxidation as indicated in voltammogram C of Fig. 3 with: $\theta_{\text{Ru}} = (Q_{\text{Ru(OH)}_2}) / (Q_{\text{Ru(OH)}_2} + 2Q_{\text{H}})$. The only assumption in this calculation is that one Ru atom replaces one Pt atom. The calculated coverages are summarized in Table 3 and agree reasonably well with the values obtained by SEM/EDX. In this table also another estimate of the Ru content is given; this was obtained from the position of the oxide reduction potential: if it is assumed that for codeposited electrodes the shift of the oxide reduction peak with increasing Ru content is the same as for adatom systems, the Ru content can be determined via the EQCMB measurements. This resulted in larger values in particular at higher Ru content; the difference may be due to surface segregation.

In Table 3 the activities of the different Pt–Ru electrodes for the methanol oxidation are compared at -0.2 V versus MSE. These activities are expressed with respect to the real(true) Pt surface area, calculated with the Ru coverages (a) from Table 3 assuming that 1 cm^2 of real surface area contains 1.41×10^{15} atoms and that the Pt surface structure is not distorted by the presence of Ru. The table shows that for these electrodes the highest activity is obtained with relatively low Ru content as was discussed in the introduction. Although it is obvious that there exists an optimum for the Ru coverage, the

Table 3

Pt–Ru codeposited electrodes: Ru content established by different methods and comparison of the activities for the methanol oxidation at -0.2 V versus MSE with that of Pt in $0.5\text{M H}_2\text{SO}_4/0.1\text{M CH}_3\text{OH}$

	SEM/EDX	Coverage calculated via Ru-oxide charge ^a	Coverage estimated from reduction peak potential	Activity at -0.2 V (mA cm^{-2})
Pt–Ru	13%	11%	10%	0.1
	18%	24%	30%	0.09
	25%	33%	45%	–
	27%	33%	48%	0.04
	28%	28%	60%	0.02
Pt	–	–	–	0.01

^a See text.

data do not allow to ascertain its exact value. Our results are in agreement with the results of Gasteiger et al. [9] on well-characterized smooth Pt–Ru surfaces. Watanabe et al. [4] concluded that the maximum activity was obtained at $\theta_{\text{Ru}} = 0.5$; this Ru coverage however was based on the assumption that RuOH is formed. With $\text{Ru}(\text{OH})_2$ as oxide species this coverage is 0.25, which is in reasonable agreement with the result of us and others [9,11,12].

3.4. Carbon supported Pt–Ru catalysts

It is known that the onset of Pt oxidation can be enhanced by decreasing the Pt particle size. However, we found [26] that the specific activity of carbon supported Pt for the methanol oxidation remains constant for Pt sizes down to about 4 nm and that below that value the specific activity decreases with smaller particles. We attributed this to the much stronger water activation by the smaller particles at low potentials, resulting in a thwarting of the methanol adsorption reaction. It is therefore of interest to measure the methanol oxidation at carbon supported Pt–Ru catalysts with very small particles. Pt–Ru/C catalysts (5 wt%) were prepared with different ratios of Pt:Ru viz. [2:1], [4:1], [8:1]; with TEM it was established that the Pt–Ru [8:1] catalyst consists of particles from 1 to 2 nm with both Pt and Ru; the [2:1] and [4:1] catalysts consist of particles of 3 to 4 nm. In Table 4 the activities for the methanol oxidation are compared at -0.2 V versus MSE; the activity of Pt/C is also included. The highest activity for the methanol oxidation was obtained for the Pt:Ru [8:1] catalyst. Again as with electrodeposited Pt–Ru the results here seem to indicate that the highest activities for the methanol oxidation are obtained with a low Ru content (ca. 10%),

although the promotor effect still has to be separated from the Pt particle size effect, because in our preparation method the particle size increases with the Ru content. The potential of the oxide reduction peak for the carbon supported Pt–Ru electrodes is the same as without Ru.

The presence of Ru appears to be quite effective: the activity of these Pt–Ru particles in the potential region -0.2 to -0.05 V versus MSE was a factor 10 higher than for Pt/C catalysts with particles of the same size. As for such small particles water activation is already too effective, the role of Ru can hardly be simply that of an oxygen donor, but may rather be ascribed to its modification of the electronic properties of Pt.

4. Conclusions

The ellipsometric measurements at codeposited Pt–Ru show that Ru–surface oxide disappears in the presence of methanol. This was also found both for adatom coverage of Ru and Sn on Pt. The absence of these oxides during the methanol oxidation indicates that the metals act via the bifunctional mechanism in which an oxygenated species of Ru or Sn oxidizes the methanolic adsorbate. With EQCMB it was established that on Pt–Ru(ad) $\text{Ru}(\text{OH})_2$ is formed.

Activity and DEMS measurements at Pt electrodes with partial coverage of Sn or Ru reveal that in the presence of the promoting metal not only the activity for the methanol oxidation changes but also the current efficiency for CO_2 production; moreover the onset potential for the methanol oxidation is lowered with increasing amounts of promotor metal. These phenomena are difficult to explain with a bifunctional mechanism and may indicate that the electronic properties of Pt are changed as well. This is further corroborated by the results at carbon supported Pt–Ru electrodes, which show that the methanol oxidation at very small particles can be enhanced by Ru in spite of the fact that Pt particles (< 4 nm) alone are too active for water activation. The activity for the methanol oxidation for the electro-codeposited Pt–Ru systems is found to be the highest for a low Ru content.

It seems clear then that the promoting action of Sn and Ru involves both water activation and plat-

Table 4
Activity at -0.2 V versus MSE for methanol oxidation of carbon-supported Pt and Pt–Ru catalysts in $0.5\text{M H}_2\text{SO}_4/0.1\text{M CH}_3\text{OH}$

Carbon-supported catalyst	Current density (mA cm^{-2})
Pt	0.02
Pt–Ru (2:1)	0.15
Pt–Ru (8:1)	0.30

inum modification. Their relative importance in each particular case remains to be more accurately determined, e.g. through in situ IR spectroscopy.

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