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Pt–Ru Anodes for Methanol Electrooxidation: A Ruthenium-99 Mössbauer Study

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^{99}Ru Mössbauer spectra have been obtained for a series of Pt–Ru methanol oxidation anodes. For the most catalytically active sample, XPS and Mössbauer data indicate the presence of Ru(IV) species with a small quadrupole splitting. For highly dispersed samples the Mössbauer data indicate that the Ru is present as a mixture of rutile-phase RuO_2 and a second Ru(IV) species. Comparison with electrocatalytic results suggests that the second Ru(IV) species is the active catalytic copromoter. The possible identity of this species is discussed. © 1990 Academic Press, Inc.

INTRODUCTION

It is well established that the catalytic activity of platinum for the electrooxidation of methanol to CO_2 at low temperatures can be increased by the addition of a promoter such as Ru, Sn, or Ti (*1–5*). On pure platinum a rapid poisoning is observed due to the build-up of a carbonaceous residue, and three possible mechanisms by which the promoters may work have been postulated. For Ru it has been proposed that the enhanced behavior is due to the direct reaction of an oxide of the second metal with the chemisorbed Pt_3–COH residue, yielding CO_2 (*6, 7*). The metal oxide is then regenerated via a second redox process. For Pb it is believed that the enhanced performance of the bimetallic electrode is due to a blocking effect (*8*), in which the second metal is assumed to inhibit the strong chemisorption of the intermediate Pt_3–COH species. Finally there is the promoter model which appears appropriate for Ti and Sn, where the second metal promotes the formation of active Pt–O groups capable of completing the oxidation reaction (*2, 6*).

Platinum–ruthenium mixtures have been identified a one of the most promising catalysts, yet especially for carbon-supported electrodes the nature of the Ru atoms remains uncertain (*9, 10*). XPS studies have proved extremely valuable in the characterization of other bimetallic systems (*2, 6, 11*); however, the binding energy of the diagnostic Ru 3*d* line is approximately the same as that of the much stronger C 1*s* line. Early temperature-programmed reduction (TPR) studies suggest that for carbon-supported Pt–Ru electrocatalysts the Ru is present as an oxide species (*12*). The stable oxide of Ru is the rutile-phase RuO_2 (*13*); however, in confirmation of previous studies (*14*) we have observed that this is a poor promoter for the methanol oxidation reaction. This apparent anomaly prompted us to undertake a detailed study of the physical properties of carbon-supported Ru and Pt–Ru systems. Mössbauer spectroscopy with the 89-keV γ-rays of ^{99}Ru has proved a useful technique for the analysis of the chemical state of ruthenium in metal-oxide-supported Ru catalysts (*15*) and mixed metal Ru oxides (*16, 17*). The Mössbauer parameters of many ruthenium compounds are known (*15, 18*). By comparison with these, unknown compounds can be identified, albeit not always unequivocally. Moreover, the isomer shift depends in a systematic

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way on the valence state of ruthenium (*15, 18*), which often allows the oxidation state to be determined even if the exact nature of the compound cannot be identified.

Recently we reported the preparation of a Pt–Ru system which showed both high short-term activity for methanol electrooxidation and very low tendency to poison (*10*). In order to identify the nature of the Ru atoms in this and related catalyst systems we have combined Mössbauer spectroscopy with X-ray photoelectron spectroscopy, electron microscopy, and electrochemical studies.

EXPERIMENTAL

(*i*) *Sample Preparation*

The unsupported Pt–Ru electrode 7:3 (at.%) was prepared from H_2PtCl_6 and $RuCl_3 \cdot xH_2O$ (Johnson Matthey) by the coprecipitation and low-temperature reduction (H_2 at 200°C for 12 h) as described recently (*10*). Catalytic studies were performed on a 13-mm-diameter disk pressed at 1.7 tons/cm^2 for several minutes.

The carbon-supported Pt–Ru sample, Pt–Ru/C_u, with a Pt:Ru ratio of 7:4 (at.%) was prepared using untreated Vulcan XC-72 as support. The carbon was suspended in distilled water, and a neutralized aqueous solution containing the required amounts of H_2PtCl_6 and $RuCl_3 \cdot xH_2O$ was added. The mixture was boiled for 2 h, dried at 100°C overnight, and then resuspended in boiling distilled water, at which time an excess of sodium formate was added. After 1 h the resulting mass was filtered, washed repeated with hot distilled water, and finally air dried at 110°C for 12 h. The Ru/C_t sample was prepared using CO_2-comminuted XC-72 (*2*). The carbon was suspended in distilled water and heated to 80°C. $RuCl_3 \cdot xH_2O$ was then added and the mixture boiled for 2 h, after which time an excess of 1% formaldehyde solution was added and the mixture was boiled for a further 1 h. The resulting mass was filtered, washed repeatedly with hot distilled water, and finally air dried at 110°C for 12 h. The Pt/C_t catalyst was prepared in an identical manner using H_2PtCl_6 as the metal source.

For electrochemical studies of the carbon-supported catalysts, Teflon-bonded electrodes were prepared, by cold pressing a Teflon/carbon mixture at 125 kg/cm^2 for 5 min followed by sintering at 360°C for 30 min. The final Teflon loading was 27 wt%. More detail is given elsewhere (*2*).

(*ii*) *Instrumentation*

The Mössbauer spectra were obtained at 4.2 K with a source of ^{99}Rh in enriched ^{100}Ru metal. They were fitted with appropriate superpositions of Lorentzian lines as previously described (*19*). In all cases, the electric field gradient was assumed to have axial symmetry. The observed electric quadrupole splittings were too small for the sign of the electric quadrupole interaction to be determined. The absorbers had Ru loadings between 50 and 100 mg/cm^2.

Photoelectron spectra were recorded on a VG ESCALAB spectrometer using MgKα as an excitation source (*20*).

Electron micrographs were obtained on a JEOL 200FX electron microscope.

Electrochemical studies were performed at 60°C in a rapidly stirred argon-saturated 1 *M* CH_3OH/2.5 *M* H_2SO_4 solution with a Thompson Electrochem Ministat. Potentials were measured against a Hg/Hg_2SO_4 reference electrode and are not iR corrected. The accurate determination of the iR drop in porous electrodes is not straightforward and its minimization is an engineering problem. In the present electrodes neglect of such a correction may lead to an underestimation of the catalytic performance, especially at high current densities.

RESULTS

(*i*) *Catalytic Properties*

The short-term polarization behavior of the Pt/C_t and Ru/C_t electrodes in 1 *M* CH_3OH/2.5 *M* H_2SO_4 is shown in Fig. 1. The half reaction for the electrochemical

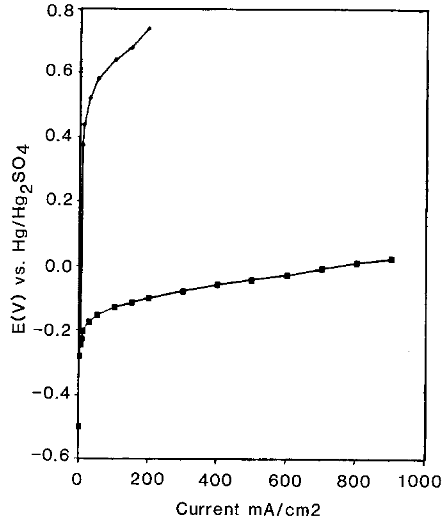


FIG. 1. Current-potential curves for (■) Pt/C_t and (◆) Ru/C_t in 2.5 *M* H_2SO_4 1 *M* CH_3OH at 60°C.

oxidation of methanol to CO_2 in acid solutions is

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e,\quad E^\circ = -0.66 \text{ V vs Hg/Hg}_2\text{SO}_4.$$

In practice more anodic potentials are needed to achieve an appreciable rate of reaction. In the case of Ru/C_t, application of an oxidizing current results in a rapid increase in potential from −300 to 300 mV. In keeping with previous studies there is no evidence for appreciable oxidation of methanol at relatively low potentials (*1*), although a catalytic current begins around 400 mV indicating that the partial oxidation of methanol can occur on the Ru/C electrode. At still higher potentials the major chemical reaction to occur may be the oxidation of water above 600 mV, viz.,

$$2H_2O \rightarrow O_2 + 4H^+ + 4e,\quad E^\circ = 0.56 \text{ V vs Hg/Hg}_2\text{SO}_4.$$

The Pt/C_t electrode has a lower open circuit voltage, −400 mV, indicating that the major electron transfer reactions occurring on the Pt surface at open circuit are those which occur at low potentials, e.g., chemisorption of methanol and protons. Application of an oxidizing current results in a rapid increase in the resultant potential to −100 mV and the catalytic oxidation of methanol becomes the dominant reaction. After the initial dramatic increase in potential there is a slow increase in potential as the current is progressively increased from 200 to 600 mA/cm². This slow increase is probably due to iR losses. The behavior of a platinum black electrode was essentially identical, save that the highest achievable current was considerably lower, 300 mA/cm².

The short-term polarization behavior of the 2 Pt–Ru electrodes in 1 *M* CH_3OH/2.5 *M* H_2SO_4 at 60°C is shown in Fig. 2. The activities of both the Pt–Ru and Pt–Ru/C_u electrodes are considerably enhanced compared to those of their pure Pt analogues (*20*). The highest activity, or current density at a given potential, was observed for the unsupported electrode, although as apparent from Fig 2 the specific activity or current per milligram of Pt is unacceptably low for this material, presumably since only those Pt particles on the surface of the electrode are involved in the catalytic reaction. The rapid stirring of the solution apparently ensures that mass transport of the fuel is not a limiting factor.

Lifetime measurements at a constant load of 250 mA/cm² indicate the unsupported Pt–Ru electrode to be exceptionally stable, operating in excess of 1000 h. This behavior is in marked contrast to the rapid poisoning observed for both Pt black and the supported Pt–Ru/C_u electrode, which was inoperative after 125 h at 25 mA/cm². A full account of the lifetime performance of Pt–Ru/C electrodes will be presented elsewhere (*10, 21*).

(*ii*) *Electron Microscopy*

An electron micrograph of the Ru/C_t is shown in Fig. 3. It is apparent that the metal crystallites are relatively small (ca. 25 Å diameter) and that a high degree of dispersion has been achieved. In some preparations some agglomeration of the crystallites was apparent; however, we note that

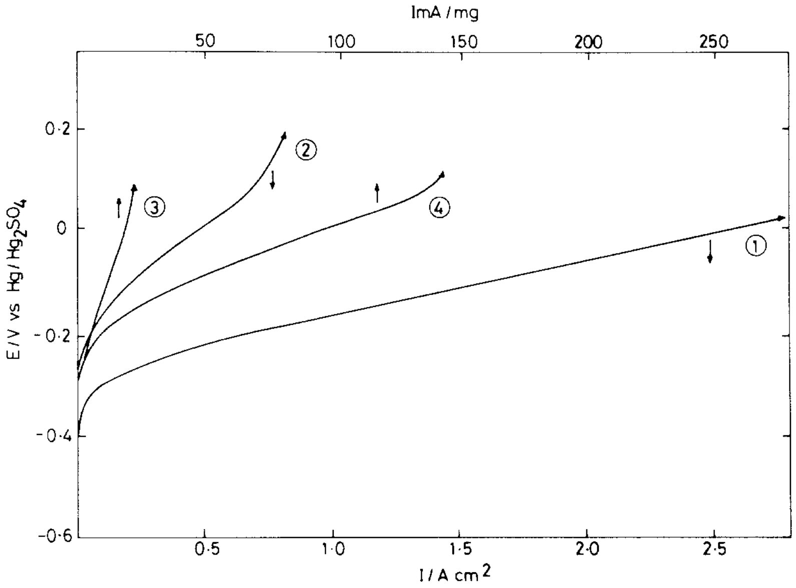


FIG. 2. Current-potential curves for methanol oxidation in 2.5 *M* H_2SO_4 1*M* CH_3OH at 60°C on (1) Pt–Ru (A/cm²), (2) Pt–Ru/C_u (A/cm²), (3) Pt–Ru (mA/mg Pt), and (4) Pt–Ru/C_u (mA/mg Pt). The unsupported catalyst had 224 mg Pt. The Pt–Ru/C_u catalyst had 6.3 mg Pt.

the deposition method used to prepare this sample was optimized for the Pt-containing catalysts. A high degree of dispersion was observed for the Pt–Ru/C_u catalyst with a relatively narrow particle size distribution. The metal particles in this sample are somewhat larger, the average particle size being ca. 65 Å, as a result of the intermediate drying step used in the deposition method.

The specific surface area of the Ru/C_t catalyst was calculated to be ca. 100 m²/g, assuming a spherical geometry of the crystallites. The larger particle size of the Pt–Ru/C_u crystallites results in a smaller specific surface area of ca. 40 m²/g. That all the catalyst was accessible to the electrolyte was confirmed by altering the catalyst loading per square centimeter of electrode; the specific activity of the catalyst for methanol oxidation remained constant. This result is somewhat surprising since BET measurements indicated a decrease in surface area on electrode fabrication. The surface area of the catalyzed powder was found to be 250 m²/g whereas the surface area of the fabricated electrode was 100 m²/g. Attempts to determine the catalyst surface area by a potentiodynamic sweep technique were inconclusive, presumably because of hydrogen spillover to the support (*11*). We note, however, that previous workers have found the specific surface area calculated from electron micrographs to be in good agreement with the electrochemically determined surface area (*22, 23*).

The BET surface area of the unsupported electrode was not determined, although it is expected to be relatively low as a consequence of the high pressure used in electrode fabrication.

(*iii*) *X-ray Photoelectron Spectra*

The X-ray photoelectron spectra of the Ru 3*d* and 3*p* regions were recorded for all three samples. In all cases fabricated electrodes were utilized in the XPS studies. For the carbon-supported samples the Ru 3*d* level overlaps with the much stronger C 1*s* signal and could not be used (Fig. 4). The Ru 3*p* signals were generally weak and poorly resolved for these samples, and attempts to identify the nature of the Ru cen-

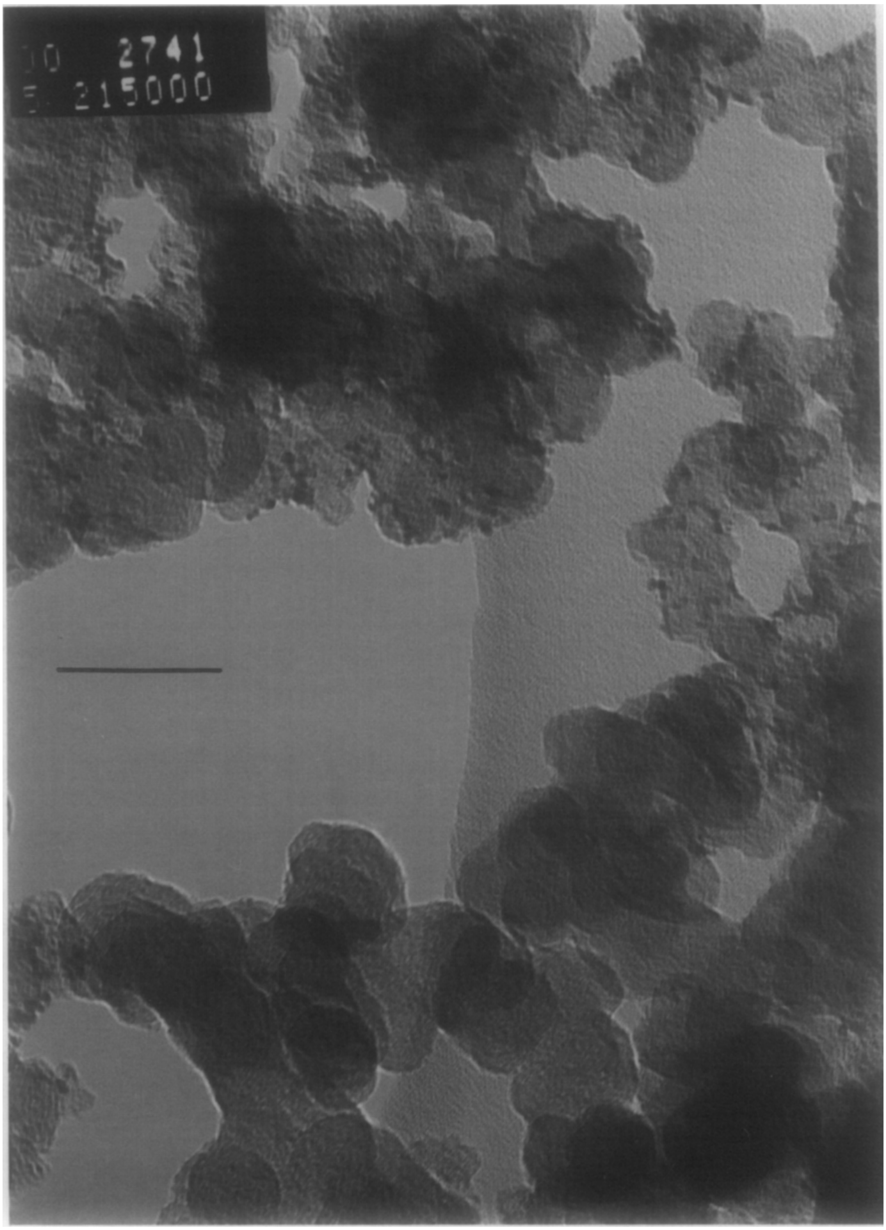


FIG. 3. TEM photograph of a Ru/C_t catalyst supported on Vulcan XC-72. The marker shows 50 nm.

ters were inconclusive. Likewise analysis of the O 1*s* signal, which could have offered some information about the presence of metal oxides/hydroxides, was invalidated by the strong signal from oxidized groups on the carbon support. For the unsupported material a well-resolved Ru 3*d* doublet signal was observed with Ru 3*d*(5/2) at 281.0 eV, indicative of tetravalent Ru (*24*). The intensity of the Ru 3*d*(3/2) line is greater than expected from simple multiplet theory; however, this is probably due to the presence of adventitious carbon. No signal from zero-valent Ru was observed. Unfor-

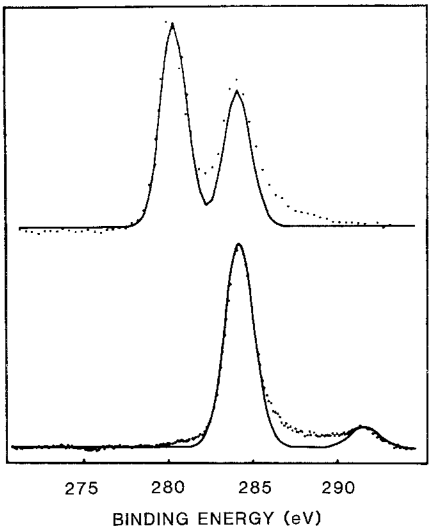


FIG. 4. Ru 3*d* and C 1*s* electron spectra of (1) unsupported Pt/Ru catalyst, upper trace, and (2) carbon-supported Pt–Ru/C_u catalyst, lower trace.

tunately the O 1*s* signal of this unsupported material was relatively broad, perhaps indicating the presence of a number of oxygen-containing species, including strongly adsorbed water from the atmosphere.

The Pt 4*f* electron spectra of Pt–Ru and Pt–Ru/C_u are shown in Fig. 5. In both cases the major Pt species is Pt(0), Pt 4*f*(7/2) = 71.4 eV. In addition a small amount of an oxidized Pt species is present. For the unsupported Pt–Ru catalyst the Pt 4*f* BE of the signal, estimate using a Gaussian deconvolution indicated the species to be Pt(IV), 74.8 eV, while for the supported sample the BE of the oxidized species was notably lower, 73.4 eV, perhaps indicating the presence of Pt(II) (*25*). It is uncertain if this difference is a result of limitations in the deconvolution routine used, or if it is due to the presence of different Pt oxide species on the two samples. No evidence for any chloride was observed. Interestingly the Pt 4*f* spectra of a Pt/C_t sample was deconvoluted into three doublets with Pt 4*f*(7/2) BE of 71.2, 73.8, and 74.9 eV, respectively (*20*).

(*iv*) *Mössbauer Spectra*

The ^{99}Ru Mössbauer spectra of the three materials at 4.2 K are shown in Fig. 6. All three spectra have lines with isomer shifts, δ, near -0.22 mm/s, which are typically assigned to Ru(IV) species. There is, however, a complication in the assignment of these lines. On the one hand, Ru(IV) species have been found to have isomer shifts between about -0.15 and -0.35 mm/s and quadrupole splittings between zero and 0.50 mm/s. On the other hand the Mössbauer resonance of Ru metal is a single narrow line (despite Ru having a *hcp* structure) at zero velocity when a Ru metal source is used. Dilute alloys of Ru in Pt metal give a narrow line with an isomer shift of $\delta = -0.38$ mm/s (*15, 26*). Isomer shifts for $Ru_{1-x}Pt_x$ alloys have not yet been measured, but it is expected that they will have a linear dependence on x between zero for $x = 0$ and -0.38 for $x = 1$. A linear dependence on the isomer shift has been observed in Pt–Ir alloys (*27*). While the quadrupole splittings in such alloy systems are

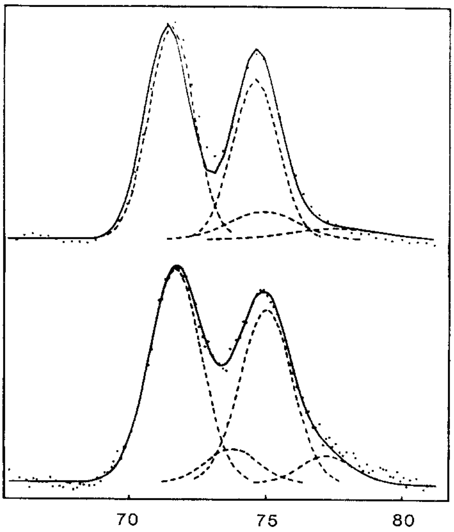


FIG. 5. Pt 4*f* electron spectra of (1) unsupported Pt/Ru catalyst, upper trace, and (2) carbon-supported Pt/Ru/C_u catalyst, lower trace.

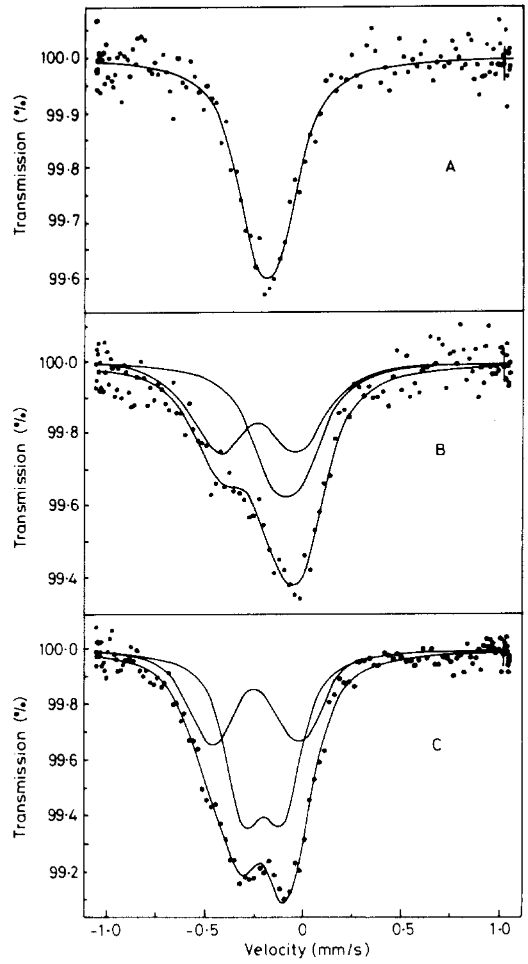


FIG. 6. Mössbauer spectra at 4.2 K of (A) Pt–Ru, (B) Pt–Ru/$\mathrm{C_u}$, and (C) Ru/$\mathrm{C_t}$.

expected to be too small to be resolved, inhomogenieties in the Ru–Pt alloys may give rise to a distribution of isomer shifts and thus lead to line broadening. Also, in bimetallic Pt–Ru clusters there is the possibility of segregation into a Pt-rich and a Ru-rich phase (*28*, *29*), thus giving rise to an apparent quadrupole split doublet. As a consequence, single but somewhat broadened peaks between about −0.15 mm/s and −0.38 mm/s may be from either Ru–Pt alloys or Ru(IV) species with small or vanishing electric quadrupole interactions. Mössbauer spectroscopy alone thus will not always yield an unambiguous identification of the state of Ru in bimetallic Pt–Ru catalytic systems.

The spectrum for Ru/$\mathrm{C_t}$ consists of at least two doublets. Analysis of the spectrum indicated that the two species present have similar isomer shifts, $\delta = -0.20$ mm/s for the inner doublet and −0.22 mm/s for the outer doublet. These values are characteristic of tetravalent Ru (*15*, *18*). Furthermore, we note that the quadrupole splitting of the 3/2 excited state of ^{99}Ru for the outer doublet, $\frac{1}{2}eQ_{3/2}V_{zz} = 0.43$ mm/s, is somewhat smaller but still comparable to that found for polycrystalline samples of $\mathrm{RuO_2}$ (Table 1). Thus it is likely that the outer doublet is due to the rutile-phase $\mathrm{RuO_2}$ species. This species is the most stable Ru ox-

TABLE 1

Mössbauer Parameters of the Samples and of Some Relevant Reference Compounds

Sample	Isomer shift δ mm/s vs Ru	Quadrupole splitting (mm/s)	FWMH (mm/s)	Area (%)	Ref.
Pt–Ru	−0.18(1)	0.14(2)	0.22(3)	100	—
Ru/$\mathrm{C_t}$	−0.20(1)	0.19(2)	0.15(2)	53	—
	−0.22(1)	0.43(3)	0.15(2)	47	
Pt–Ru/$\mathrm{C_u}$	−0.09(9)	0.16(10)	0.24(5)	48	—
	−0.23(8)	0.43(19)	0.24(5)	52	
$\mathrm{RuCl_3 \cdot xH_2O}$	−0.34	0	—	—	(*15*, *30*)
$\mathrm{CaRuO_3}$	−0.30	0	—	—	(*15*, *31*)
$\mathrm{BaRuO_3}$	−0.26	0	—	—	(*15*, *31*)
$\mathrm{RuO_2}$	−0.26(1)	0.50	—	—	(*15*, *31*)

ide and has been identified in a number of oxide-supported Ru systems (*16, 32*).

According to its isomer shift the inner doublet is due to a second Ru(IV) species, which has, however, a substantially smaller quadrupole splitting than the rutile species, whose quadrupole splitting is, in fact, quite large for Ru(IV). Because of the absence of a strong Cl 1*s* signal in the XPS this second species cannot be a chloride. We therefore conclude that it is a badly crystallized form of Ru(IV) oxide or hydroxide.

For the unsupported Pt–Ru sample a somewhat broadened peak at $\delta = -0.18$ mm/s is observed. As indicated above, this isomer shift is typical of Ru(IV) species. On the other hand, a metallic $Ru_{1-x}Pt_x$ alloy with a mean composition of $Ru_{0.53}Pt_{0.47}$ should yield a similar Mössbauer spectrum, if there was a certain variation in composition leading to the large linewidth. The assignment of the Ru to a metallic alloy would mean that the bulk of the platinum exists as discrete Pt crystallites, and the exceptional catalytic activity is due to only a small portion of the material. The XPS, however, indicates that the material is indeed a Ru(IV) species and not a metallic Ru–Pt alloy. Therefore the Mössbauer spectra were fitted to a quadrupole doublet. It is apparent from the small quadrupole splitting that the Ru is not present as the rutile RuO_2. It is interesting to note that a number of nonmagnetic perovskites of the type $M^{II}RuO_3$ (M = Ba, Ca, Sr) also have a single poorly resolved quadrupole split doublet at 4.2 K, (*31*) and that XPS measurements on the present sample indicate that ca. 15% (or 1 Pt : 1 Ru) of the total Pt is present as a Pt(II) species. From this it might be tempting to assign a perovskite structure $PtRuO_3$ to the present unsupported Pt–Ru sample, together with a large amount of Pt(0). However, such an assignment would be tenuous at best, and we have observed that all other Ru(IV) perovskites studied (M = Ba, Ca, Sr) are both poor copromoters for methanol oxidation and unstable under the experimental conditions employed in methanol oxidation.

The third sample, Pt–Ru/C_u has a broad and asymmetric Mössbauer spectrum that was deconvoluted into two doublets. Here the isomer shift and quadrupole splitting of the outer doublet are again typical of polycrystalline RuO_2. The second poorly resolved doublet, or broadened single line, has parameters similar to that found for the unsupported Pt–Ru sample (Table 1). The isomer shift is notably higher, −0.09 instead of −0.20 mm/s, but it is still compatible with the notion that it represents a Ru(IV) species and it is definitely lower than the isomer shifts reported for Ru(V) species such as Na_3RuO_4, $\delta = +0.04$ mm/s. The higher isomer shift may be a result of donation of some of the Ru *d* electrons onto either the carbon support or onto nearby Pt atoms, although this appears unlikely since the Pt 4*f* BE shows no apparent shift. An alternate possibility involving the presence of a mixed-valence Ru(IV/V) species with rapid electron transfer between the two valence states appears unlikely. The possibility that the component at −0.09 mm/s represents $Pt_{0.75}Ru_{0.25}$ alloy, however, cannot be definitely discounted on the basis of the present data.

DISCUSSION

There are, in principle, two possible explanations for the observed Mössbauer spectra for the carbon-supported ruthenium species. The first postulates the existence of two types of particle on the support and is analogous to the two-particle model recently postulated to explain the ^{57}Fe Mössbauer spectra of supported iron crystallites (*33*). The second possibility is that there are two distinct chemical species present, associated with a single type of particle, perhaps corresponding to interior and surface species.

The possibility of a two-particle model arises because XC-72 has a reasonably high surface area, in which there are a limited number of "active sites" on the carbon at which very small Ru(IV) or Pt–Ru(IV) crystallites might form. In these very small crystallites the local environment of the ruthenium apparently gives rise to a small field gradient. At other less active sites, decomposition of $PtCl_6^{2-}$ and/or $RuCl_3$ results in the formation of larger particles, 25 Å in diameter for the Ru/C_t and 65 Å for the Pt–Ru/C_u catalysts, in which Ru–Ru bonding interactions can occur, resulting in a rutile-like Mössbauer spectrum.

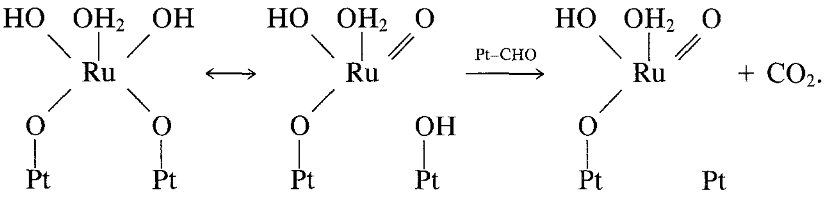
Of these two models, the second, or single-particle model, would appear to be better supported by the experimental data. Electron micrographs of the samples show no evidence for appreciable numbers of particles smaller than 25 Å; however, the failure to observe these may simply be a resolution problem. It would seem likely, therefore, that at least for the ruthenium deposited on carbon, there is essentially one type of particle composed of two different chemical forms of Ru(IV). Now it is noteworthy that for the highly active unsupported bimetallic catalyst, there is no rutile RuO_2 present, but for the inactive Ru/C_t electrode, a signal characteristic of rutile RuO_2 is seen, as well as one that apparently corresponds to that form of Ru(IV) found in the active unsupported catalyst. In addition, electrodes formed from Pt and rutile-RuO_2 alone are known to be rather inactive for the oxidation of methanol (*14*). These two facts suggest that either there are two types of particles, both of identical size, with one composed purely of rutile RuO_2 and the other of an active form of Ru(IV), or there is a single composite type of particle with an interior of rutile RuO_2 and an exterior of some form of active Ru(IV). The latter would appear more probable.

Interestingly, the areas of the Mössbauer signal from the two species are approximately the same. Since in the 25 Å particles approximately half the Ru atoms will exist as surface species, the Mössbauer data apparently support the idea of an interior and surface species model. Against this we have no idea about the relative recoil-less fractions of the two species and note that the areas do not necessarily represent the actual amounts of the differing species.

In the case of the mixed Pt–Ru supported catalyst, the picture is somewhat more complicated. While it is possible that the poorly resolved line at $\delta = -0.09$ mm/s represents metallic clusters, the absence of a Mössbauer signal due to Ru(0) in the Ru/C_t sample together with the absence of an XPS signal due to Ru(0) in the unsupported Pt–Ru sample argues against such an assignment. The ^{99}Ru Mössbauer signal from the supported ruthenium is rather similar whether or not platinum is present, the main difference being that the spectrum is less well resolved, especially for the active Ru(IV) species, in the latter case. An attempt was made to use electron microprobe analysis to establish the composition of the particles in the Pt–Ru supported catalyst, but the smallness of the particles leads to very poor counting statistics; the only conclusion that may be stated with confidence is that all the particles analyzed showed the presence of both Pt and Ru. The most plausible model that can be advanced with our data is then that particles exist with either a platinum metal or a RuO_2 core and a mixed Pt(II)/Pt(0)/Ru(IV) outer layer. It is of course possible that the inner core of all particles contains a mixture of Pt(0) and RuO_2. One unexplained observation in this model is the great similarity of the Mössbauer signal from the RuO_2 phase for both Ru/C_t and Pt-Ru/C_t catalysts, although this may simply indicate that rutile RuO_2 does not interact with metallic platinum to any great extent.

The form of the second active phase of Ru(IV) remains to be considered. XPS data indicates there is no detectable amount of chloride present, which would rule out a chloro complex, and the N 1*s* signal was also very small, effectively disposing of a ruthenium nitrosyl complex. The balance of probability is, therefore, that the species is some sort of oxide/hydroxide with a small field gradient, and lacking any strong Ru–Ru interactions characteristic of RuO_2 itself. Clearly additional structural work is desirable here using EXAFS or XANES.

The final question is the mode of action of ruthenium. XPS data, presented elsewhere (*2*), have indicated that extensive oxygen spillover from ruthenium to platinum appears to be possible with Ru(IV), in contrast to Ir(IV) and Os(IV). Thus facile spillover appears to be associated with the active form of Ru(IV) and may arise from the possibility of very intimate association between Pt and Ru(IV) at the surface of the particles. One possibility is that the active oxide/hydroxide Ru(IV) phase can nucleate extremely easily at the surface of the stable RuO_2 form. It would be tempting to speculate that ruthenium was capable of efficient oxide spillover as the Ru(IV)/(III) couple was close to the potential at which hydroxy species form on platinum; however, no evidence from XPS and Mössbauer studies has been found for any other oxidation state except Ru(IV), and it seems likely at the moment that all redox processes actually take place at platinum. If so it is possible to propose a mechanism for methanol oxidation similar to that suggested for the valve-metals (*2*).



A **B** **C**

The active Ru surface species **A** is bonded to a Pt oxide and can supply the oxide groups necessary to complete the oxidation of methanol via a facile oxygen spillover process to give a species such as **B**. It is the Pt–OH group on **B** which reacts with Pt–CHO residue to complete the oxidation of methanol to CO_2. The reformation of **A** from **C** possibly involves oxidation of a water molecule that is part of the Ru coordination sphere. Future work is aimed at better characterizing the nature of the active Ru(IV) material, using both *in situ* and *ex situ* methods.

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