Mössbauer Characterization of Carbon Supported Ruthenium-Tin Catalysts

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¹¹⁹Sn and ⁹⁹Ru Mössbauer spectroscopy was used to investigate catalysts of ruthenium and tin supported on activated carbon (Ru–Sn/C) containing 2 wt % ruthenium and having Sn:(Sn+Ru) ratios between zero and 0.4. Samples were subjected to different reducing and oxidizing treatments, and suitable precursor products were studied. Four major components in the ¹¹⁹Sn Mössbauer spectra are attributed to oxidic Sn(II) and Sn(IV) and to Ru–Sn and Ru–Sn–O_x species forming on the surface of ruthenium metal particles. In addition to this, the ¹¹⁹Sn spectra reveal the presence of minor amounts of Ru₃Sn₇. While some of the features of the ⁹⁹Ru Mössbauer spectra cannot be interpreted unambiguously, the presence of tin leads to a substantial increase of the Lamb–Mössbauer factor of the metallic ruthenium particles, which shows that tin strengthens the attachment of the particles to the support even at very low tin loadings. None of the ruthenium–tin phases on the catalysts can be clearly identified as those responsible for the development of the catalytic activity and selectivity. The observed close contact between the two metals, however, appears to be decisive for the formation of catalytically active sites during the induction period at the beginning of the reaction.

Introduction

Among the group VIII metals, metallic ruthenium has long been known as an active catalyst for many processes, such as the hydrogenolysis of paraffins and olefins, 1,2 the Fischer— Tropsch synthesis,³ and the hydrogenation of alkenes and carbonyls.^{4–10} When supported ruthenium is used in hydrogenation reactions, the addition of small amounts of tin decreases the rate of hydrogenation of C=C groups in favor of the hydrogenation of C=O groups. 11-20 The development of highly selective heterogeneous catalysts for the hydrogenation of carbonyls in the presence of olefinic bonds is of interest, for instance, in the preparation of various fine chemicals²¹ and in the perfumery industry.²² The catalytic activity of ruthenium and ruthenium-tin supported on activated carbon has been studied for the selective reduction of α,β -unsaturated aldehydes such as citral^{23,24} and cinnamaldehyde.^{5,13} The reduction of both aldehydes can lead to a large variety of products obtained by addition of hydrogen, cyclization, or reaction with the solvent.

The catalytic activity of carbon-supported ruthenium—tin toward C=O groups decreases again, however, when the Sn: (Ru+Sn) atomic ratio becomes too high, the optimum value being close to 0.2.12 The suppression of the hydrogenation of C=C groups by tin has been attributed to electronic and/or structural modifications of the metallic ruthenium, i.e., to a decrease of the active surface of the ruthenium in the presence of tin.19 On the other hand, the increased hydrogenation rate of the carbonyl group has been related to the presence of ionic tin, which should enhance the reactivity of C=O groups by increasing their polarization.13 In this way, the polarized carbonyls are believed to become more reactive toward the

attack of a weak nucleophilic agent such as the hydrogen chemisorbed on the adjacent ruthenium atoms.

A previous HRTEM characterization of Ru-Sn/C catalysts showed that, in the absence of tin, the metallic ruthenium is present on the carbon support as small particles displaying the hexagonal lattice of bulk ruthenium with a mean diameter of about 6 nm. On addition of up to 20 at % (atomic %) of tin, the average size of the ruthenium particles decreases to about 3.5 nm. A further increase of the tin loading leads to a massive agglomeration of smaller particles and the appearance of a few particles with the fcc structure of the Ru₃Sn₇ intermetallic compound. The small content of metallic tin even at high tin loadings suggests that tin is mainly in the ionic form, probably covering the ruthenium particles. The presence of a tin layer on the surface of the ruthenium particles explains the observed decrease of the adsorption of carbon monoxide when the tin loading increases. Without the tin decoration, the decrease of the average size of the ruthenium crystallites going along with the addition of tin should increase the ruthenium surface available for CO adsorption.¹²

In the present work we report on a study of a series of Ru—Sn/C catalysts by ⁹⁹Ru and ¹¹⁹Sn Mössbauer spectroscopy. The study was undertaken to elucidate the physical and chemical state of tin and ruthenium on specimens containing different amounts of the two elements and subjected to different treatments. The presence of two Mössbauer isotopes makes this system an interesting case for the application of Mössbauer spectroscopy. Whereas in the past 20 years ¹¹⁹Sn Mössbauer spectroscopy has been widely applied in catalysis, mainly in the study of the supported Pt—Sn system,^{25–36} the ⁹⁹Ru Mössbauer resonance³⁷ has been used but rarely in studies of catalysts.^{38–41} Reasons for this may be the high energy of the nuclear transition, which requires cryogenic temperatures for both source and absorber, and also the short lifetime of the ⁹⁹Rh

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TABLE 1: Overview of the Pretreatment Conditions of the Catalysts

method	treatment after reduction in H_2 at 300 °C for 2 h
(a)	none
(b)	flushed with dried argon at room temperature for 1 h
(c)	flushed with argon saturated with water at room
	temperature for 1 h
(d)	exposed to air at room temperature for about 1 week

TABLE 2: Composition, CO Chemisorption, and Mean Ruthenium Particle Size of the Catalyst Specimens

sample ^a	Ru %	Sn %	100Ru/ (Ru+Sn)	100Sn/ (Ru+Sn)	CO:Ru ^b	d^{c} (nm)
Ru100/C Ru95/C Ru80/C Ru70/C Ru60/C	2.00 2.00 2.00 2.00 2.00	0.12 0.58 1.01 1.56	100 95 80 70 60	5 20 30 40	0.261 0.220 0.096 0.003	5.9 3.5 3.4 d

^a The number behind **Ru** indicates the ruthenium content in percent of the total metal content. ^b CO chemisorption capacity given as the number of molecules of CO chemisorbed per ruthenium atom. ⁷ Average diameter of the ruthenium particles according to TEM evaluations. ⁷ ^d Not evaluated. ^e Below the limit of detection.

source isotope, which is relatively expensive and difficult to prepare. 42 Despite their scarce application, the 89.4 keV γ -rays of ^{99}Ru are a useful tool to determine the chemical state of ruthenium. 42

Experimental Section

Materials. An overview of the different methods of preparation is given in Table 1. The names and the composition of the catalyst specimens are listed in Table 2. The samples were prepared by the conventional incipient wetness technique, i.e., by impregnating the activated carbon (Chemviron SCXII, 80–100 mesh, surface area 900–1100 m²/g) with hydrous solutions of RuCl₃ and SnCl₂·2H₂O of appropriate concentrations. After impregnation, the samples were dried in air at 120 °C for 1 h. Some samples were subdivided into several parts, which were then treated under the following slightly different conditions:

- (a) The samples were filled into cylindrical glass ampules with a diameter of about 1.0 cm, a height of about 1.5 cm and two attached glass tubes. They were then reduced at 300 °C for 2 h by hydrogen entering and leaving the ampule through the glass tubes. After cooling to room temperature and before sealing off the tubes, the hydrogen flow was changed to helium. The helium atmosphere guarantees the sample material to cool rapidly to 4.2 K when the sealed ampules are immersed into liquid helium for the Mössbauer measurements. The same sealed catalyst samples were used in both ⁹⁹Ru and ¹¹⁹Sn Mössbauer experiments.
- (b) The samples were reduced by flowing hydrogen in a fixed-bed glass reactor at 300 °C for 2 h and then cooled to room temperature in flowing hydrogen. They were then flushed with argon for 1 h and the reactor was immersed into liquid nitrogen. The argon used for flushing the samples was dried by passing it first through concentrated $\rm H_2SO_4$ and then through a bed of silica gel. During the subsequent preparation and handling of the Mössbauer absorbers, the sample material was kept in liquid nitrogen. The catalyst samples were measured by 99 Ru and 119 Sn Mössbauer spectroscopy using the same absorbers for both measurements.
- (c) A portion of sample **Ru70/C** was treated as described in (b), except that the argon flushed through the sample was saturated with water vapor by bubbling it through distilled water at room temperature.

TABLE 3: ¹¹⁹Sn Mössbauer Parameters at 4.2 K for the Reference Materials

				chemical
	QS	IS^a	area	form
sample	(mm/s)	(mm/s)	(%)	of Sn
SnCl ₂ ·2H ₂ O	1.30(1)	3.66(1)	100	SnCl ₂ •2H ₂ O
frozen aq soln	1.30(1)	3.64(1)	97(1)	$SnCl_2 \cdot 2H_2O$
of SnCl₂ 2H₂O , 48 mmol/L	0.7(2)	-0.1(2)	3(1)	Sn(IV)
Sn100/C	1.90(1)	3.12(1)	31(1)	Sn(II) adsorbed
as prepared, wet	0.62(1)	0.00(1)	69(1)	Sn(IV)
Sn100/C	1.87(2)	3.10(1)	18(1)	Sn(II) adsorbed
as prepared, dried in vacuo	0.64(1)	0.02(1)	82(1)	Sn(IV)
Sn100/C	1.88(3)	3.11(2)	19(1)	Sn(II) adsorbed
reduced in H ₂ at 300 °C for 2 h	0.62(2)	0.01(1)	81(1)	Sn(IV)
Sn100/C	2.24(4)	2.87(2)	14(1)	Sn(II)
reduced in H ₂	0.55(2)	0.01(1)	24(1)	Sn(IV)
at 400 °C for 2 h	0.00	2.54(1)	62(1)	β -Sn metal
aq soln of	0.52(1)	0.01(1)	69(1)	Sn(IV)
SnCl ₂ and RuCl ₃	2.21(1)	1.84(1)	31(1)	oxidic Ru-Sn
Ru70/C	0.62(1)	-0.01(1)	79(1)	Sn(IV)
dried in vacuo, before reduction	2.22(3)	1.81(2)	9(1)	oxidic Ru-Sn

^a The isomer shift scale is referred to the CaSnO₃ source.

(d) The samples were prepared as in (b) and then exposed to air for about a week at room temperature before the $^{99}\mathrm{Ru}$ and $^{119}\mathrm{Sn}$ Mössbauer measurements.

The samples prepared by method (a) are supposed to resemble most closely the in situ conditions of the catalysts. The slightly different methods of preparation were chosen to facilitate the interpretation of the complicated ¹¹⁹Sn Mössbauer spectra, since slight modifications in the method of preparation were expected to cause changes mainly in the relative intensity of the different spectral components.

For comparison, a monometallic sample labeled **Sn100/C** and containing 2% of Sn was prepared according to method (b). In this case, the reduction was performed not only at 300 °C as for the catalyst specimens, but also at 400 °C. Moreover, to compare the reduction behavior of supported and unsupported ruthenium, pure ruthenium dioxide was reduced at 300 °C under the same experimental conditions as the catalysts (method (b)).

Mössbauer Spectroscopy. The 89.4 keV transition in ⁹⁹Ru takes place between the first excited state with spin 3/2 and the 5/2 ground state. The ⁹⁹Rh isotope feeding the 89.4 keV Mössbauer transition has a half-life of 16 d and was produced by cyclotron irradiation of isotopically enriched ¹⁰⁰Ru metal, using the ¹⁰⁰Ru (p,2n) ⁹⁹Rh reaction with 30 MeV protons. The irradiated Ru metal was used in the Mössbauer experiments without further treatment. Ru metal is well-suited as the source matrix although its hcp structure gives rise to a small unresolved electric quadrupole interaction.⁴³ Despite this splitting, the experimental line width obtained with ruthenium metal sources is close to the natural width of 0.149 mm/s expected for the half-life of 20.5 ns of the 89.4 keV excited state. 44 In the fits of the ⁹⁹Ru spectra, the electric field gradient was always assumed to be axially symmetric and the small splitting of the 5/2 ground state was taken into account as well as the small quadrupole splitting in the source.⁴²

The source of ^{119m}Sn in a matrix of CaSnO₃, used for the Mössbauer measurements with the 23.9 keV resonance of ¹¹⁹Sn,

was purchased from Amersham International. The ^{119m}Sn isomer shifts are given with respect to the CaSnO₃ source.

For all Mössbauer experiments, the source and the absorber were cooled to 4.2 K in a liquid helium bath cryostat. The Mössbauer spectrometer was operated with a sinusoidal velocity wave form. For γ -ray detection an intrinsic Ge detector was used. The 99 Ru spectra were fitted with appropriate superpositions of Lorentzian lines. The 119 Sn Mössbauer spectra were fitted with transmission integrals by using the MOS-90 computer program. In the case of 119 Sn, the lines were grouped into quadrupole doublets, which were assumed to be symmetric, i.e., it was assumed that there is no Goldanskii—Karyagin effect. This assumption is justified by the fact that the spectra could be fitted consistently in this way.

The quadrupole components of the ¹¹⁹Sn Mössbauer spectra were often found to be broadened. This line broadening was taken into account by assuming Gaussian distributions of the electric quadrupole interaction. The width of the Gaussian distributions never exceeded 0.25 mm/s.

The least-squares fits of the ⁹⁹Ru and ¹¹⁹Sn Mössbauer spectra yielded the mean electric quadrupole splitting (QS), the mean isomer shift (IS), and the relative resonance areas (area) of the different components of the spectra. These parameters are listed in Tables 3–5.

For the fitting with transmission integrals,⁴⁶ the program calculates the transmission integral spectrum according to the formula

$$I(v) = I_0 \left\{ 1 - f_S \left[1 - \int_{-\infty}^{\infty} \frac{\Gamma_S/2\pi}{(\Gamma_S/2)^2 + (v - v')^2} \times \exp \left(-\sum_i \frac{d_i(\Gamma_i/2)^2}{(\Gamma_i/2)^2 + (v_i - v')^2} \right) dv' \right] \right\}$$

where I_0 is the baseline, $f_{\rm S}$ is ideally the f-factor of the source, $\Gamma_{\rm S}$ is the width of the source spectrum (in mm/s), and v_i , Γ_i , and d_i are position, width, and depth of the ith Lorentzian in the absorption cross-section of the absorber.

In reality, f_S is not the true Lamb—Mössbauer factor of the source, but is usually reduced by resonant self-absorption in the source and by the background radiation detected in the single-channel window set on the γ -ray spectrum. Therefore, its value must be determined separately for a given experimental arrangement by measuring the spectra of a reference material of known thickness, for which the Lamb—Mössbauer factor and the resonant absorption cross-section are known at the temperature of interest.⁴⁷

Since it is not possible to rigorously separate the different components of transmission integral patterns, Lorentzian lines are shown in the figures of spectra fitted by transmission integrals to approximate the individual spectral components.

Results and Discussion

119Sn Mössbauer Spectroscopy. 119Sn Mössbauer spectra were measured after the different treatments of the samples. For comparison, measurements of frozen solutions and other reference materials were taken. Some of the spectra are shown in Figures 1, 2, and 3. The Mössbauer parameters of the frozen solutions and of the reference materials are reported in Table 3. The Mössbauer parameters of the catalysts are reported in Table 4

Reference Materials. The Mössbauer spectrum of crystalline SnCl₂•2H₂O (Figure 1) consists of a doublet with a quadrupole

TABLE 4: ¹¹⁹Sn Mössbauer Parameters at 4.2 K for the Catalyst Samples

					chemical
prep		QS	IS^a	area	form
method	sample	(mm/s)	(mm/s)	(%)	of Sn
(a)	Ru95/C	1.7(1)	1.60(5)	15(3)	oxidic Ru-Sn
		1.12(3)	2.28(3)	73(3)	surface Sn
		1.86(6)	2.91(4)	12(3)	Sn(II)
	Ru80/C	0.50(8)	0.10(7)	2(2)	Sn(IV)
		1.54(9)	1.50(6)	16(2)	oxidic Ru-Sn
		1.29(2)	2.38(2)	59(2)	surface Sn
		1.86(8)	2.90(5)	23(2)	Sn(II)
	Ru70/C	0.7(1)	0.1(1)	3(2)	Sn(IV)
		1.62(6)	1.47(7)	25(2)	oxidic Ru-Sn
		1.33(8)	2.27(5)	32(3)	surface Sn
		1.96(5)	2.92(3)	40(2)	Sn(II)
(b)	Ru95/C	0.65(5)	0.06(5)	22(3)	Sn(IV)
		1.52(5)	1.48(5)	28(3)	oxidic Ru-Sn
		1.33(5)	2.18(3)	36(2)	surface Sn
	D 0010	1.90(6)	2.94(5)	14(1)	Sn(II)
	Ru80/C	0.54(5)	0.08(7)	10(2)	Sn(IV)
		1.44(7)	1.43(6)	25(2)	oxidic Ru-Sn
		1.30(5)	2.27(4)	33(2)	surface Sn
	D =0/G	1.89(8)	2.89(4)	32(1)	Sn(II)
	Ru70/C	0.54(4)	0.09(5)	8(2)	Sn(IV)
		1.58(3)	1.53(2)	28(2)	oxidic Ru-Sn
		1.29(4)	2.32(3)	28(1)	surface Sn
	Ru60/C	2.00(3)	2.90(2)	36(1)	Sn(II)
	Ruou/C	0.40(7)	0.08(6)	2(2)	Sn(IV) oxidic Ru-Sn
		1.64(1) 1.44(2)	1.67(2) 2.30(2)	27(1) 32(1)	surface Sn
		1.44(2)	2.93(1)	39(1)	Sn(II)
(c)	Ru70/C	0.62(1)	0.04(1)	51(1)	Sn(IV)
(C)	Ku/0/C	1.64(3)	1.55(2)	30(1)	oxidic Ru-Sn
		2.12(4)	2.91(2)	19(1)	Sn(II)
(d)	Ru95/C	0.71(2)	0.13(1)	98(1)	Sn(IV)
(u)	Russic	0.00	1.5(1)	1(1)	Ru_3Sn_7 (I)
		0.7(1)	2.7(1)	1(1)	Ru_3Sn_7 (II)
	Ru80/C	0.78(1)	0.12(1)	97(1)	Sn(IV)
		0.00	1.5(1)	2(1)	Ru ₃ Sn ₇ (I)
		0.7(1)	2.67(9)	1(1)	Ru ₃ Sn ₇ (II)
	Ru70/C	0.78(1)	0.11(1)	91(1)	Sn(IV)
		0.00	1.49(7)	4(1)	$Ru_3Sn_7(I)$
		0.70(8)	2.65(5)	5(1)	Ru_3Sn_7 (II)
	Ru60/C	0.77(1)	0.11(1)	92(1)	Sn(IV)
		0.00	1.49(6)	4(1)	$Ru_3Sn_7(I)$
		0.71(8)	2.68(5)	4(1)	Ru_3Sn_7 (II)

^a The isomer shift scale is referred to the CaSnO₃ source.

splitting of 1.30(1) mm/s and an isomer shift of 3.66(1) mm/s. The frozen aqueous solution of SnCl₂·2H₂O (48 mmol/l) used for preparing the monometallic sample **Sn100/C** exhibits two components, of which the main one has the same Mössbauer parameters as SnCl₂·2H₂O and is probably representing SnCl₂·2H₂O precipitated from the aqueous solution during freezing. The weaker component, with a relative intensity of 3%, is attributable to Sn(IV) formed by incipient oxidation of the Sn(II) in the solution.

The Mössbauer spectra collected before and after drying the monometallic sample Sn100/C (prepared by impregnation of carbon with the aqueous solution of $SnCl_2 \cdot 2H_2O$) also exhibit two components, attributable to Sn(II) and Sn(IV) (Figure 1). The Sn(IV) component, which probably represents an oxidic species, is now the stronger one, whereas the Mössbauer parameters of the weaker Sn(II) doublet are different from those of crystalline $SnCl_2 \cdot 2H_2O$. Although the Sn(II) component cannot be attributed to a specific species, its Mössbauer parameters (Table 3) are comparable to those reported for hydrated Sn(II) oxides or hydroxides, such as $SSnO \cdot 2H_2O$ (QS = 2.04 mm/s, IS = 2.85 mm/s), SIS = 2.85 mm/s, SIS = 2.85 mm/s, and SIS = 2.85 mm/s, and SIS = 2.85 mm/s, SIS = 2.85 mm/s, and SIS = 2.85 mm/s, SIS = 2.85 mm/s, and SIS = 2.85 mm/s, SIS = 2.85 mm/s, and SIS = 2.85 mm/s, SIS = 2.85 mm/s, and SIS = 2.85 mm/s, SIS = 2.85 mm/s, and SIS = 2.85 mm/s, SIS = 2.85 mm/s, and SIS = 2.85 mm/s, SIS = 2.85 mm/s, and SIS = 2.85 mm/s, and SIS = 2.85 mm/s, SIS = 2.85 mm/s

TABLE 5: ⁹⁹Ru Mössbauer Parameters at 4.2 K for the Catalyst Samples

Cuturyst	Catalyst Samples					
		0.0	10.		chemical	
prep		QS	IS^a	area	form	
method	sample	(mm/s)	(mm/s)	(%)	of Ru	
(a)	Ru100/C	0.00	0.00(5)	6(9)	Ru metal	
		-0.36(5)	-0.20(4)	94(9)	Ru(IV)	
	Ru95/C	0.00	0.00(2)	71(5)	Ru metal	
		0.00	-0.16(5)	14(4)	Line A	
		0.00	-0.43(4)	15(3)	Line B	
	Ru80/C	0.00	0.01(1)	64(4)	Ru metal	
		0.00	-0.20(2)	24(4)	Line A	
		0.00	-0.56(3)	12(3)	Line B	
	Ru60/C	0.00	-0.01(2)	55(7)	Ru metal	
		0.00	-0.22(3)	30(5)	Line A	
		0.00	-0.48(4)	15(4)	Line B	
(b)	Ru100/C	0.00	0.00(3)	22(7)	Ru metal	
		-0.33(4)	-0.22(5)	78(7)	Ru(IV)	
	Ru95/C	0.00	0.00(1)	68(5)	Ru metal	
		0.00	-0.19(5)	16(4)	Line A	
		0.00	-0.39(3)	16(4)	Line B	
	Ru80/C	0.00	0.01(1)	61(5)	Ru metal	
		0.00	-0.19(3)	28(4)	Line A	
		0.00	-0.48(4)	11(3)	Line B	
	Ru70/C	0.00	0.00(2)	60(6)	Ru metal	
		0.00	-0.21(3)	32(5)	Line A	
		0.00	-0.47(8)	8(5)	Line B	
(d)	Ru100/C	-0.46(2)	-0.29(3)	100	Ru(IV)	
	Ru95/C	0.00	0.00(1)	51(4)	Ru metal	
		0.00	-0.21(3)	29(4)	Line A	
		0.00	-0.49(3)	20(4)	Line B	
	Ru80/C	0.00	0.00(1)	56(3)	Ru metal	
		0.00	-0.23(2)	30(3)	Line A	
		0.00	-0.54(3)	14(3)	Line B	
	Ru60/C	0.00	-0.01(1)	60(4)	Ru metal	
		0.00	-0.25(3)	28(4)	Line A	
		0.00	-0.47(4)	13(4)	Line B	

^a The isomer shift scale is referred to ruthenium metal.

mm/s).⁴⁹ It is likely that in **Sn100/C** the tin is adsorbed onto the activated carbon with a nearest coordination shell containing hydroxyl ions and/or water molecules in addition to chlorine ions. In fact, the decrease of the isomer shift observed for the adsorbed Sn(II) reveals a decrease of the s-electron density at the tin nucleus with respect to that of $SnCl_2 \cdot 2H_2O$. The decrease in s-electron density and the concomitant increase of the electric quadrupole splitting indicate a more covalent bonding for tin in the adsorbed species than in $SnCl_2 \cdot 2H_2O$.

In a subsequent step, Sn100/C was exposed to hydrogen gas at 300° and 400 °C in a gas flow reactor. At 300 °C the Mössbauer spectrum is practically identical to that of the sample before reduction, indicating that no reduction has taken place. At 400 °C the reduction takes place since the single line of metallic β -Sn is observed in addition to two weaker quadrupole doublets. One of these doublets is attributable to oxidic Sn(IV) and the other to Sn(II) species with parameters very close to those of the Sn(II) on the unreduced specimen.

The ¹¹⁹Sn Mössbauer spectrum of a frozen solution containing both SnCl₂•2H₂O and RuCl₃•xH₂O (Figure 1) is different from that of the frozen solution containing only SnCl₂•2H₂O. The most prominent spectral component is an unresolved quadrupole doublet attributable to Sn(IV), whereas the other component is a doublet with an isomer shift clearly attributable to neither Sn(IV) nor Sn(II). The dominance of Sn(IV) in the solution of SnCl₂•2H₂O and RuCl₃•xH₂O shows that Sn(II) is oxidized to Sn(IV), accompanied by the reduction of Ru(III) to Ru(II). ⁵⁰ It is known⁵¹ that in acidic aqueous solutions of RuCl₃•xH₂O and SnCl₂•2H₂O, the mixed metal complex [Cl₂Ru(SnCl₃)₂]²⁻ forms, in which tin bonds to the ruthenium and to three chlorine atoms.

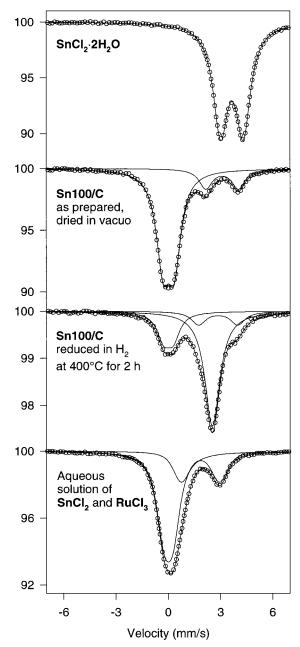


Figure 1. ¹¹⁹Sn Mössbauer spectra at 4.2 K of some of the reference materials

The ¹¹⁹Sn Mössbauer parameters of the corresponding salts (QS = 1.93 mm/s, IS = 1.84 mm/s for the tetramethylammonium salt; QS = 1.97 mm/s, IS = 1.83 mm/s for the triphenylphosphonium salt)^{52,53} are very close to those observed in the spectrum of the solution of SnCl₂•2H₂O and RuCl₃•xH₂O (Table 3), which indicates that a mixed-metal ruthenium—tin complex with ruthenium—tin bonds is formed.

It is also interesting to note that the Mössbauer parameters of the weaker component in the solution are close to those of the main component in the $^{119}\mathrm{Sn}$ spectrum of $Ru_3Sn_{15}O_{14}$ (QS = 2.26 mm/s, IS = 1.56 mm/s). 54 The tin atoms in this case are bonding to four oxygen ligands and a ruthenium atom. The crystalline $Ru_3Sn_{15}O_{14}$ mixed oxide, however, is obtained by the reaction of an appropriate mixture of RuO_2 , SnO_2 , and Sn metal at about 900 °C in a sealed quartz tube. 54 Therefore, it is unlikely that this phase forms in solution. The similarities of the Mössbauer parameters, however, suggest the presence of oxygen-bonded tin species with intermetallic bonds between ruthenium and tin in the solution. One thus concludes that the

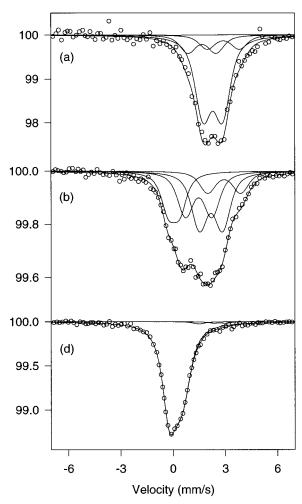


Figure 2. 119Sn Mössbauer spectra of the Ru95/C catalysts obtained by preparation methods (a), (b), and (d).

tin in the ruthenium-tin solution forms metal-metal bonds with ruthenium and additionally has oxygen or chlorine ligands, or both. We will henceforth call this species "oxidic Ru-Sn".

The tin species observed in the Mössbauer spectrum of an unreduced precursor sample of the Ru-Sn/C catalysts (Ru70/ C, Table 2) are very similar to those of the frozen solution of SnCl₂•2H₂O and RuCl₃•xH₂O, but the Sn(IV) component is more intense, showing that the deposition on the carbon goes along with a further oxidation of the stannous component.

Catalyst Samples. Selected 119Sn Mössbauer spectra of the specimens Ru95/C and Ru70/C prepared by the different methods are shown in Figures 2 and 3. The samples Ru95/C, Ru80/C, Ru70/C, and Ru60/C were prepared according to the methods (a), (b), and (d). Ru70/C was also made according to method (c). It appears reasonable to assume that, on going from preparation method (a) to method (d), the specimens are increasingly exposed to oxidation, either by traces of water present in the helium or argon gas flushed through the samples after reduction or by contact with air in the case of the method (d). The Mössbauer spectra of the samples treated according to the different methods were fitted assuming that the same components should be present in the different samples, but with relative areas depending on the reactivity toward oxidation.

The Mössbauer spectra of the catalysts prepared by method (d), i.e., by exposing the previously reduced samples to air at room temperature for about a week, are the least complicated. They consist of a main component with the typical parameters of Sn(IV) and of a shoulder at the positive velocity side of the

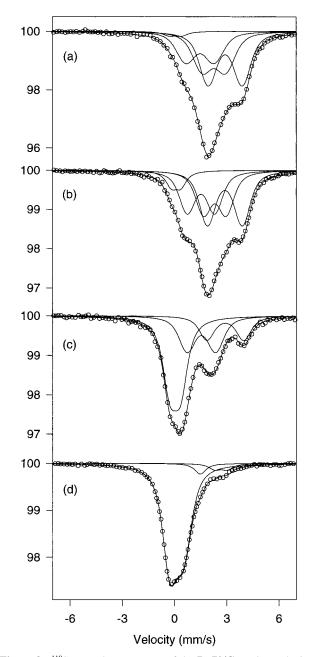


Figure 3. 119Sn Mössbauer spectra of the Ru70/C catalysts obtained by preparation methods (a), (b), (c), and (d).

spectra. This shoulder is very weak at low tin loadings (Ru95/C and Ru80/C), but becomes more intense for samples with higher tin contents (Ru70/C and Ru60/C). The shoulder can be fitted by the two typical components of Ru₃Sn₇. The ¹¹⁹Sn Mössbauer spectrum of Ru₃Sn₇ consists of a single line (IS = 1.487(5)mm/s) and of a doublet (QS = 0.704(7) mm/s, IS = 2.671(7)mm/s) attributable to the two different crystallographic tin sites.⁵⁴ The presence of small amounts of Ru₃Sn₇ is in agreement with previously reported HRTEM studies of similar samples after exposure to air. These studies revealed minor amounts of Ru₃-Sn₇ in the samples Ru70/C and Ru60/C but its absence in Ru95/C and Ru80/C. This is in agreement with the Mössbauer results which show traces of the alloy in the latter samples.

The samples not exposed to oxidation in air, i.e., those prepared by methods (a) and (b), yield more complicated ¹¹⁹Sn Mössbauer patterns (Table 4 and Figures 2 and 3). At least four different spectral components are necessary to fit the spectra of the samples prepared by method (a). These four components are present in all spectra of samples prepared according to method (a) with nearly the same Mössbauer parameters, but with different relative intensities. The four spectral components are discussed in the following:

(1) The component with the most positive isomer shift (about 2.9 mm/s) is similar to that observed in stannous hydrous oxides or hydroxides^{48,49} and in the monometallic sample **Sn100/C** (Table 3).

(2) The component with an isomer shift between 2.2 and 2.4 mm/s, which is slightly less than the shift of metallic β -Sn (IS = 2.56(1) mm/s), has a noticeable quadrupole splitting of about 1.3-1.4 mm/s. The values of isomer shift and quadrupole splitting are too small to be attributed to divalent tin. Bulk β -Sn does not exhibit a quadrupole splitting, but a quadrupole doublet very similar to the component described above has been observed by Bowles et al.,55 who identified it with monolayers of metallic tin on platinum. For these monolayers, the isomer shift was found to be slightly smaller than that of β -Sn, as expected for tin in a platinum host. In fact, for tin in transition metal hosts, the increase of the effective p- and d-electron population at the tin results in a decrease of the isomer shift with respect to β -Sn, a result of the shielding effect of p and d electrons on the s electrons.⁵⁶ A similar effect is also expected in the case of monolayers of tin on ruthenium.

In previous studies of supported platinum—tin catalysts, 26,28,29,31,36 the Mössbauer components with an isomer shift smaller than that of β -Sn and a small quadrupole splitting were assigned to platinum—tin alloys. In contrast to platinum, tin is virtually insoluble in ruthenium and only two intermetallic compounds, Ru_2Sn_3 and Ru_3Sn_7 , are known. The Mössbauer patterns of both intermetallics are different from those of the component found in the Ru–Sn/C catalysts. The Mössbauer

In bimetallic particles consisting of metals with a miscibility gap in the binary phase diagram, a surface segregation of the metals is expected. Two models account for surface enrichment in such alloys: the first is the broken-bond model, which predicts an enrichment of the component with the lower heat of sublimation at the surface of the particle. The second is the size-difference model, which proposes an enrichment of the component with larger atomic volume at the surface. Both models suggest a segregation of tin on the surface of ruthenium—tin particles. Therefore, it is plausible to assign the second component in the Mössbauer spectra to metallic tin covering the ruthenium particles.

One should note, however, that on small aggregates such as the ruthenium crystallites on carbon detected by HRTEM (Table 2), there are surface sites of different topologies such as low index planes, kinks, edges, and corners. In principle, the distribution of the two components of the bimetallic particles could be ordered, with one component preferentially occupying sites of a given topology.⁶⁰ The differences between different surface sites may, however, be too small to be resolved in the Mössbauer spectra.

The spectral component with an isomer shift, as well as a quadrupole splitting of about 1.5 mm/s, is similar to the component attributed to "oxidic Ru-Sn" in the unreduced samples and in the frozen hydrous solution of SnCl₂•2H₂O and RuCl₃•xH₂O. The difference between the Mössbauer parameters of this component in reduced catalysts and the unreduced precursor of **Ru70/C** (Table 3) suggests a rearrangement in the structure of the mixed oxide during reduction.

The spectral component near zero velocity is observed in all but the spectrum of **Ru95/C** prepared according to method (a)

and is attributable to Sn(IV), most probably present as a SnO₂-like oxidic species.

The spectra of the samples prepared by method (b) contain the four components detected in the spectra of the samples prepared by method (a), but with different relative intensities. In particular, the component attributable to surface tin on ruthenium particles is weaker, whereas the components attributable to the various oxidic species are more intense.

The addition of water to the argon flushed through the sample Ru70/C after the reduction treatment (method (c)) caused the disappearance of the component attributed to metallic tin at the surface of the ruthenium particles. The Mössbauer spectrum was fitted with the remaining three components (Table 3) attributable to Sn(IV), Sn(II) oxide, and the oxidic Ru—Sn species. The disappearance of the surface tin component leaves the relative intensity of the Sn(II) oxide and the oxidic Ru—Sn nearly unchanged, whereas that of the Sn(IV) oxide component increases noticeably, indicating that the surface tin becomes stannic oxide. The oxidation of the surface component thus reveals its sensitivity to small amounts of water in the atmosphere surrounding the catalyst sample.

In the spectra of the samples prepared by methods (a), (b), and (c), small amounts of Ru₃Sn₇ may be present but could not be detected in the Mössbauer spectra because of the presence of the much stronger Mössbauer patterns of the other tin species. The presence of Ru₃Sn₇ in the catalyst samples is suggested by HRTEM⁷ and by the Mössbauer spectra of the samples exposed to air (method (d)). Its presence in the latter Mössbauer spectra (Figures 2 and 3), in fact, suggests that Ru₃Sn₇ was already present before the exposure of the respective samples to air, since it is highly improbable that Ru₃Sn₇ forms in the course of the oxidation process. On the other hand, Ru₃Sn₇ is supposed to be sufficiently stable toward oxidation to be left over after all other tin species were oxidized to Sn(IV). When the spectra of the samples made according to methods (a) and (b) were fitted with the two components of Ru₃Sn₇ added to the other four spectral components, however, the fit would converge only when the relative intensities of the two Ru₃Sn₇ components were fixed, for instance, to the values obtained from the spectra of the oxidized samples. Even then the quality of the fit increased but marginally, while the values of the other fit parameters changed only slightly. The components of Ru₃Sn₇ were therefore omitted in the fits yielding the results given in Table 4.

To summarize the ¹¹⁹Sn Mössbauer results, the hyperfine parameters of the different tin species obtained for the different samples are displayed on the QS vs IS diagram in Figure 4. The Mössbauer parameters of the four components present in the catalyst samples form four compact groups. Two further groups represent the two spectral components of Ru₃Sn₇ observed in the samples prepared by method (d). The fact that within each group the Mössbauer parameters vary but slightly for samples prepared by the different methods supports the interpretation of the spectra in terms of these components, while the comparison with literature data, also displayed in Figure 4, allows the identification of these groups with specific tin species.

One should note, however, that the relative spectral areas given in Tables 2 and 3 are proportional to the products of the respective amounts of tin and the Lamb—Mössbauer factors of the individual species. Since the latter are unknown and could not be determined in the course of this work, the Mössbauer spectra represent changes in the abundance of the individual species correctly, but not necessarily the abundances themselves.

Finally, it is also worth noting that consistent fits of all spectra could be obtained without allowing for an asymmetry of the

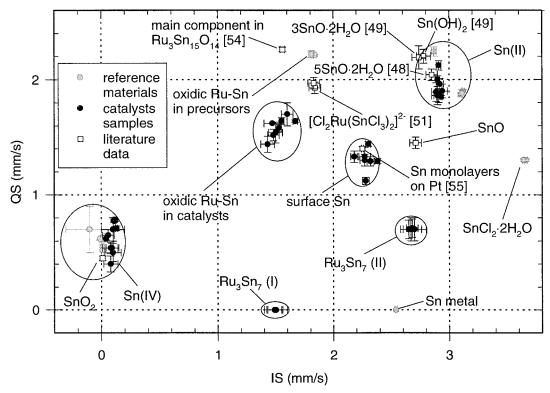


Figure 4. ¹¹⁹Sn Mössbauer quadrupole splitting vs isomer shift for reference and catalyst samples. The parameters for SnO₂ and SnO are taken from Greenwood, N. N.; Gibb, T. C. Mössbauer Spectroscopy; Chapman & Hall: London, 1971. The references to the other literature data are the numbers in square brackets following the names of the compounds.

quadrupole doublets caused by the Goldanskii-Karyagin effect, i.e., by an anisotropy of the Lamb-Mössbauer factor. A substantial influence of the Goldanskii-Karyagin effect on the spectra of Pt-Sn catalysts supported on alumina was reported by Bacaud et al.²⁶ for spectra taken at ambient temperature and attributed to surface tin atoms. The absence of the Goldanskii-Karyagin effect in the Ru-Sn/C catalyst spectra reported here may be due to smaller vibrational anisotropies at liquid helium temperature.

99Ru Mössbauer Spectroscopy. 99Ru Mössbauer spectra were measured for several reference materials and for the catalyst samples. Some of the spectra are shown in Figures 5, 6, and 7. The 99Ru Mössbauer parameters of the catalysts are reported in Table 5.

Reference Materials. The 99Ru Mössbauer spectrum of metallic ruthenium (Figure 5) is a single line with zero isomer shift, since a Ru metal matrix is also used for the source. The spectrum of bulk RuO2 (Figure 5) is an electric quadrupole pattern with an isomer shift of -0.26(1) mm/s and a quadrupole splitting of -0.50(1) mm/s, in agreement with the early results published by Kaindl et al.61 The negative sign of the electric quadrupole interaction, determined from the shape and asymmetry of the spectrum assuming an axially symmetric electric field gradient, is in agreement with the literature. When wellcrystallized RuO2 is reduced under the same conditions as the catalyst specimens and then exposed to air, the Mössbauer spectrum shows only metallic ruthenium (Figure 5).

Catalyst Samples. The Mössbauer spectra of the reduced monometallic ruthenium catalyst Ru100/C obtained by methods (a) and (b) (Table 5 and Figure 6) show a strong quadrupole component and, at least in the case of method (b), an additional single line of metallic ruthenium at zero velocity. The quadrupole pattern has an isomer shift of -0.20 mm/s and a quadrupole splitting of 0.35 mm/s, whose sign cannot be determined unambiguously because of the insufficient resolution and

statistical accuracy of the spectra. The parameters of this component fall into the range found for Ru(IV) compounds⁴² and are compatible with a badly crystallized form of RuO₂,⁴¹ particularly if one assumes the sign of the electric quadrupole interaction to be negative, as has been done in the fits (Figure 6) and in Table 5. After exposure to air (method (d)), the monometallic Ru100/C sample shows only a quadrupole pattern with a larger splitting, which brings the parameters closer to those of crystalline RuO₂.

The ⁹⁹Ru Mössbauer results for the monometallic samples contrast with those obtained by HRTEM studies, which revealed only metallic ruthenium particles even in a sample exposed to air before the measurement.7 The observation of mainly ruthenium oxide in the Mössbauer spectra can have different reasons. At a first glance, it suggests the presence of ruthenium in the oxidized state. Preparation according to methods (a) and (b) appears to cause no or at best a partial reduction, and on subsequent exposure to air (method (d)) a virtually complete reoxidation to ruthenium oxide seems to take place, in blatant contrast to the HRTEM results.

An explanation for this discrepancy could be that the Lamb— Mössbauer *f*-factor for the small metallic ruthenium particles is much smaller than that of bulk metallic ruthenium and also much smaller than that of both bulk and supported ruthenium oxide. Such an effect was reported by Clausen et al.,38 who found a dramatic reduction of the Lamb-Mössbauer f-factor of metallic ruthenium particles supported on silica over that of bulk ruthenium metal. In this case the f-factor for the metallic ruthenium particles was in fact so low that the metallic ruthenium was not visible in the Mössbauer spectra at all. This was attributed to the weak binding of the metallic ruthenium particles to the silica support. Clausen et al.³⁸ claim that only particles with a diameter bigger than about 40 nm can be detected in the Mössbauer spectra, if they are but losely bound to the support. A rather different picture emerged for metallic

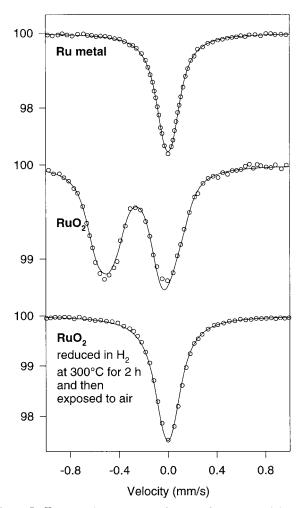


Figure 5. 99Ru Mössbauer spectra of some reference materials.

ruthenium supported on alumina, where stronger interactions with the support resulted in a larger Lamb—Mössbauer *f*-factor.³⁸

Although a direct measurement of the Lamb-Mössbauer f-factor was not attempted for the catalyst samples, a rather good estimate of f-factor ratios between different samples can be obtained by comparing the values of the total resonance area of the spectra with the ruthenium content per unit absorber area. The 89.4 keV line in the γ -ray spectrum obtained with a germanium detector is well separated from other lines and is much stronger than the background. A determination of the lineto-background ratio was performed for several measurements and consistently gave about 8-9% of background counts in the window set on the 89 keV line. This background does not change noticeably during the aging of the source. Therefore one can confidently assume that the total resonance area is directly proportional to the product of the absorber thickness expressed in mg(Ru)/cm² and the respective f-factor. The ratio of the f-factors for the bulk RuO2 and the bulk ruthenium metal standards (Figure 5) has been determined in the course of this work as $f(RuO_2)/f(Ru\text{-metal}) = 1.47(3)$.

For the monometallic **Ru100/C** samples obtained by methods (a) and (b), the observed total resonance area is about an order of magnitude smaller than that expected for the *f*-factor of bulk RuO₂ and the thickness of the catalyst absorber, indicating a dramatic decrease of the overall *f*-factor in the catalysts. A similar though less drastic result is obtained for the sample exposed to air, i.e., prepared by method (d), for which the total resonance area is half of that expected for bulk RuO₂. If one assumes that the ruthenium oxide supported on carbon has the

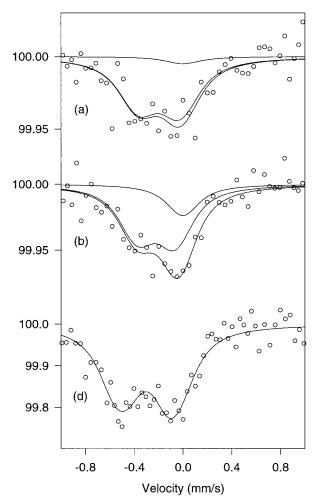


Figure 6. ⁹⁹Ru Mössbauer spectra of the **Ru100/C** catalysts obtained by preparation methods (a), (b), and (d).

same or a slightly smaller *f*-factor than bulk RuO₂, the Mössbauer spectra suggest that the metallic ruthenium particles are largely underrepresented because of weak bonding to the carbon surface, such as in the case of ruthenium on silica.³⁸ The weak interaction of the metallic ruthenium particles with the support thus leads to an underestimate of the content of metallic ruthenium. The *f*-factor considerations, however, suggest that for samples prepared by methods (a) and (b), the majority of the ruthenium is metallic in the form of particles that escape observation because of their small size and weak binding to the support. The increase of the total resonance area in the monometallic sample exposed to air will then be due to the transformation of some of the metallic ruthenium into ruthenium oxide.

The ⁹⁹Ru Mössbauer spectra of the bimetallic samples **Ru95**/ **C, Ru80/C, Ru70/C,** and **Ru60/C** are different from those of the monometallic **Ru100/C**. Samples prepared by methods (a) and (b) give almost identical Mössbauer spectra (Table 5 and Figure 7), with a dominant component at zero velocity typical of metallic ruthenium and additional components at the negative velocity side of the spectra, where there is a shoulder at about -0.2 mm/s and another component at about -0.5 mm/s. Owing to their different intensities, these two components cannot be fitted by a quadrupole doublet as for the monometallic samples, and therefore were fitted by two broad single lines with different isomer shifts, called line A and line B. Although the isomer shift of the two components is quite constant in the spectra of the different samples, both components could be either single lines or belong to quadrupole doublets, the second component

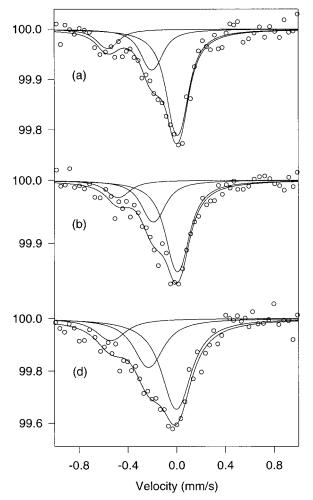


Figure 7. 99Ru Mössbauer spectra of the Ru80/C catalysts obtained by preparation methods (a), (b) and (d).

of which may coincide with the line of metallic ruthenium at zero velocity.

In particular, line B, which has an isomer shift of about -0.5mm/s, could be one of the two components forming a doublet attributable to RuO₂, as in the case of the monometallic samples. On the other hand, also the mixed phases Ru_3Sn_7 (QS = 0.26(1), IS = -0.67(1) mm/s, and $Ru_3Sn_{15}O_{14}$ (QS = 0.13(1), IS =−0.54(1) mm/s) give Mössbauer spectra similar to line B.⁵⁴

Line A could be considered as one of the components of the doublet attributable to badly crystallized ruthenium oxide, as in the case of the monometallic Ru100/C, or to a ruthenium chloride or oxychloride. 42 In fact, it is known that chlorine is retained by ruthenium particles in catalyst samples even after severe reduction treatments.⁶²

In addition to these possible interpretations, two further effects are expected to become important for small bimetallic particles: first of all, the small particle size of about 3.5 nm (Table 2) suggests that surface atoms become important in the Mössbauer spectra, as has recently been shown for gold clusters. 63 Second, the presence of tin or tin oxide on the surface of the metallic ruthenium particles may also be expected to give rise to particular surface components in the 99Ru Mössbauer spectra. Because of both the lack of reliable Mössbauer data on nanometer size ruthenium metal clusters or bimetallic layers and the impossibility to predict the spectral components produced by both free or tin covered surfaces, it appears impossible to unambiguously attribute any of the components observed in the Mössbauer spectra to these effects.

A striking difference between the bimetallic samples prepared by methods (a) or (b) and the monometallic **Ru100/C** specimen is that the component representing metallic ruthenium increases in intensity already in the presence of very small amounts of tin, and remains almost unchanged on increasing the tin concentration. This effect may be due to a stronger interaction of the metallic ruthenium particles with the carbon support in the presence of small amounts of tin, perhaps the result of a modification of the surface or shape of the metallic crystallites. The notion that tin acts as a glue fixing the ruthenium particles to the carbon surface is also in agreement with the observed increase of the total resonance area in the spectra of the bimetallic samples by about a factor of 2 compared to the monometallic specimens.

In the spectra of the bimetallic samples prepared by methods (a) and (b), the relative intensity of component A increases with the tin loading, although the increase is only slight (Table 5). In contrast to this, the relative area of line B does not change with the tin content. The increase of the relative intensity of line A with the tin loading suggests that this component might be related to the interaction of ruthenium with the tin covering the surface of the metallic particles. However, component A is also present in the 99Ru Mössbauer spectra of the samples prepared by method (d), where both the surface tin and the oxidic Ru—Sn components are absent in the corresponding ¹¹⁹Sn Mössbauer spectra.

Moreover, when the Ru-Sn/C catalyst samples are exposed to air (method (d)), the ⁹⁹Ru Mössbauer spectra show the presence of the same three components as in the case of preparation methods (a) and (b). The line positions as well as the relative areas change only slightly, except in the case of sample Ru95/C, where the intensity of the component attributable to metallic ruthenium decreases noticeably while component A increases. This suggests that at least part of line A is due to the oxidation of the surface of metallic ruthenium particles and the formation of badly crystallized ruthenium oxide.

Thus, component A and component B can be related to various species, e.g., badly crystallized ruthenium oxide, surface ruthenium atoms, or other tin-containing compounds. An unambiguous interpretation is therefore impossible.

Summarizing, the ⁹⁹Ru Mössbauer spectra reflect the importance of the presence of small amounts of tin on the state of the ruthenium and on its interaction with the support, but they do not allow a unique interpretation of some of the observed features. However, the picture that emerges seems more detailed than that drawn by the HRTEM studies, which detected only metallic ruthenium particles even in the bimetallic samples.⁷

Discussion of Catalytic Properties and Conclusions. To obtain as complete a picture as possible of the structure of the ruthenium-tin catalysts, the Mössbauer results must be seen in the light of the catalytic activity of the samples. As already mentioned in the Introduction, the catalytic activity of bimetallic ruthenium-tin supported on activated carbon has been widely investigated.12,13

The hydrogenation of β -methylstyrene with H_2 in ethanol at 343 K for 1 h yielded phenylpropane without any side product, but a steady decrease of the catalytic activity with the amount of tin was observed.¹² At a tin concentration of about 20% of the total metal loading, the activity of the catalysts practically vanished. However, the turnover number, i.e., the activity per ruthenium surface atom, was found to be constant in the whole range of composition. 12 These results suggest that in this reaction the main effect of the tin is to block part or all of the ruthenium surface atoms, whereas the specific activity of the accessible ruthenium surface atoms is not affected by the addition of tin. On the other hand, the hydrogenation of hydrocinnamaldehyde under the same experimental conditions 12 yielded phenylpropanol through the reduction of the carbonyl group. In this case, the activity of the catalyst first increased toward a maximum at a tin concentration of about 20% of the total metal loading and then decreased again. Moreover, in contrast to the case of β -methylstyrene, the turnover number increased linearly on addition of tin. These results suggest that the tin promotes the hydrogenation of carbonyl groups by supported ruthenium catalysts. This activating effect has been ascribed to the presence of ionic tin, which polarizes the carbonyl group, while the ruthenium is activating the hydrogen molecules. 12

Similarly, in the hydrogenation of cinnamaldehyde¹³ the number of surface ruthenium atoms decreases on addition of tin. In this case, the hydrogenation produces mainly hydrocinnamaldehyde and cinnamyl alcohol, with minor quantities of other side products. A modification of the catalyst surface during the first minutes of reaction has been observed.¹³ After this induction period, the rate of hydrogenation of the carbonyl group increases with respect to that of the allyl group, and the selectivity remains constant up to 90% conversion. The rate of disappearance of cinnamaldehyde decreases continuously on addition of tin, whereas the selectivity to cinnamyl alcohol increases from 30% without tin to 90% for a tin content of 30% of the total metal loading. As in the case of the hydrogenation of β -methylstyrene and hydrocinnamaldehyde, the higher selectivity has been related to the presence of ionic tin which activates the carbonyl group of the cinnamaldehyde. 13

The catalytic activity data, in agreement with the HRTEM results, suggest that the ruthenium is present as metallic particles both in the monometallic and in the bimetallic specimens, and that in the bimetallic samples the tin is mainly present as tin ions on the surface of the ruthenium particles. The Mössbauer results confirm and complete this picture.

In fact, the presence of small metallic ruthenium particles in the monometallic catalysts, although not directly detectable, can be inferred from the small overall ⁹⁹Ru resonance area of the samples and from the change of the spectral area on exposure to air. These results also reveal a weak interaction of the metallic ruthenium particles with the support. Small quantities of ruthenium oxide are also detected. In the bimetallic specimens, the average f-factor of the ruthenium particles increases somewhat despite the decrease of the particle size. This indicates an increase of the binding forces between the ruthenium particles and the support. Interactions between the ruthenium particles and the tin are also suggested, although they are not unambiguously visible in the 99Ru Mössbauer spectra. Small quantities of ruthenium oxide, as well as small amounts of the Ru₃Sn₇ intermetallic compound, may also contribute to the ⁹⁹Ru Mössbauer spectra.

 119 Sn Mössbauer spectroscopy shows that the tin is present as at least four different chemical species, plus minor amounts of the Ru_3Sn_7 intermetallic compound. The latter can unambiguously be detected only in the spectra of the samples exposed to air, where all the other tin species are oxidized to Sn(IV). Two of the four major components have been attributed to species where the ruthenium and the tin are in direct contact. This notion is supported by the absence of these components when no ruthenium is present on the carbon. It is suggested that these two components represent thin layers of metallic tin on the surface of the ruthenium particles and a mixed oxidic phase in which ruthenium and tin atoms forming metal—metal bonds. The latter could, in fact, represent tin atoms bonded to the

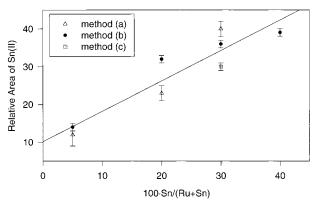


Figure 8. Relative area of the Sn(II) component in the ¹¹⁹Sn Mössbauer spectra of the catalysts obtained by preparation methods (a), (b), and (c) plotted vs the overall tin concentration.

surface of the ruthenium particles and to oxygen or retained chlorine atoms on the outer surface, forming, e.g., $Ru-Sn-O_x$ -like species on the surface of the metallic particles.

The other two species are attributable to Sn(IV) and Sn(II), probably present as oxides or hydrated oxides. The Mössbauer results give no indication whether these species are in contact with the ruthenium particles or not. However, in the Mössbauer spectra of the samples prepared by method (a), negligible amounts of Sn(IV) were detected. It is therefore likely that, after the reduction with H₂ at 300 °C for 2 h, all of the tin is reduced and that the Sn(IV) shown in the Mössbauer spectra of the samples prepared by methods (b) and (c) is mainly the oxidation product of the surface tin and the oxidic Ru-Sn species. The surface tin species have, in fact, turned out to be very sensitive to oxidation by traces of water contained in the argon used to flush the samples after the reduction, since the amount of Sn(IV) increases with the exposure of the samples to water mainly at the expense of the surface tin. Finally, when the samples are exposed to air, virtually all of the tin transforms into Sn(IV). It is likely that at least part of the Sn(IV) formed in this way is still in contact with the ruthenium particles. In the ⁹⁹Ru Mössbauer spectra (Table 5 and Figure 7), the interaction of the tin with the ruthenium cannot be clearly identified. Presumably both the ruthenium-tin bonds and the oxidation of ruthenium contribute to the components in the 99Ru Mössbauer spectra designated as lines A and B, which cannot be assigned unambiguously.

A different picture emerges for the Sn(II) species. Except for preparation method (d), the relative area of the Sn(II) component increases with the tin content of the samples. At the same time, for a given tin concentration, the amount of Sn(II) changes only slightly in the presence of water (method (c), Figure 8). This suggests that, for small tin concentrations, almost all of the tin interacts with the ruthenium, whereas with increasing tin concentration an increasing fraction of the tin forms oxidic Sn(II) species, either in contact with or separated from the metallic ruthenium particles.

This conclusion is in contrast with the recent results of Poilloux et al., ²⁰ who studied ruthenium—tin supported on Al₂O₃ prepared by coimpregnation with RuCl₃ and SnCl₂•2H₂O solutions and reduction with NaBH₄. These authors reported that, for a tin content lower than 80% of the total metal loading, ruthenium and tin are dispersed on the support as noninteracting tin oxide and ruthenium metal particles. Only at higher tin concentrations was the tin found to interact with the ruthenium particles forming SnO—Ru species. Thus, there appears to be a tendency for segregation of tin and ruthenium on Al₂O₃, whereas the two metals interact already at low tin loadings when

supported on carbon. The reason for the different behavior may lie in the different method of reduction or other differences in the preparation, or in differences in the metal—support interaction

The interaction of tin with platinum, rhodium, and ruthenium on different supports has been the subject of many studies, since a more electropositive metal is known to modify the catalytic properties of the platinum group metals. ¹⁹ Such bimetallic catalysts have been prepared mostly by conventional wetness impregnation from inorganic salts, but also by more specific methods, such as controlled surface reaction (CSR)⁶⁴ or solvated metal atom dispersion. ³⁰ These novel methods of preparation improve the interaction between the two metals and avoid their segregation, which usually occurs in catalysts prepared from inorganic salt precursors. On Rh–Sn/SiO₂ catalysts prepared by the CSR method, for instance, Mössbauer spectroscopy showed the formation of a RhSn alloy only, without any traces of oxidized tin. ⁶⁵

Most of the studies on Sn-containing bimetallic systems, however, refer to catalysts supported on different oxides (mainly Al₂O₃ and SiO₂).^{25–36,65} The use of different supports, however, may play a significant role in controlling the type of interactions that occur between tin and the other metal and between tin and the support, as has been shown by Weishen et al.³⁴ in a study of Pt–Sn catalysts on different supports prepared from inorganic precursors. In the case of the Ru–Sn/C catalysts investigated in the present work, the observed low degree of segregation of the two metals may arise from the weak interaction with a support such as activated carbon compared with oxide supports such as alumina or silica.

Among other authors, Deshpande et al., 11 Kikuchi et al., 66 and Poillux et al.²⁰ suggested that in the hydrogenation of α,β unsaturated carbonyl compounds on supported ruthenium-tin catalysts the Sn(II) oxide, acting as a Lewis acid site, is responsible for the activation of the carbonyl group. The results reported here do not reveal any correlation between the amount of Sn(II), of surface tin or of oxidic Ru-Sn with the activity or the selectivity in the hydrogenation reactions. The pronounced tendency of the tin species on the catalysts to oxidize already in the presence of traces of water, however, suggests that the tin contained in the catalyst may change from its state after the reduction to its active form during the induction period at the beginning of the hydrogenation, as reported by Galvagno et al.¹³ Such a restructuring of the surface involving the production of oxidic tin on the surface of the ruthenium metal has recently been suggested by Sordelli et al.⁶⁷ in a study of supported rhodium-tin catalysts prepared under similar conditions as the samples studied here.

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