Preparation and Surface Characterization of Nonsupported Ruthenium Catalysts

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A study of the preparation of ruthenium powder catalysts, starting from ruthenium compounds from various sources, has been made. In many cases it is found that the extent of the chemisorbed hydrogen monolayer is lower than expected on the grounds of the BET surface area of the powder. From TGA, XPS, and EM observations it is concluded that this is caused by the presence of tightly bound chlorine and oxygen on the surface. These poisoning substances can be removed by reduction in hydrogen at room temperature, but above 700 K the metal surface is repoisoned by chlorine and oxygen originating from the bulk of the metal and diffusing to the surface. Methods are indicated to circumvent this difficulty and to prepare very pure samples.

INTRODUCTION

Ruthenium can be applied as a catalyst in the Fischer-Tropsch synthesis of paraffins, in the methanation of carbon monoxide, and in the partial hydrogenation of benzene to cyclohexene. In the fundamental study of these reactions it is attractive to work with nonsupported catalysts in order to exclude a possible direct or indirect influence of the support on the catalyst performance.

Nonsupported ruthenium is also used by many investigators in the determination of the number of hydrogen atoms chemisorbed in a monolayer per square meter of surface area, the knowledge of this number being essential in calculating the free-metal surface area of *supported* ruthenium catalysts from hydrogen chemisorption isotherms. For this purpose the powder surface area following from the extent of a chemisorbed monolayer of hydrogen,

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 $S_{\rm H}$, is compared with the BET surface area, $S_{\rm BET}$, which follows from the physical adsorption isotherm of nitrogen or methane at 78 K. Provided the right suppositions are made concerning the number of adsorption sites per unit surface area and the chemisorption stoichiometry of hydrogen, the ratio $S_{\rm H}/S_{\rm BET}$ should be unity.

In this article it will be shown that a ratio of unity is seldom arrived at, neither in our own work nor in that of other investigators. It will further be shown that this is mainly due to the presence of tightly bound chlorine and oxygen on the surface of ruthenium and in the bulk of the metal. Methods are indicated for achieving a better result.

EXPERIMENTAL

Apparatus

Volumetric adsorption measurements of methane and of hydrogen were carried out in a "micro-BET apparatus" (1), provided with a Baratron pressure gauge (from MKS Instrument Inc., Burlington, Mass.) with a Type BH-100 single-sided sensor, pressure range 0.133 to 0.133×10^5 Pa. BET surface areas were calculated from methane adsorption isotherms at 78 K, taking the cross-sectional area of a methane molecule

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to be 0.194 nm². Hydrogen chemisorption isotherms were measured at 295 K. The ruthenium samples were prepared by *in situ* reduction of various ruthenium compounds at temperatures between 473 and 973 K for 3 hr, followed by degassing at the same temperature for 3 hr, by means of an oil diffusion pump, down to a pressure of 1.33 $\times 10^{-4}$ Pa.

Thermogravimetric measurements were carried out in a balance from Mettler, Switzerland, Type TA-1. Gases leaving the balance were analyzed with a mass spectrometer from Leybold-Heraeus, West Germany, Type MS-Quadruvac 2000. Samples of 2 to 4 g were investigated in a gas flow of $1.7 \text{ cm}^3 \cdot \text{s}^{-1}$.

Surface analysis was carried out in a Leybold-Heraeus Type LHS-10 XPS/AES apparatus, provided with a Hewlett-Packard dedicated computer. A MgK α excitation source (energy 1253.6 eV) was applied at the operating conditions of 13 kV and 20 mA. Spectral lines were compared with standard values (2). Samples were pretreated *in vacuo*, or prereduced in a 90% Ar + 10% H₂ mixture in a preparation chamber connected to the XPS/AES chamber via a valveless UHV lock.

Electron micrographs were taken with a Philips EM 300 apparatus. Suspensions of the ruthenium powders in methanol were brought onto a small-mesh wire netting, coated with a carbon film.

Materials

Table 1 lists the ruthenium compounds from which the metal powders were prepared, their suppliers, the impurity concentrations as determined by neutron activation analysis (3), and the BET surface areas after reduction of the compounds in hydrogen at 673 K for 3 hr, followed by degassing at the same temperature for 3 hr.

Note that in general the samples have a high level of purity. However, the chlorine concentration is relatively high, in the chlorides as a matter of course, but also in the oxides.

RESULTS AND DISCUSSION

Ruthenium Free-Metal Surface Areas as Compared with the BET Surface Areas

By way of example, Fig. 1 represents the hydrogen chemisorption isotherm at 294 K on ruthenium powder prepared *in situ* from RuO₂, sample A, by reduction in flowing hydrogen at 673 K for 3 hr, followed by degassing for 2 hr at the same temperature.

In accordance with Taylor's findings (4), equilibration was slow, and especially at the lower pressures 1 to 2 hr were needed for equilibration. The isotherm consists of two parts, representing respectively strongly and weakly chemisorbed hydrogen. The weakly chemisorbed part is easily reversible at room temperature, and is known as "type C hydrogen." This type of hydrogen is found on many group VIII metals, and, according to Bond (5) and Basset et al. (6), it should be looked upon as hydrogen in excess of the strongly held monolayer.

From the hydrogen chemisorption isotherms, $S_{\rm H}$, the free-metal surface area following from the extent of the chemisorbed monolayer of hydrogen, was calculated according to two different methods.

In the first method, advocated by Anderson (7), the transition point between strongly and weakly bound hydrogen is arbitrarily taken to be 133.22 Pa (1 Torr). The chemisorption stoichiometry of hydrogen, X_m , is assumed, according to Anderson, to be 2, which means that one hydrogen molecule is chemisorbed per two surface ruthenium atoms. Furthermore, also according to Anderson, the concentration of surface ruthenium atoms for polycrystalline material is supposed to be 1.63×10^{19} atoms m⁻².

The second method is based on work by Dalla Betta (8), Taylor (4), Goodwin (9), and Kubicka (10). They all suppose equal contributions of the (001) (101), and (100) planes to be present in the surface of polycrystalline ruthenium, and in this way arrive at 1.2×10^{19} atoms $\cdot m^{-2}$. Again the

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TABLE 1

Ruthenium Compounds, Impurity Analysis, and BET Surface Areas of the Ruthenium Powders Prepared from these Compounds

Sample code	Ruthenium compound	Supplier	Impurities (ppm)	BET surface area, after reduction (m ² /g Ru)	
A	RuO ₂	Drijfhout, Amsterdam, Dec. 1977	Not analyzed	2.3	
В	RuO ₂	Drijfhout, Amsterdam, March 1979	Ag: 100, Al: 68, Au: 47, Cl: 6100, Cu: 135, Mn: 15	10.0	
С	RuO ₂	= RuO_2 (B), but calcined in air at 1473 K	Ag: 3, Al: 113, Au: 15, Cu: <200, Mn: 55, Sc: 4, V: 2	3.6	
D	RuO ₂	Alpha Ventron, USA	Ag: 30, Cl: 1800, Mn: 11, Na: 10,000.	10.0	
Е	RuO ₂	From RuCl ₃ (F), by calcining in air at 1473 K.	Al: 157, Cl: 375, Ir: 10, Mn: 36, Na: 75, V: 2	3.3	
F	$RuCl_3 \cdot xH_2O$	Drijfhout, Amsterdam.	Al: 30, Au: 9, Ir: 28	1.5	
G	$RuCl_3 \cdot xH_2O$	Alpha Ventron, USA	Not analyzed	6.0	
Н	Ru ₃ (CO) ₁₂	Strem Chemicals, USA	Not analyzed	1.7	

transition point between strongly and weakly chemisorbed hydrogen was taken by us to be 133.32 Pa, but X_m is now taken as 2.2, on the basis of the most recent findings by Goodwin (9).

The free-metal surface areas calculated

in this way are presented in Table 2 for a

pounds mentioned in Table 1. In the table, $S_{\rm H}(1)$ refers to the first method of calculation, and $S_{\rm H}(2)$ to the second. Immediately after completion of the hydrogen chemisorption measurements, the BET surface areas were determined in the same appa-

series of ruthenium powders from the com-

TABLE 2

Free-Metal Surface Areas of Ruthenium Powders as Compared with their BET Surface Areas

Sample code	Ruthenium prepared from	Temp of reduction and degassing (K)	S _H (1) (m ² /g)	S _H (2) (m²/g)	S _{BET} (m²/g)	$\frac{S_{\rm H}(1)}{S_{\rm BET}}$	$\frac{S_{\rm H}(2)}{S_{\rm BET}}$
A	RuO ₂	673	2.21	2.73	2.8	0.79	0.98
\mathbf{B}^{b}	RuO ₂	553	1.53	1.89	17.0	0.09	0.11
\mathbf{B}^{b}	RuO ₂	653	1.87	2.32	11.0	0.17	0.21
B ^b	RuO ₂	698	1.62	2.01	9.0	0.18	0.22
B ^b	RuO ₂	803	1.03	1.28	4.9	0.21	0.26
F	$RuCl_3 \cdot xH_2O$	673	0.65	0.80	2.7	0.24	0.30
G	RuCl ₃ · xH ₂ O ^a	673	2.48	3.07	5.9	0.42	0.52
н	Ru ₃ (CO) ₁₂	673	1.19	1.48	1.7	0.70	0.87

Note. The samples are prepared by reduction in flowing hydrogen (1.7 cm³ hydrogen (STP) \cdot s⁻¹), at the temperatures indicated, followed by degassing at the same temperature.

^{*a*} Prior to reduction with hydrogen, this sample was reduced with hydrazine in the liquid phase, according to the method of Sinfelt *et al.* (11).

^b These measurements were performed with the same sample B in succession.

Table 2 demonstrates that, whether we prefer the first or second method of calculation, the free-metal surface areas are in many cases very low in proportion to S_{BET} , and this must be due to impurities not easily removable by reduction. Furthermore, the choice of a higher reduction temperature slightly improves the situation (see samples B in Table 2). Sample A had a very pure surface, also according to XPS analysis (see later section on XPS analysis). Preparation of ruthenium powders from Ru₃(CO)₁₂ appears to be a good method for obtaining a high surface purity (see ruthenium prepared from sample H, Table 2).

In Table 3 the same quantities are presented as tabulated in Table 2, but now calculated from literature data published by others. From this table the same conclusion is arrived at as from Table 2: especially the ruthenium powders prepared from chlorine-containing compounds show $S_{\rm H}(1)/$ S_{BET} values or $S_{\text{H}}(2)/S_{\text{BET}}$ values pointing to surface poisoning, whereas for a sample of high surface cleanliness (last line Table 3), $S_{\text{H}}/S_{\text{BET}}$ approaches a value of unity.

Thermogravimetric Reduction of Passivated Ruthenium Powder

In order to elucidate the nature of the ruthenium surface poison(s) mentioned above, a thermogravimetric study was performed of the reduction of a passivated ruthenium powder. We started from RuCl₃, sample G, see Table 1, which was reduced in flowing hydrogen (1.7 cm³ hydrogen (STP) \cdot s⁻¹) at 673 K, and, after cooling down to 300 K, passivated in 5% O₂ in nitrogen at 300 K.

The thermogravimetric result, together with the mass spectrometric analysis of the off-gas with respect to the water content, is given in Fig. 2. The part of the figure to the left of the dashed line represents the roomtemperature reduction of the passivation layer. The observed weight change, integrated over a period of about 45 min, is equivalent to 3.3 mg H₂O per g Ru, and corresponds with a passivation layer of ap-

TABL	E	3
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Quotients of the Free-Metal Surface Areas and the BET Surface Areas of Ruthenium Powders, as Calculated from Literature Data, According to the First and Second Methods Indicated in this Paper

Ruthenium or Ru prepared from	Temp of reduction in H ₂ (K)	S _H (1) (m²/g)	S _H (2) (m²/g)	S _{BET} (m²/g)	$\frac{S_{\rm H}(1)}{S_{\rm BET}}$	$\frac{S_{\rm H}(2)}{S_{\rm BET}}$	Authors	Reference
(NH ₄) _x RuCl _y O _z	773	1.75	2.16	3.5	0.45	0.62	Engels et al.	(12)
Ru powder, not specified	673	0.22ª	0.28ª	0.34	0.66	0.82	Dalla Betta	(8)
RuCl ₃	673 ^{<i>b</i>}	2.51	3.11	5.1	0.49	0.61	Sinfelt et al.	(11)
RuCl ₃	723	0.34	0.42	1.0	0.34	0.42	Urabe et al.	(13)
Ru powder, not specified	673	0.06 ^a	0.09	0.34	0.19	0.25	Kubicka	(14)
Monocrystal ^d								
Ru (0001)	673				0.86 ±	± 0.15 ^c	Shimizu <i>et al</i> .	(15)

^a These values are calculated supposing the strong chemisorption to be 75% of the total adsorption.

^b Before reduction with hydrogen, RuCl₃ was reduced in the liquid phase with hydrazine.

^c Value calculated by Shimizu et al. (15).

^d Surface cleaning was performed by oxidation and degassing at 1873 K. The concentration of surface ruthenium atoms for Ru (0001) is 1.59×10^{19} atoms $\cdot m^{-2}$.



FIG. 1. Hydrogen chemisorption isotherm at 294 K on ruthenium powder, prepared by reduction of RuO_2 , sample A, in flowing hydrogen at 673 K. Point a indicates the arbitrarily chosen transition point between strongly and weakly bound hydrogen.



FIG. 2. Weight change of passivated ruthenium powder, ΔW , during reduction in a flowing mixture of 80% hydrogen and 20% argon; flow rate: 1 cm³ · g⁻¹ · s⁻¹. Heating rate: 4°C · min⁻¹. Ruthenium powder prepared from RuCl₃, sample G. On the right-hand ordinate the water concentration in the offgas during reduction is plotted in arbitrary units, as a function of time and of temperature.

prox 1.7 oxygen atoms per surface Ru atom $(S_{\text{BET}} = 6 \text{ m}^2/\text{g}; 1.2 \times 10^{19} \text{ surface Ru atoms per m}^2).$

After removal of the passivation layer, the linear time/temperature program started, with a heating rate of 4 K min⁻¹. It is seen that from 270 to 700 K, the weight change and the accompanying water production is relatively low, but above that temperature a new weight change of about 4 mg/g Ru sets in, and the water production increases again.

Obviously, a ruthenium sample, after being reduced at 673 K and after removal of the passivation layer, may still contain a certain amount of hard to remove oxygen, either strongly adsorbed or bound in the bulk of the metal. However, the amount of oxygen removed, as calculated from the integrated amount of water, is 2 mg/g Ru only, whereas the total weight change above 673 K was 4 mg/Ru. It follows that there is another compound besides water leaving the sample.

Though HCl was not detected mass spectrometrically (HCl adheres strongly to the inside wall of the mass spectrometer), we could show that the second component leaving ruthenium above 673 K is chlorine, by analysis of the ruthenium powder before and after the thermogravimetric run. For this purpose the ruthenium sample was slurried in a 50% alcohol/50% water mixture to which 0.5% HNO₃ was added, in order to increase the electrical conductivity. From a coulometric titration of the slurry it was found that in a period of 19 hr, 790 ppm of chlorine was extracted from the freshly passivated ruthenium sample, whereas after completion of the thermogravimetric run, only 1.5 ppm of chlorine was extractable in the same period.

Preparation of Ruthenium Powders of High Surface Purity

In the foregoing paragraph it was demonstrated that above 700 K oxygen and chlorine desorb from ruthenium in a reducing atmosphere, up to 1200 K. It follows that strongly bound oxygen and chlorine are the main cause of the suppression of hydrogen chemisorption on many samples.

In order to prepare ruthenium samples of high surface purity we made use of the findings of Pizzini et al. (16), who reported that ruthenium oxides may also contain large amounts of chlorine. They showed that the chlorine content can be strongly diminished by calcining ruthenium oxide in oxygen or in clean air at temperatures up to 1500 K. Table 4 shows the importance of such pretreatment in the preparation of pure ruthenium. The higher the temperature of calcination of the oxide, the higher the $S_{\rm H}/S_{\rm BFT}$ ratios of the ruthenium powders prepared from it, and after calcining at 1473 K a very high surface purity is attained $(S_{\rm H}(2)/S_{\rm BET})$ approaches unity).

TABLE 4

The Influence of Calcination of Ruthenium Oxide (Sample B) at High Temperatures and in Clean Air, on the $S_{\rm H}/S_{\rm BET}$ Ratios of the Ruthenium Powders Prepared from the Oxide by Reduction

Temp of calcination of	Calcination time	Reduction temp	$S_{\rm H}(1)$ (m ² /g)	$S_{\rm H}(2)$ (m ² /g)	S_{BET} (m^2/g)	$\frac{S_{\rm H}(1)}{2}$	$\frac{S_{\rm H}(2)}{2}$
the oxide (K)	(hr)	(K)	(,8)	(,8)	(, 8)	SBET	S _{BET}
No calcination		803	1.03	1.28	4.9	0.21	0.26
773	3	673	1.55	1.92	5.2	0.30	0.26
1273	1	673	2.79	3.44	4.1	0.68	0.84
1473	1	673	2.81	3.48	3.7	0.76	0.94
1473	1	773	0.94	1.17	1.6	0.59	0.73
1473	1	828	0.45	0.56	1.1	0.41	0.51

The last two lines in Table 4 demonstrate that by increasing the reduction temperature to 773 and 828 K, respectively, stronger sintering of the ruthenium powder is initiated and the $S_{\rm H}/S_{\rm BET}$ values again drop.

This is an indication that at these higher temperatures impurities, originating from the bulk of the metal, diffuse to the metal surface, poisoning it once more. Further evidence for this effect may be found in the following paragraphs.

XPS Analysis of Ruthenium Powders

A ruthenium powder was prepared by reduction of RuO₂, sample A, in flowing hydrogen (1.7 cm³ H₂ (STP) \cdot s⁻¹) at 893 K for 3 hr, followed by degassing at the same temperature, and passivation in a stream of 5% O_2 in nitrogen at 300 K. The upper curve in Fig. 3 represents the O(1s) line in the XPS spectrum of the passivated sample, after evacuation down to 0.67×10^{-8} Pa. The experimental ratio of the integrated peak intensities, $I_{O(1s)}/I_{Ru(3d 5/2)}$, was found to be 0.31. This is a factor of 4 higher than the intensity ratio for a monolayer of oxygen on ruthenium, as estimated theoretically (17-19), and is in accordance with the presence of at least two layers of passivating oxygen.

The passivated sample was reduced statically for half an hour in the preparation chamber, in an excess of a mixture of 90% Ar/10% H₂ of pressure 1500 Pa, at 673 K. It was then transferred again to the XPS/AES chamber and analyzed (see Fig. 3, the lower spectrum). It appears that after the reduction treatment, the position of the O(1s) line is shifted to a lower kinetic energy; the maximum shift calculated from five measurements was 0.7 ± 0.1 eV. Furthermore, the difference in the position of the baseline on the left and right of the peaks is not proportional to the peak heights: with the reduced sample this difference is relatively higher. Both facts point to the oxygen in the reduced sample being mainly present in the bulk of the ruthenium, not at the surface.



FIG. 3. The O(1s) lines in the XPS spectra (narrow scan) of passivated (upper line) and reduced (lower line) ruthenium powder. The ruthenium is prepared from RuO_2 , sample A.

From the experimental intensity ratio $I_{O(1s)}/I_{Ru(3d 5/2)}$ the bulk oxygen concentration was estimated to be $\sim 7 \operatorname{atom}\%$ (19). This finding is in good accordance with the result of the thermogravimetric experiments (see above), where it was found that above 700 K a few percent of oxygen is removed by reduction up to 1273 K.

At 1053 eV, XPS Cl(2p) peaks were found, both in the passivated and in the reduced sample. The intensity ratios $I_{Cl(2p)}/I_{Ru(3d 5/2)}$ were <0.01 and <0.005, respectively, pointing to a very low concentration of chlorine in this sample in the bulk and/or the surface, in accordance with the high surface purity found from hydrogen chemisorption (see Table 2, sample A).

A second ruthenium sample was prepared by reduction of RuCl₃, sample G, in flowing hydrogen (1.7 cm³ H₂ (STP) \cdot s⁻¹), at 673 K for 3 hr, followed by degassing at the same temperature, and passivation in a stream of 5% oxygen in nitrogen at 300 K. The spectra of the passivated and *in situ* reduced sample are presented in Fig. 4.

The observations with respect to the intensities of the O(1s) peaks were fully in line with the results described above for the sample prepared from RuO₂. The much higher chlorine concentrations are striking, however. For the passivated sample $I_{Cl(2p)}$



FIG. 4. The XPS spectra of passivated (upper line) and reduced (lower line) ruthenium powder (wide scan). The ruthenium is prepared from RuCl₃, sample G.

 $I_{\text{Ru}(3d 5/2)}$ was 0.064, and for the passivated sample, after reduction in the preparation chamber under the same conditions as indicated for the foregoing sample, $I_{Cl(2p)}$ $I_{Ru(3d 5/2)}$ was 0.031. A comparison of these values with the theoretically calculated intensities for a monolayer of chlorine (19) results in chlorine coverages of the order of 50%. The presence of an Auger line of chlorine at the low kinetic energy value of 184.5 eV (see Fig. 4) establishes the presence of chlorine at the surface. Obviously, the low extent of hydrogen chemisorption on this sample $(S_{\rm H}(1)/S_{\rm BET} = 0.42)$ is due to adsorbed chlorine. After reduction of the sample in the preparation chamber at 1200 K, $I_{Cl(2p)}/I_{Ru(3d 5/2)}$ decreased dramatically to a value lower than 0.01, in accordance with what has been stated on the removal of chlorine in the foregoing paragraphs.

The strong decline in intensity of the oxygen peaks due to reduction (see Fig. 4), attended by a nearly constant intensity of the chlorine peaks, is striking.

In accordance with expectations, the Auger peaks of ruthenium at low kinetic energy increase as a result of the removal of the oxygen passivation layers.

Electron Microscopy of Ruthenium Powder

In the preceding paragraphs evidence is presented for the presence of oxygen and chlorine on the surface and in the bulk of ruthenium. The surface oxygen is quite easily removable by reduction, but chlorine is more tightly bound. Furthermore, a ruthenium surface, totally purified by reduction, is repoisoned by oxygen and especially by chlorine, on continuing reduction above 700 K. It follows that above that temperature, oxygen and chlorine are diffusing from the bulk to the surface, and we may ask ourselves where these impurities are bound in the bulk, and why so strongly. Electron microscopy of ruthenium throws some light on this matter.

A ruthenium powder was prepared by reduction of ruthenium oxide, sample A, in flowing hydrogen at 575 K, and, after careful passivation as described above, investigated in the electron microscope.

Micrograph a, Fig. 5, shows the sample to be composed of conglomerates of small particles, the mean diameter of which is estimated to be 50 ± 10 nm. From the BET



FIG. 5. (a) Electron micrographs of ruthenium powder prepared by reduction of RuO_2 , sample A. (b) Dark-field micrograph of the same powder fraction as depicted in (a).

surface area $(9.2 \text{ m}^2/\text{g})$ a mean particle diameter of 58 nm is calculated, supposing the particles to be spherical. From X-ray line broadening we found the mean diameter of the elementary *crystallites* to be only 20 nm; this is a first indication that we are dealing with a polycrystalline material, each particle being composed of several smaller crystallites. This was substantiated by a dark-field micrograph, Fig. 5b, in which the diffracted beam in a certain direction is depicted. The particles appear to consist of conglomerates of smaller crystallites of varying orientation, interconnected by crystallite boundaries. Such boundaries may be looked upon as lattice defects, where the coordination of the Ru atoms will be lower than in the undisturbed crystal.

We now tentatively suppose that oxygen and chlorine impurities in the bulk are relatively strongly bound to these sites of lower higher temperatures coordination. At (above 700 K; see, for instance, Table 4) sintering commences, attended by the disappearance of the lattice defects. Simultaneously with this process, the chlorine and oxygen atoms are expelled from the bulk, and diffuse to the surface of the particles. In the presence of hydrogen (see Fig. 2) this process is attended by the gradual reduction of these impurities originating from the bulk. This obviously continues up to 1200 K (see Fig. 2).

CONCLUSIONS

The difficulties encountered in the preparation of ruthenium powder catalysts with a high degree of surface cleanliness is clearly demonstrated in this work. Evidence is presented that these difficulties are mainly caused by the polycrystalline nature of the ruthenium powders investigated, in combination with the presence of impurities in the compounds from which we started.

It is to be expected that in working with supported ruthenium catalysts, where the mean metal crystallite size is much smaller, crystallite boundaries are practically absent. Moreover, the length of the diffusion path to the surface is much shorter in this case, and therefore impurities are more readily removable. Another advantage of such systems is, of course, the high surface atom/bulk atom ratio: this means that a certain weight percentage of impurity attains a much smaller coverage at the surface than in the case of large powder particles.

The determination of the concentration of surface ruthenium atoms in a polycrystalline surface, and the determination of the chemisorption stoichiometry of hydrogen, calls for further research, in view of the results presented in Tables 2–4. Perhaps the best approach to this problem is a study of the extent of the hydrogen chemisorption of UHV-evaporated ruthenium films as compared with the BET surface areas of these films, determined from krypton physisorption.

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