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Adsorption of CO on Ru and Pt blacks and catalysts and the possibility of its utilization for the determination of the ruthenium-free surface

Abstract Electrochemical voltammetric curves on Ru and Pt blacks of a different surface area were measured in potential intervals 0.05–1.05 V in pure 0.5 M H_2SO_4 and after CO adsorption. It was proved that after the CO adsorption, the outset of ruthenium oxidation is shifted by about 150 mV towards the positive potentials, e.g. to the region of oxidation of adsorbed CO. This fact made possible the determination of a double-layer charging current of Ru electrodes and, subsequently, also the determination of the amount of adsorbed hydrogen on the Ru surface. An evaluation of the amount of CO and hydrogen adsorption showed that the ratio of adsorbed CO:H on the Pt surface was about 1:1, while on Ru electrodes this ratio was around twice as large. The amount of hydrogen adsorbed on Ru blacks depends on the preliminary preparation of the electrodes. The CO adsorption could also be employed in the determination of a charging current of electrode double-layers during voltammetric oxidation of adsorbed hydrogen on ruthenium supported on Al_2O_3, SiO_2, or TiO_2 carriers. However, a similar determination of hydrogen adsorbed on the tin-modified Ru catalysts is not very reliable.

Keywords Hydrogen/carbon monoxide adsorption · Platinum/ruthenium catalysts · Specific surface

Introduction

The specific surface area of active metals is one of many characteristics that has a great impact on activity in catalytic reactions. In order to determine the specific surface area of a catalyst without a support, the most commonly used method is the one based on physical gas adsorption. However, for a surface area determination of an active supported component, it is necessary to apply a method of selective chemisorption of hydrogen, oxygen, carbon monoxide, or nitric oxides, followed by titration of the adsorbed molecules with another suitable gas or other titration agent. These determination methods which employ adsorption from gas phase could be replaced by electrochemical techniques, which have, in comparison with techniques based on gas methods, a number of advantages, such as a simple experimental device, short-time measurements, and the need for only a small amount of a sample. The most commonly used electrochemical methods applied in the determination of Pt surface and Pt catalyst surface areas are based on hydrogen adsorption. Bett et al. [1] showed that both methods gave analogous results in H and CO adsorption on Pt/C catalysts.

A method that employs hydrogen chemisorption for the determination of active metal surface areas on metals other than Pt encounters several problems. In the case of ruthenium, one such problem is the non-specific stoichiometric ratio of H and Ru adsorbed from the gas phase. This ratio diverges in the work of different authors [2–8]. Application of the electrochemical potentiodynamical sweep, or galvanostatic technique, for the determination of hydrogen adsorption is not possible because the oxidation of adsorbed hydrogen continuously results in the oxidation of ruthenium. Therefore, it is possible neither to distinguish between these two processes nor to determine the corresponding electric charge of oxidation [9, 10]. Furthermore, the ruthenium surface easily undergoes oxidation together with an oxide formation of a different stoichiometry. The reduction of these oxides, which is often irreversible [11], and the preparation of a pure ruthenium surface without oxides, strongly depends on the chosen method of ruthenium preparation and the conditions of its storing. Contrary to platinum, a simple electrochemical reduction under the potential $E \approx 0.0$ V (RHE) does not result in a preparation of an oxide-free surface, which is the reason why the method based on the electrochemical

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oxidation of adsorbed hydrogen is not used anymore. Occasionally, a method is used based on the voltammetry or coulommetry of RuO_2, which in a potential range of 1.25–0.3 V, reversibly changes only the Ru/O stoichiometry of the surface oxide. This fact could be used as a basis for Ru surface area determination [12]. The experimentally demanding electrochemical method for determining the specific surface area was proposed by Fernández et al. [13]. This method is based on the analysis of the potential transients where the equilibrium potential of the quinone/hydroquinone red–ox couple is perturbed with a periodic current signal of low amplitude.

Voltammetry of ruthenium oxide gives satisfying results if a smooth electrode [12] or RuO_2 black is used [14]. However, it has been shown that the voltammetric curves of supported RuO_2 catalysts have a shape markedly distinct from that of RuO_2 electrodes [14]. It is not certain that stoichiometric changes of Ru/O ratio in ruthenium oxides, on different supports and in given potential range, are the same as those for pure oxides. Therefore, it is not clear whether the values of red–ox electrical charges for pure oxides, with its recalculating factors, could also be used for ruthenium oxide on carriers. This method allows one to determine the surface area covered by an oxide. It was shown in Ref. [11] that some oxides are poorly reducible. It is only the free ruthenium surface which is covered by adsorbed hydrogen takes part in many reactions.

Another method used to evaluate the amount of CO adsorbed onto a metal surface based on the determination of charge, and which requires the oxidization of the adsorbed CO, has been briefly described and evaluated in Ref. [15]. This method has already been used for the determination of an Ru surface area [16], but without detailed description. Recently two papers have appeared [17, 18] that use an evaluation method based on the oxidation of copper, which is underpotential deposited (upd), and adsorbed CO on ruthenium and platinum–ruthenium high-surface electrocatalysts. This method has been used in the determination of ruthenium and platinum–ruthenium specific surface areas. It has been followed from these papers that the ratio of the oxidation charges of upd copper and adsorbed CO were about 0.5. The authors have concluded that the stoichiometry between adsorbed CO and surface ruthenium sites must be different than 1:1. The value of the specific surface area determined by upd Cu stripping is in relatively good agreement with the BET determination; however, the area of the ruthenium surface calculated using CO stripping was around twice as large as that by the BET method.

The work presented here was motivated by an effort to determine the ruthenium surface area supported on a carrier using the application of electrochemically adsorbed hydrogen. The complications, connected with a difficult differentiation of electric charge of oxidation of adsorbed hydrogen from that of ruthenium surface, were solved by CO adsorption. We assumed that hydrogen would not be adsorbed after the CO adsorption, enabling the assessment of the value for the charge current of the double-layer. Thus, it was possible to define an electric charge of hydrogen oxidation by appropriate extrapolation of a voltammetric curve of the adsorbed hydrogen to the value of charge current in a pure electrolyte. Our work also set out to clarify the possibility of applying the measuring electrical charge of the oxidation of adsorbed CO. We studied the CO adsorption on Pt blacks to verify the usefulness of the applied method.

Experimental

Ruthenium black was prepared by the reduction of $RuCl_3 \cdot xH_2O$ using $NaBH_4$ as the reducing agent [19, 20]. Platinum black was prepared by the reduction of H_2PtCl_6 using formaldehyde. Ru and Pt blacks of smaller specific surfaces areas were prepared by heating the original blacks at a higher temperature (500–700 °C) in H_2 atmosphere. Supported Ru catalysts (on SiO_2, Al_2O_3, or TiO_2 carriers) were prepared by a conventional impregnation technique [14].

The prepared catalysts were ground to powder in agate mortar and the powder was passed through a sieve with a mesh size of 0.125. The fraction, which passed through this sieve, was used for further measurements. With respect to the fact that supported catalysts are non-conductive particles, they were mixed up with the fine powder of ground graphite (particle size < 0.125 mm) which made possible electrical charge transfer. The homogenization of both powdered substances was carried out in a ratio 1:1 using a (Janke & Kunkel GBMH Type A10) homogenizer.

In order to ensure a good level of adherence of the prepared mixture to the electrode collector, which was platinum gauze (on the surface with thin layer of electrodeposited gold) with a mesh size of 0.38 mm, the PTFE dispersion, diluted by water, was added into the mixture until a diluted mash-like suspension was obtained. This suspension was dried to a constant weight at a temperature of about 100 °C. After the evaporation of excess water, the waxy solid that remained was spread as a thin layer using a pallet knife over the supporting gauze. The PTFE content in the mixture (calculated on a dry substance) was about 3%. The gauze (having a disc-like shape with a diameter of 1 cm) was put into a mould and pressed under a pressure of 500 MPa. The weight of prepared electrodes was approximately 15 mg. The electrodes were reduced in a H_2 atmosphere at 200 °C for 4 h shortly before measurements.

All electrochemical measurements were conducted in 0.5 M H_2SO_4. A conventional three-compartment glass cell was used for the measurements. The compartments with a counter electrode (2×2 cm^2 platinum sheet) were separated from the compartment with the sample as the working electrode by fritted glass. A saturated calomel electrode (SCE) placed in the Luggin capillary was used as the reference electrode [all potentials mentioned

throughout this article are made in reference to the hydrogen electrode (RHE) scale]. The dissolved oxygen was removed from the solution by bubbling nitrogen through the compartment with the working electrode before measurements. The sample, affixed to a holder (platinum wire with a thin layer of electrodeposited gold and insulated with PTFE tubing), was electrically connected as the working electrode to the potentiostat (Wenking ST 72). The Ru–Sn electrodes were immersed in the electrolyte under 0.05 V potential in order to avoid the dissolution of Sn component of the electrode. The electrode was firstly polarized at $E_p \approx 0.00$ V (vs. RHE) for 15–30 min, then polarized at $E_i = 0.05$ V for 15 min. After this polarization period, a voltammetric curve with a potential sweep (v) usually $v = 2$ mV s^{-1} was recorded using a generator of triangle voltage (UNIPAM 711). The current response was detected in digital form by A/D converter (S 711 Advantech) and processed by a personal computer.

The poisoning of Pt and/or Ru electrodes with CO was performed using 0.5 M H_2SO_4 with dissolved carbon monoxide. For this purpose, CO was purged into the cell for 0.5–4 h to allow complete adsorption of CO. Adsorption proceeded at zero-current potential (mainly at Pt and Ru blacks) or at a potential of approximately $E \approx 0.15$ V. The excess CO in the solution was then purged with N_2 for at least 0.5 h. Before the voltammetry measurements the electrodes were pre-polarized at $E_i = 0.05$ V for 5 min.

The specific surface area of Ru black electrodes was determined by the electrochemical voltammetric method [12, 14]. In this method, the charges needed for the reduction and the reverse oxidation of RuO_2 blacks in

the potential range $\Delta E = 1.15$–0.45 V (reduction) and vice versa were measured. Sweep rates v between 0.2 and 1.0 mV s^{-1} were used. The value $Q = 1.08$ C m^{-2} [14] was used for the evaluation of the specific surfaces of Ru blacks. Before measurements, Ru blacks were oxidized by heating electrodes at 200 °C for 5 h. The specific surface of Pt black was determined using the conventional electrochemical voltammetric method [1] based on the determination of adsorbed hydrogen.

Results

Pt black

The voltammetric curves of Pt blacks are displayed in Fig. 1. Curve 1 represents Pt black in pure electrolyte, curve 2 represents Pt black after CO adsorption under bubbling of the electrolyte with CO for 3 h at an open circuit potential (a steady state value of $+0.165$ V) and finally curve 3 shows Pt black after CO adsorption under bubbling of the electrolyte with CO at the imposed potential of $E = +0.290$ V also for 3 h. The voltammetric oxidation curve of adsorbed CO resembles the curves in formerly published articles [1, 20]. A certain difference is in the potential of the CO oxidation peak E_p. In our experiments, E_p was shifted from about 0.1 [1] to 0.18 V [21] towards lower positive potentials. Furthermore, a wide oxidation peak, which was not observed previously in the above-mentioned papers, arose on an oxidation direction of the voltammetric curve of Pt blacks in the potential range of 0.35–0.55 V (a similar pre-peak was, however, observed for monocrystalline Pt(111) electrode [22]). Of importance is the finding that the charging current of the Pt black electrode with the adsorbed CO layer i_{COd} in the potential range 0.165–0.23 V is only fractionally smaller than the double-layer charging current i_{dl} measured in the CO-free solution in the potential range 0.45–0.65 V. In more exact terms the ratio of both currents is $i_{dl}/i_{COd} \approx 1.55$. This value is similar to the ratio of capacitances $C_{dl}/C_{CO} < 1.78$ found on monocrystalline Pt(111) [21] at corresponding potentials [C_{dl}, capacitance of Pt(111) electrode in 0.1 M $HClO_4$, ($C_{dl} < 25$ µF cm^{-2}) [22]; C_{CO}, capacitance evaluated at potentials below where CO electrooxidation proceeds (C_{CO} about 14 µF cm^{-2}) [22, 23]].

The charge of the adsorbed hydrogen oxidation Q_H for Pt in pure electrolyte (curve 1) was determined by integration of the area I–E in the potential range from 0.05 V to about 0.4 V. The oxidation charge Q_{CO} of adsorbed CO was determined by integration of the area defined by curve 2 in the potential range 0.2–0.8 V. When comparing oxidation charges of the oxidation of hydrogen with those for CO into CO_2, it is necessary to include the fact that the first process is a one-electron reaction, while the oxidation of CO is a two-electron transfer. From the curves in Fig. 1 the ratio R of adsorbed CO–H particles $R = Q_{CO}/(2Q_H) = 0.92$ was calculated for curves 2 and 1, and $R = 0.51$ for curves 3 and
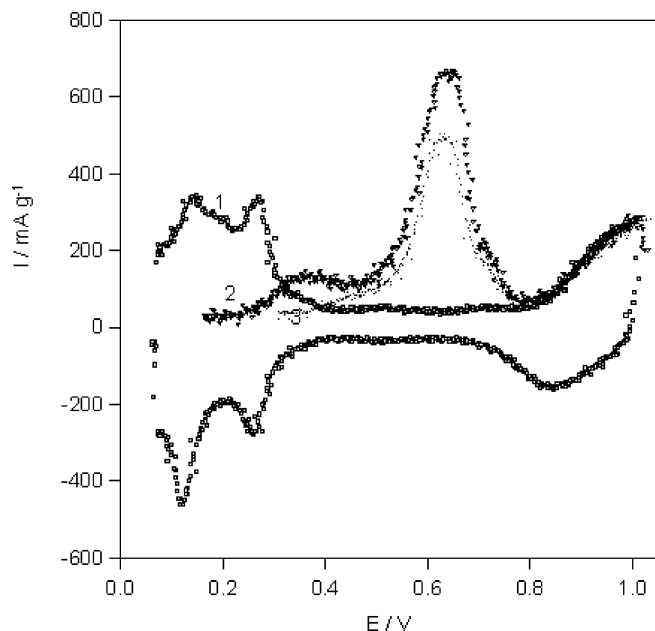

Fig. 1 Voltammograms of Pt black. *1* Before CO adsorption, *2* after 3 h of CO adsorption at open circuit potential, *3* after 3 h adsorption of CO at $E \approx 0.29$ V. Sweep rate $v = 2$ mV s^{-1}

1. Moreover, the ratio R of CO adsorbed onto the electrode in a zero-current state was calculated (the curve is not included in the figure for better clarity); then the electrode was bubbled with N_2 and polarized for 5 min at $E_i = 0.05$ V (in contrast to the curve 2 in Fig. 1 where $E_i \approx 0.18$ V) and voltammetric curve was measured. In this case, the measured ratio value was $R = 0.85$. Measured values of R for CO adsorption in the case of zero-current adsorption correlate with values given in the literature 0.87–0.89 [1] and 1.0 ± 0.1 [19]. The R ratio was markedly lower at CO adsorption under a more positive potential of $E \approx 0.29$ V, even though adsorbed CO does not oxidize under such potential. Described R rates were obtained on Pt blacks with a specific surface area of 14.8 m^2 g^{-1}. Similar R values were obtained on Pt blacks with specific surface area of 8.27 and 4.27 m^2 g^{-1}.

Ru black

Voltammetric curves of Ru black are shown in Fig. 2. Curve 1 represents the course in pure electrolyte. Curve 2 is the voltammetric curve in an electrolyte saturated with CO for 30 min and curve 3 after 4 h of saturating. From the oxidation branches of the curves it follows that the commonly used saturation time of 30 min is insufficient for total replacement of adsorbed hydrogen with adsorbed CO. A shift of the oxidation peak in curve 3, e.g. reaction with more adsorbed CO than that demonstrated in curve 2 shows that CO oxidation is an irreversible reaction even at a low sweep rate v. A considerable different behavior of Ru and Pt blacks is

apparent mainly in the potential region of around 0.3 V. The oxidation current decreased noticeably in Ru blacks with adsorbed CO than those without adsorbed CO. It could be concluded from a comparison of curve 2 with curve 3 that a current decrease in this potential range is proportional to the degree of the surface coverage with adsorbed CO. The main oxidation peak of adsorbed CO is, in comparison to Pt blacks, shifted towards less positive potentials and its value ranges 0.5–0.59 V; this is about 0.1–0.15 V more negative than that of Pt electrodes. For further explanation of a course of the voltammetric curves in Fig. 2, voltammograms of pure Ru black were measured with different values of initial potential E_i, at which the potential sweep began, and different turn potential E_t (Fig. 3). Their course shows that the current increase at $E \approx 0.25$ V is caused by the initiation of the ruthenium oxidation. The oxidation proceeds in the form of a current plateau until a potential of approximately 0.7 V, where a further oxidation reaction begins. An identical peak potential in anodic branches of VCs 1–3 demonstrates that Ru oxides formed at potentials from about 0.25 V to about 0.95 V are almost reversibly reduced in the cathodic branches of the VCs.

When determining the charge of the oxidation of adsorbed CO, it is necessary to analyze the shape of the voltammetric curves 1 and 3 (Fig. 2) and also consider reduction branch of the curves. It can be concluded from the curves that the adsorbed layer CO_{ad} prevents the oxidation of the ruthenium surface up to a potential of at least 0.35 V. At this potential the oxidation of CO_{ad} into CO_2 starts, followed with CO_2 desorption from the ruthenium surface. The bare ruthenium surface is then instantly oxidized with to form a RuO_x surface layer.
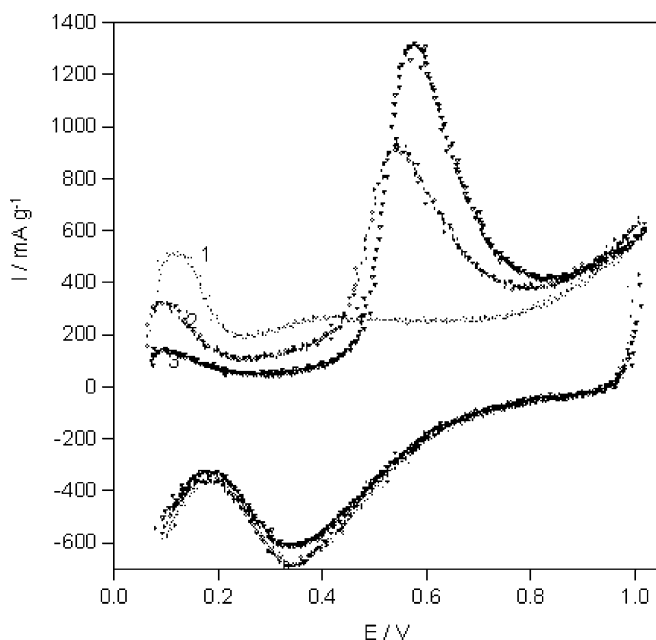

Fig. 2 Voltammograms of Ru 1 black. *1* Before CO adsorption, *2* 0.5 h of CO adsorption, *3* after 4 h CO adsorption at $E \approx 0.15$ V. Sweep rate $v = 2$ mV s^{-1}
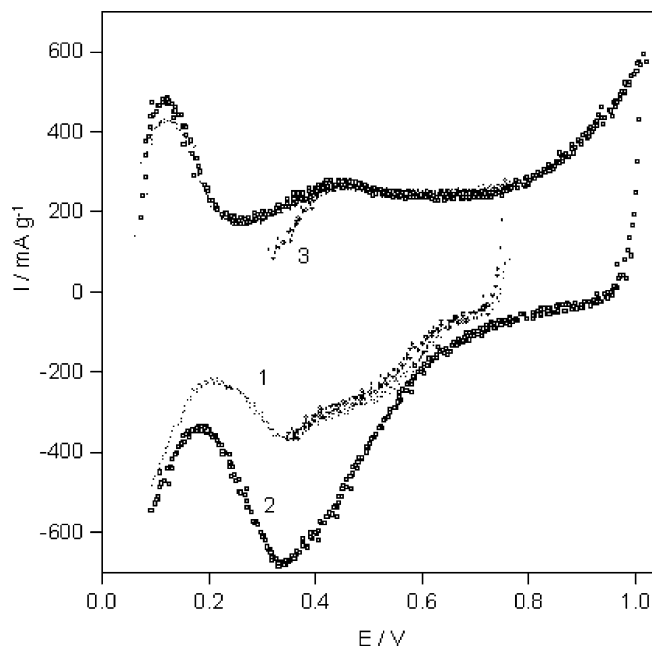

Fig. 3 Voltammograms of Ru 1 black. *1* Initial potential $E_i = 0.05$ V, turn potential $E_t = 0.73$ V, *2* $E_i = 0.05$ V, $E_t = 0.96$ V, *3* $E_i = 0.30$ V, $E_t = 0.73$ V. Sweep rate $v = 2$ mV s^{-1}

Electric charge, which is defined by the area beneath an oxidation peak, is formed by a sum of an oxidation charge of adsorbed CO (Q_{CO}) and a charge of ruthenium surface oxidation (Q_O): $\Sigma Q = Q_{CO} + Q_O$. ΣQ was obtained by integration of the area enclosed by the voltammetric curve 3. The integrated value of the envelope curve 1 Q_O (e.g. without CO adsorption) was subtracted from the sum ΣQ in the same potential range and $Q_{CO} = \Sigma Q - Q_O$. The suitability of the used procedure confirms the courses of cathodic branches of VCs. The reduction charge of curve 3 is evidently almost the same as the charge of curve 1, which implicates that in the oxidation branch of the voltammetric curve both oxidations occurred; the oxidation of adsorbed CO and also the oxidation of ruthenium surface. The Q_O value is evidently the same in both solutions.

The charge of the oxidation of adsorbed hydrogen was determined by an integration of an area defined by the envelope in curve 1 (e.g. non-poisoned electrode) from above in the potential range from 0.05 V to about 0.21 V and by the value of poisoned electrode current (a segment of curve 3) from below (Q_{H1}). The remaining area between 0.21 and 0.3 V, where the curve bends due to oxidation of the ruthenium surface at the non-poisoned electrode, was also determined by the integration of an area where the upper part of the curve was replaced with a straight line connecting the current value at $E \approx 0.21$ V and the current value of poisoned electrode at $E = 0.300$ V (Q_{H2}), and the bottom part was limited with the current value of poisoned electrode. The total charge of the oxidation of adsorbed hydrogen Q_H is $Q_H = Q_{H1} + Q_{H2}$. Q_H values for individual Ru blacks evaluated by this way are summarized in Table 1.

This procedure supposes that the current of the totally poisoned electrode at $E \approx 0.3$ V is equal to the double-layer charging current of the electrode in pure solution. It was stated above that this assumption for the Pt electrode was not valid as the capacitance of the Pt/CO–solution was lower than that of the Pt–solution interface. For this same reason the charging current of poisoned Pt electrode is also lower than the double-layer charging current of the clean Pt electrode. With the assumption that the ratio $i_{dl}/i_{COd} \approx 1.55$ found for Pt was also valid for Ru electrodes, it was possible to evaluate the corrected charge of adsorbed H oxidation Q_{HC}. All obtained H oxidation charges calculated by this way are also summarized in Table 1.

The ratio R of CO/H adsorbed particles was determined similarly as it was done for the Pt blacks. It could not be possible to entirely poison the Ru 1 blacks as even after long-term CO adsorption, remnants of adsorbed hydrogen remained on the electrode surface and a charge of residual adsorbed hydrogen Q_{HR} was measured during voltammetric oxidation. Hence, the values Q'_H ($Q'_H = Q_H - Q_{HR}$) instead of Q_H were employed in the calculation of R. The summary of obtained results is displayed in Table 1. The table comprises further of the following data: P_{VT} (m^2 g^{-1})—a surface of Ru blacks obtained from voltammetric curves in the potential range $0.45 < E < 1.15$ V after previous oxidation by heating in air at ≈ 200 °C for 5 h; P_{CO} (m^2 g^{-1}) calculated from Q_{CO} provided that a specific charge of an oxidation of adsorbed CO is 420 μC cm^{-2} [1], $\Theta_H = 2Q'_H/Q_{CO}$ and $\Theta_{CO} = P_{VT}/P_{CO}$. Non-constant values of Θ_H for individual Ru blacks are in agreement with the findings [11] that the amount of adsorbed hydrogen on the ruthenium depends considerably on history and a treatment of the Ru electrode. This also applies to the used Ru 2 blacks. In this case, prepared Ru black was first oxidized for 3 h at 300 °C into RuO$_2$. The specific surface area of oxidized Ru black, determined by the method described earlier, was $P_{VT} = 5.6$ m^2 g^{-1}. After the determination of the surface area, the voltammetric curve of the RuO$_2$ electrode in the potential range 0.05–0.945 V was measured (Fig. 4, curve 1). Then the RuO$_2$ black was reduced for 4 h at 200 °C in a hydrogen atmosphere. The reduced electrode was put in the electrochemical cell, maintained at $E = 0.00$ V for 30 min and at $E = 0.050$ V for further 15 min and the voltammetric curve 2 (Fig. 4) was recorded. The process (without reduction in gas phase) was repeated so as to obtain curve 3. Curve 4 was obtained after two further activations. Then after CO adsorption, the values Q_H and Q_{CO} were determined by the method described earlier. After these processes Ru electrode was again oxidized for 5 h at 200 °C in air, after which the surface area of RuO$_2$ black was determined. The specific surface area $P_{VT} = 8.47$ m^2 g^{-1} was found after the described procedures. All the measured and evaluated quantities are summarized in Table 1, row Ru 2. It could be concluded from these values that the ruthenium black surface prepared by H$_2$ reduction of RuO$_2$ in gas phase adsorbs only a small amount of hydrogen. The amount of adsorbed hydrogen increased

Table 1 Summary of evaluated data for various Ru blacks

Ru black	P_{VT}	Q_{CO}	Q_H	Q_{HC}	$Q_{CO}/(2Q'_H)$	P_{CO}	Θ_H	Θ_{HC}	Θ_{CO}
1	18.3	96.2	22.6	21.0	2.12	22.9	0.47	0.43	1.25
2	8.47	39.05	9.11	8.45	2.14	9.29	0.46	0.43	1.09
3	1.81	8.05	1.41	1.24	2.85	1.91	0.35	0.33	1.05

P_{VT} specific surface (m^2 g^{-1}) determined from VCs of RuO$_2$, Q_{CO} oxidation charge (C g^{-1}) of adsorbed CO, Q_H oxidation charge (C g^{-1}) of adsorbed hydrogen, Q_{HC} corrected oxidation charge of adsorbed hydrogen, $Q'_H = Q_H - Q_{HR}$ where Q_{HR} is remnant adsorbed hydrogen after CO adsorption, P_{CO} surface area (m^2 g^{-1}) determined from Q_{CO}, $\Theta_H = 2Q'_H/Q_{CO}$, $\Theta_{HC} = 2Q'_{HC}/Q_{CO}$ and $\Theta_{CO} = P_{CO}/P_{VT}$
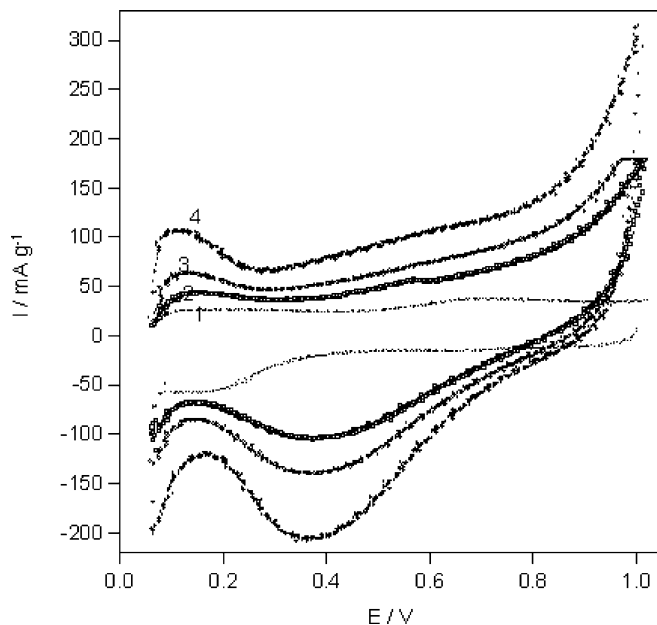
Fig. 4 Voltammograms of Ru 2 black. *1* Original RuO$_2$ black, *2* immediately after the reduction in H$_2$, *3* after first cycle of reduced electrode, *4* after fourth cycle. Sweep rate $v = 2$ mV s^{-1}

after an activation of the Ru black by potential cycling in a potential range 0.00–0.945 V. The shape of voltammetric curves of reduced and successively activated Ru black electrodes and P_{VT} values of RuO$_2$ electrodes, determined before the reduction and after the activation showed that during activation a number of centers for hydrogen adsorption (on the surface unit) as well as total ruthenium surface increased.

Supported catalysts and bimetallic Ru–Sn catalysts

A method of measuring the charge of oxidation of adsorbed CO cannot be applied for determining an Ru surface area on carrier catalysts because on the anodic branch of the voltammetric curve not only ruthenium but also a ruthenium support and conductive additive graphite are oxidized. Charges of oxidation of the ruthenium support and conductive additive graphite were not sufficiently reproducible. Thus the use of these values in the evaluation of the oxidation charge of CO adsorbed on Ru surface would lead to serious inaccuracies.

Adsorption of CO was only useful for the determination of the double-layer charging current i_{COd}. It was then possible to determine Q_H on Ru/carrier catalyst in a similar way as was employed for the Ru blacks. Assuming that the degree of coverage on the Ru surface by adsorbed hydrogen is about 0.46 it was possible to estimate the free Ru surface area.

The determination of free surface of Ru–Sn catalysts, where hydrogen could be adsorbed, is not highly reliable. The high error is caused by the fact that free catalyst surface depends on Sn content in the catalyst

and that it is smaller than at catalyst without Sn. Additionally the shape of the H oxidation voltammogram on Ru–Sn catalysts does not allow for the extrapolation of the voltammetric curve to the i_{COd} current density.

Discussion

Voltammetric curves measured on Pt black electrodes with adsorbed CO showed the occurrence of two adsorption peaks of adsorbed CO. It indicates the existence of energetically different adsorption centers for the adsorption of CO on used Pt blacks, similar to hydrogen adsorption.

The study of CO adsorption on Ru blacks confirmed our original aim to utilize CO adsorption for determining a free Ru surface, i.e. the Ru surface on which hydrogen can be adsorbed. It was proved that CO adsorption on Ru blocked the oxidation of ruthenium until the value for E reached about 0.35 V. This allowed the determination of charging current of a double-layer i_{COd} of Ru/CO–solution interface. Provided that this value is equal to the double-layer charging current of the electrode without adsorbed CO, we can determine the oxidation charge of adsorbed hydrogen by extrapolating the voltammetric curve to i_{COd} at $E \approx 0.3$ V (assumed end of hydrogen adsorption) and by integrating arisen area. It emerged from Table 1 and Fig. 4 that hydrogen adsorption is more complicated on ruthenium than on platinum. The amount of adsorbed hydrogen, or the degree of surface coverage, depends mostly on electrode history or its surface preliminary preparation; it was also proved qualitatively in other works [10, 11]. The specified ratio $Q_{CO}/2Q'_H$ for Ru blacks is always higher than 1 and exceeds even 2.

The surface area calculated from the upd Cu stripping analysis [17] was in close agreement with the surface area determined by the BET method, whereas that calculated from CO adsorption stripping analysis was around twice as large. On the other hand, we have found that there is a good agreement on the ruthenium surface area when determined by the voltammetry of oxidized Ru black and from the stripping of adsorbed CO (assuming the 1:1 stoichiometry between CO$_{ad}$ and Ru sites). Even though the accuracy of the surface area determination in the cited work was not great (measured values were 15 and 25 m^2 g^{-1}), it was reasonable to expect that the values of the surface area determined by the BET method were more accurate than those obtained by us. We measured the Ru surface area by the method according to Burke [12] which is based on empirical factors. Hence, the 2:1 stoichiometry found by Green and Kucernak [17] is more probable than the 1:1 stoichiometry found by us. On the other hand, it followed from many IR spectroscopy measurements that CO adsorbs on ruthenium similarly as on platinum, i.e. in the form of a single-bonded species or, to a lesser extent, dissociatively. In the recently published paper

[24] concerning the in situ FTIR spectroscopy of CO on an Ru electrode the authors showed that in acid solutions CO on Ru [0001] electrode adsorbed in a linear form, i.e. in a 1:1 stoichiometry. In another publication [25] authors described that CO can also be adsorbed onto ruthenium in the vicinity of Ru–O sites. These experimental findings suggest that the comprehensive understanding of CO adsorption onto ruthenium surfaces is a complex task and requires further investigation. It seems that it is not possible to reliably determine the real surface area of Ru electrodes using only CO stripping analysis. If the 2:1 stoichiometry between CO_{ad} and surface ruthenium sites is valid then the surface area listed in Table 1 (P_{CO}) should be around a half-value and the maximum degree of coverage by adsorbed hydrogen about twice as large.

Interestingly, however, the initiative to use CO adsorption as a means to shift the oxidation of ruthenium to more positive values, allowed the determination of the double layer charging current of the non-poisoned Ru electrode. This method is valid on the assumption that the double layer charging current density of the Ru/CO–solution interface is equal to that of the Ru–solution interface. It followed from the Refs. [22, 23] that the specific capacitance of the Pt/CO–solution interface is lower than that of the Pt–solution interface. For that reason the double layer charging current density must be different on both interfaces. It was shown in the Sect. 3 that the ratio i_{dl}/i_{COd} for Pt black electrodes is equal to about 1.55. This value is very close to the ratio of capacitances found for (111)Pt monocrystalline electrode found on both interfaces [22, 23]. Supposing that the ratio $i_{dl}/i_{COd} = 1.55$ is also valid for the Ru black electrodes, corrected values of the adsorbed hydrogen oxidation charge Q_{HC} were evaluated. The data in Table 1 show that corrected Q_{HC} values are not significantly different from uncorrected ones.

The ruthenium surface accessible to the hydrogen adsorption often depends on the method of the electrode activation before measurement. This fact is important in the determination of an active Ru surface in reactions with adsorbed hydrogen, such as catalytic hydrogenations or electrocatalytic reductions. In these cases, a surface determined by the voltammetry of RuO_2 surfaces [12, 14] is less exact than a surface calculated from the Q_H charge and for the comparison of various Ru catalysts it is not important whether the maximum degree of coverage by adsorbed hydrogen is $\Theta_H \approx 0.46$ or twice as large.

Conclusion

The achieved results confirmed that adsorbed CO effectively eliminated oxidation of ruthenium until the potential of E reached about 0.35 V. From this point, the oxidation of adsorbed CO starts and it is accompanied by the oxidation of ruthenium, which occurs on the unblocked free surface. This could be utilized in determining the value of the charging current of the electrode double-layer and for determining the amount of adsorbed hydrogen on the electrode without adsorbed CO. It was proved that contrary to Pt, where the ratio of the adsorbed particles is CO/H≈0.9, the ratio for ruthenium is approximately 2. The amount of hydrogen adsorbed on Ru blacks depends on the preliminary preparation of the electrodes. The method of CO adsorption in combination with H adsorption method can be employed in the determination of a free ruthenium surface of some Ru/support catalysts.

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