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CHEMISORPTION OF HYDROGEN AND OXYGEN ON γ-ALUMINA-SUPPORTED RHENIUM. PART 1. CHEMISORPTION OF HYDROGEN

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ABSTRACT

The chemisorption of hydrogen on γ-alumina-supported rhenium (10.4 wt.% and 1.04 wt.%) has been investigated gravimetrically, using a Cahn RG (HV) electrobalance, with respect to time (within 300 min), pressure (50–250 Torr, 1 Torr = 133.3 N m^{-2}) and temperature (20–550 ° C). Some results are compared with earlier data obtained volumetrically on rhenium powder. The chemisorption of hydrogen on supported rhenium was found to be similar to that on rhenium powder and is, in part, slow, thermally activated and, at each temperature in the applied range, partially or completely reversible. The applicability of hydrogen chemisorption, under properly chosen conditions, for the determination of the surface area and dispersion of supported rhenium is indicated and the dispersion data resulting from that determination are given.

INTRODUCTION

The study of hydrogen and oxygen chemisorption and of hydrogen–oxygen titration in a wide temperature range on supported metallic catalysts is very useful for the characterisation of the catalysts. It enables us to obtain information concerning the chemisorption features and other important properties of the catalysts such as the parameters of reduction and oxidation or the surface area and dispersion of the supported metal. Gravimetry is especially recommended in such a sorption study. Its usefulness results mainly from the possibility of continuous recording of the catalyst mass during the experiment. The method allows us to determine the kinetics and reversibility of sorption and to directly control the processes of reduction, oxidation or outgassing of the catalysts. Such a sorption study for hydrogen and oxygen on γ-alumina-supported rhenium seemed of considerable interest as it is widely used as a catalyst or catalyst promoter [1] and because there are no sufficient data on its interaction with either gas.

In our work, gravimetric investigations of hydrogen and oxygen chemisorption and of hydrogen–oxygen titration on Re/γ-alumina catalysts con-

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taining about 10 wt.% or 1 wt.% of the metal have been made with respect to time, pressure and temperature, in rather wide ranges, using a Cahn RG (HV) electrobalance. The main aims of the work were to obtain information on the interaction of hydrogen and oxygen with the supported rhenium and to use it for characterisation of the catalysts. Some results of the investigations can be compared with earlier data obtained volumetrically on rhenium powder [2,3].

Part I of this work presents the results obtained for the chemisorption of hydrogen. The sorption of hydrogen by supported rhenium catalysts has been investigated in numerous works in connection with the reducibility of the catalysts by hydrogen [4–16] or with the estimation of the surface area of rhenium by hydrogen chemisorption [17–26]. There are also a number of works in which the reducibility of supported rhenium catalysts was studied using various spectroscopic methods [27–32]. However, the results reported by various authors are not consistent. The differences refer to the reducibility of the catalysts, as well as to the chemisorption stoichiometry. The present results enable us to confirm some literature data on the system, as well as to indicate the applicability of hydrogen chemisorption for determination of the surface area and dispersion of γ-alumina-supported rhenium and to define the most advantageous conditions of that determination. The dispersion data resulting from that determination are also given.

Part II of this work presents the results obtained for chemisorption of oxygen and for hydrogen–oxygen titration [33].

EXPERIMENTAL

Apparatus

The high-vacuum sorption system (below 10^{-6} Torr), equipped with a Cahn RG electrobalance as previously described [34,35], was modified and adapted for the more exacting measurements of gas chemisorption on metallic catalysts. A zeolite pump was installed between the oil diffusion pump and the rotary forepump to allow for continuous pumping over 40 h. A glass coil immersed in liquid nitrogen was introduced into the gas-dosing system to improve the purification of the adsorbates. An iron–constantan thermocouple (Heraeus) was located in the quartz hangdown tube, sheltering the sample under study. This measured the temperature at 2 mm from the sample bulb with a nominal accuracy of 0.2 °C. A symmetrical quartz suspension was used for the sample and counterbalance, as before. The total mass of the sample container and its suspension amounted to 412 mg and was smaller by several percent than that used before. As before, the sample was protected from contamination from above by a quartz disc and, from below, by a getter placed in the bottom of the hangdown tube. The getter was made of the adsorbent under examination. Its mass, in each case, was five times as large as that of the adsorbent sample. The supply of hydrogen was identical to that given before. Oxygen was generated by thermal decomposition of $KMnO_4$ (Fluka, p.a., 99.96%), previously dried and outgassed at 150 °C. The modified system is described in detail in ref. 36.

Preparation and thermal pre-treatment of the catalysts

The catalysts were obtained by impregnation of the oxide support with aqueous solutions of ammonium perrhenate (Biddle Sawyer Co. Ltd.) [37]. The aluminium oxide was obtained by the heating of pseudo-boehmite in a stream of dry hydrogen at 400 °C for several hours and identified by the X-ray method as γ-alumina. High purity pseudo-boehmite [Si, B, Mg, Cu: 10^{-4}–10^{-3}%; Fe, Na: 10^{-3}–10^{-1}%] was prepared in another laboratory by hydrolysis of aluminium isopropoxide [38]. The surface area of γ-alumina outgassed at 400 °C, determined by the BET method from the low-temperature argon adsorption, amounted to 230 m^2 g^{-1}. It decreased to 165 m^2 g^{-1} after additional outgassing of the oxide at 500 °C and 550 °C [34]. Fresh catalysts were dried on a water bath for 24 h. After preliminary reduction in a stream of dry hydrogen at 500 °C over 10 h and then cooling in hydrogen to room temperature, the catalysts were stored in air for several months. The metal concentrations in the catalysts, 10.4 wt.% and 1.04 wt.%, were calculated from the mass of the support used for impregnation and from the mass of rhenium in the impregnation solutions, the loss of mass from the support during the reduction of the catalysts at 500 °C being considered.

The measurements were made on several samples of each catalyst by hanging them on the balance; about 350 mg of the high-percentage catalyst (10.4 wt.% $Re/\gamma\text{-}Al_2O_3$) or about 580 mg of the low-percentage catalyst (1.04 wt.% $Re/\gamma\text{-}Al_2O_3$) were used. After outgassing at room temperature, the sample was subject to repeated heating in hydrogen at 250 Torr for 12 h and in vacuo for 12 h, first at 400 °C and then at 550 °C. The reduction and outgassing cycle at 400 °C was repeated five times. At 550 °C it was repeated to constant mass of the sample in vacuo and its reproducible increment in hydrogen. In addition, prior to each measurement, the sample was heated at 550 °C until its constant mass was achieved in hydrogen (2 h) and in vacuo (12 h). The same thermal pre-treatment was applied to the samples of pure support.

Sorption and calibration measurements

The measurements were made on each catalyst sample first for hydrogen sorption, then for oxygen sorption and hydrogen–oxygen titration and, finally, for hydrogen sorption once again.

The pressures and temperatures applied for hydrogen sorption varied in the ranges of 50–250 Torr and 20–550 ° C. Gradually increasing temperatures were applied and at each temperature the total and reversible sorption were measured at increasing pressures. The total sorption of hydrogen was measured in two ways: (A) on the sample cooled in vacuo from 550 ° C to the temperature of measurement; and (B) by saturating the sample with hydrogen from 550 ° C to the temperature of measurement.

The time needed for cooling the sample in vacuo from 550 ° C to the temperature of measurement, ranging from 20 ° C to 400 ° C, varied from 180 min to 30 min, respectively. An additional 30 min were allowed for stabilisation of the sample temperature. The cooling time in hydrogen was a little shorter. The reversible sorption of hydrogen was determined after the total sorption and the subsequent outgassing of the sample at the temperature of measurement for 1 h. Changes in the mass of the catalyst samples during sorption of hydrogen were recorded for 2–5 h. They were determined with a balance sensitivity of 1 μg.

Identical conditions were applied in the calibration measurements in which, instead of catalyst, samples of pure support were used. The calibration corrections included an increase in the mass of the support sample resulting from hydrogen sorption by the support and an apparent change in the sample mass caused by various undesirable disturbances and forces [39–43]. The calibration corrections determined for the mass of support identical with the mass of catalyst, Δm_{cal}, were subtracted from the corresponding mass changes of the catalyst samples, Δm_{cat}, to obtain the corrected mass changes of the catalyst samples, Δm_{corr}. It was assumed that the corrected mass change of the catalyst sample, determined in the above manner, corresponded to the amount of hydrogen chemisorbed on the supported rhenium, $H_{2\mathrm{chem}}$.

$$H_{2\mathrm{chem}} = \Delta m_{\mathrm{corr}} = \Delta m_{\mathrm{cat}} - \Delta m_{\mathrm{cal}}$$

The change in the sample mass in hydrogen in the calibration measurements was fairly quick and was established within 20–30 min. The corrections for hydrogen were of greater importance because, in most cases, they were comparable with the changes in mass corresponding to the chemisorption on rhenium.

RESULTS AND DISCUSSION

Reduction and outgassing of the catalysts

Typical changes in mass recorded for a sample of the high-percentage catalyst during the final stages of heating in hydrogen and in vacuo at 550 ° C are presented in Fig. 1. The constant mass of the sample in vacuo

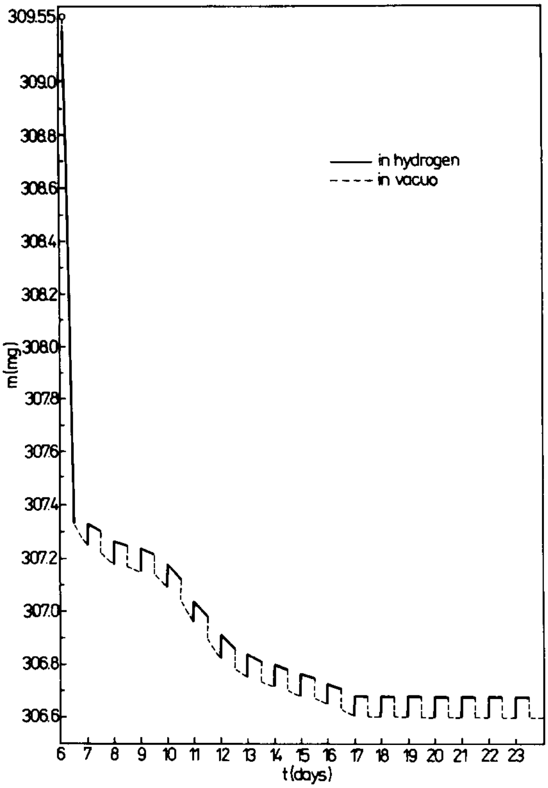

Fig. 1. Mass of a sample of the 10.4 wt.% Re/γ-Al_2O_3 catalyst during preheating at 550 ° C.

was achieved only after several days of heating in hydrogen and in vacuo, first at 400 ° C and then at 550 ° C. During the applied thermal treatment, the sample mass in vacuo decreased from 345 mg to 306.6 mg, i.e. by about 11%. More than 90% of this decrease in mass was observed as early as during the initial outgassing of the sample at room temperature and the following first five cycles of its reduction and outgassing carried out at 400 ° C. In that time the sample mass decreased from the initial value to 309.55 mg. The reproducible increase in the sample mass in hydrogen amounted to 80 μg and was attained as early as after the first cycle of reduction and outgassing at 550 ° C.

A similar course of mass changes was recorded during the thermal pre-treatment of samples of the low-percentage catalyst and of the pure support, except that the mass increment in hydrogen amounted to only 34 μg and 15 μg, respectively, and was much lower than that observed for the high-percentage catalyst. As for the catalyst samples, the total decrease in mass of the support samples amounted to 11%, and 90% of that decrease was recorded during outgassing of the samples at room temperature and their heating at 400 ° C.

From the above results, it follows that the decrease in the mass of the catalyst during thermal pre-treatment was mainly due to dehydration of the support. The large water content of the support is understandable because the catalysts were stored in air and the support had a large surface area. Following the considerations of MacIver et al. [44], it can be shown that the 11% decrease in mass observed for the catalyst and for the support having a surface area of 230 m^2 g^{-1}, may be due to removal of water which was physically adsorbed and chemisorbed on the support surface.

The results also indicate that to achieve a constant mass of the samples in vacuo, i.e. a stable state of the catalysts, it is necessary to heat them in hydrogen and in vacuo for over 100 h at 400 °C and for over 300 h at 550 °C. Such a long thermal treatment was required in spite of the use of small samples and the intensive pumping of the apparatus.

On the other hand, the results obtained in hydrogen show that the reproducible chemisorptive properties of the catalysts for hydrogen, i.e. the reproducible state of the catalyst surface, were already attained during the first reduction and degassing cycle at 550 °C, i.e. after 12 h heating in hydrogen and the following 12 h heating in vacuo at that temperature. The results suggest the reduction of the catalysts to metallic rhenium under the above conditions. This would be in accordance with much of the data published by other authors concerning the reducibility of alumina-supported rhenium catalysts by hydrogen. The catalysts are usually prepared, as in the present work, by impregnation of the support with rhenium compounds in which rhenium occurs in the +7 oxidation state. According to the data obtained under isothermal conditions or at the programmed temperature, as well as information from spectroscopic techniques, the total reduction of alumina-supported rhenium compounds by hydrogen to the metal is possible at temperatures close to 500 °C, or lower, mainly depending on the rhenium concentration in the catalysts [5–9,11,13,15,16,26,29]. However, there are also data indicating that rhenium occurs, at least partly, in similarly reduced catalysts in the +4 oxidation state [4,7,10,12,14,27,28,30–32] and that it is necessary to apply reduction temperatures exceeding 500 °C to achieve complete reduction to zero valence rhenium [4,7,10,12,15]. This is especially so in the case of catalysts with rhenium concentrations below 1% [4,10,12,15].

Chemisorption of hydrogen

The mass increment of the catalyst samples in hydrogen during the total sorption after procedure A, see above, was rapid in part only and occurred over 2–3 min. After this rapid process, slow changes in sample mass were recorded. They were found to have a linear dependence on log t, i.e. to obey Elovich kinetics, known to hold for sorption processes on a large number of catalysts [45–47].

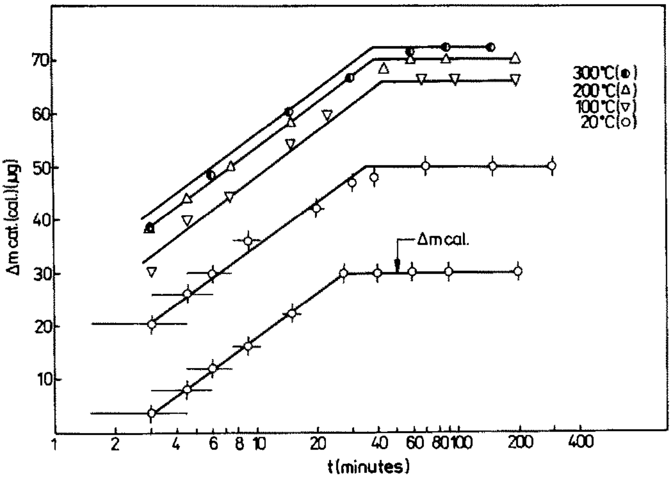

Fig. 2. Elovich plots for the total sorption of hydrogen using procedure A at 50 Torr on a sample of the 10.4 wt.% Re/γ-Al_2O_3 catalyst (m = 304.1 mg).

Figure 2 shows typical Elovich plots obtained at some temperatures during the total sorption according to procedure A on a sample of the high-percentage catalyst. The bending of the straight lines 30–40 min after contact of the catalyst with hydrogen indicates that sorption of hydrogen proceeds in two stages. Similar Elovich plots were obtained on the low-percentage catalyst. The plots were not analysed in detail because of the low accuracy of the time variable t (1.5 min) which was determined from the speed of the recorder tape. This caused considerable uncertainty as to the slope of the lines below the bending point. For the same reason, it was difficult to account exactly for the contribution of the support effect, Δm_{cal}, to that slope. The above difficulties are illustrated in Fig. 2 by presenting an Elovich plot obtained for the metal-free support at 20 °C as an example and by marking the uncertainty in the variable t at that temperature.

As a result, the final increase in mass at each pressure and temperature value was assumed after checking that it did not change over 1 h. The time necessary to achieve a constant value of the mass increase of the catalyst samples was 15 min at 550 °C and did not exceed 100 min at lower temperatures. In the case of the total sorption according to procedure B, no slow process was observed after cooling of the sample in hydrogen to the temperature of measurement. Reversible uptake in both measurements A and B was also rapid.

Figures 3–7 present the chemisorption data on supported rhenium determined by accounting for the calibration corrections in the manner given above. Figures 3 and 4 show the total and reversible chemisorption as a function of pressure at all the applied temperatures obtained according to procedures A and B on a sample of the high-percentage catalyst. For clarity,

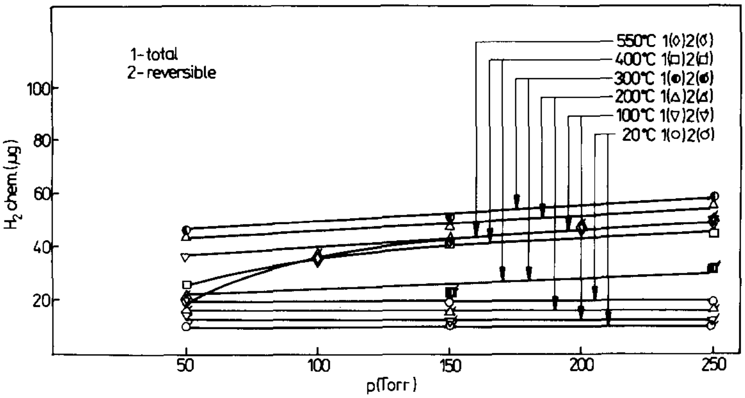

Fig. 3. Chemisorption of hydrogen using procedure A versus pressure on a sample of the 10.4 wt.% Re/γ-Al_2O_3 catalyst ($m = 304.1$ mg).

a number of experimental points were neglected. The results of analogous measurements performed on a sample of the low-percentage catalyst are given in Figs. 5 and 6. Figure 7 presents the chemisorption determined on the high-percentage catalyst at 250 Torr as a function of temperature, the amount of chemisorbed hydrogen being given in molecules per 1 g of the catalyst (molecules (g cat.)$^{-1}$).

As can be seen from Figs. 3–7, the chemisorption of hydrogen on both catalysts is activated in nature. On the samples of the catalysts cooled in vacuo to the temperature of measurement (procedure A), chemisorption increases with increasing temperatures and reaches its maximum value at 300 °C. The results obtained below 300 °C are much higher when the catalysts are saturated with hydrogen from 550 °C (procedure B). In this case, the total amount of chemisorbed hydrogen reaches its maximum value

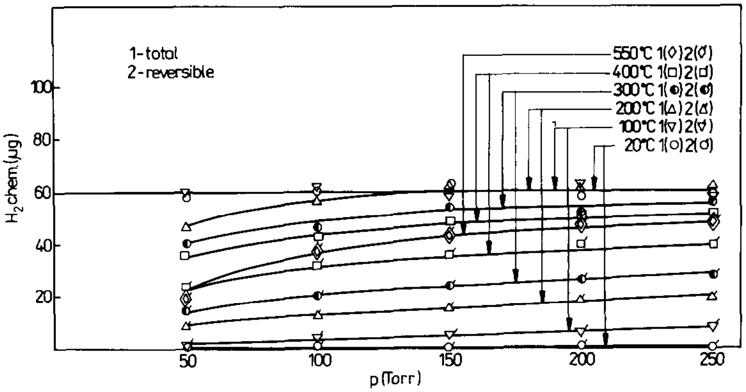

Fig. 4. Chemisorption of hydrogen using procedure B versus pressure on a sample of the 10.4 wt.% Re/γ-Al_2O_3 catalyst ($m = 304.1$ mg).

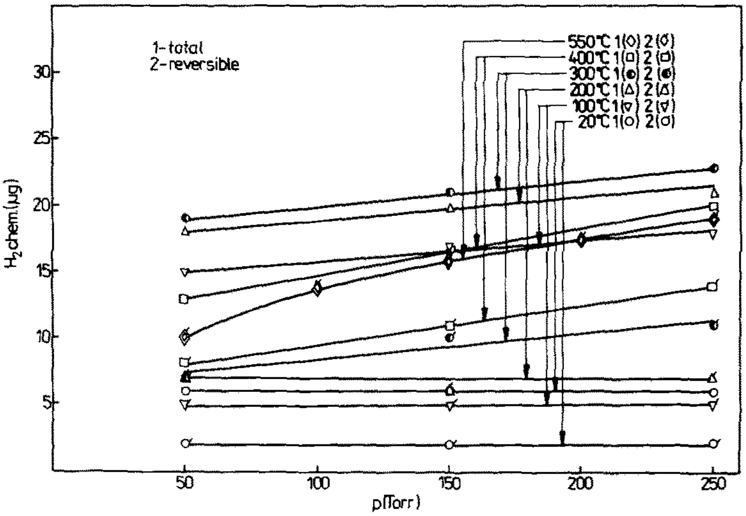

Fig. 5. Chemisorption of hydrogen using procedure A versus pressure on a sample of the 1.04 wt.% Re/γ-Al_2O_3 catalyst (m = 516.4 mg).

at 20–200 °C. At these temperatures, the chemisorbed amounts obtained according to procedure B are independent of pressure over the whole range or above 100 Torr, indicating saturation. The maximum total amount of hydrogen chemisorbed on the high-percentage catalyst at saturation at 20–200 °C, according to procedure B, is 60 µg for the sample 304.1 mg in mass, or 5.94×10^{19} molecules (g cat.)$^{-1}$. The temperature dependence of chemisorption on the low-percentage catalyst was found to be similar to that

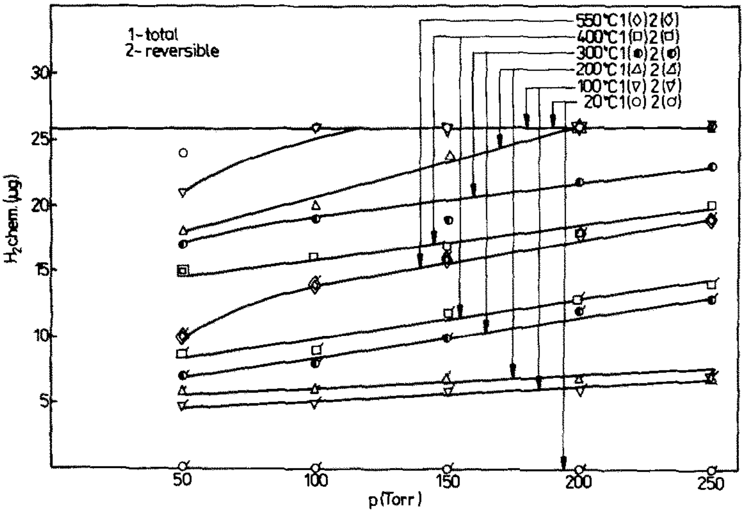

Fig. 6. Chemisorption of hydrogen using procedure B versus pressure on a sample of the 1.04 wt.% Re/γ-Al_2O_3 catalyst (m = 516.4 mg).

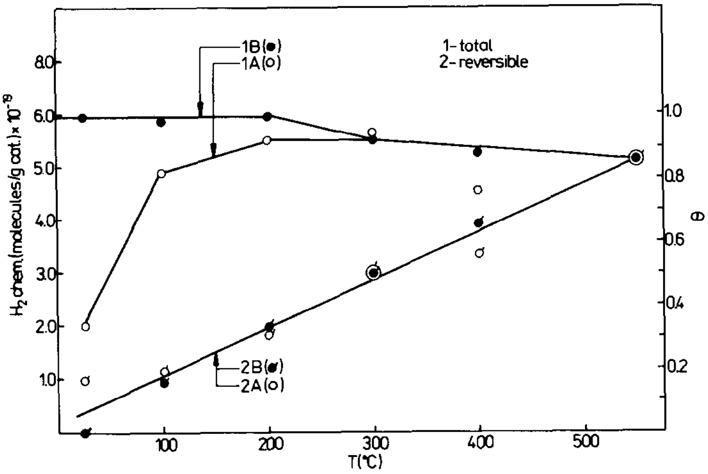

Fig. 7. Chemisorption of hydrogen versus temperature at 250 Torr on the 10.4 wt.% Re/γ-Al_2O_3 catalyst.

shown in Fig. 7, with the maximum value of the total chemisorption according to procedure B occurring at 20–200 °C and being 26 μg for the sample 516.4 mg in mass, or 1.52×10^{19} molecules (g cat.)$^{-1}$. At 20 °C these values are 3–4 times higher than those obtained according to procedure A. Thus, a larger portion of hydrogen chemisorption at room temperature at saturation is due to slow activated chemisorption. From the data given in Figs. 3–7, it also follows that at each temperature below 550 °C both irreversible and weaker reversible chemisorptions occur. At room temperature, the reversible chemisorption does not exceed 10% of the maximum value. At 300 °C it constitutes 40–60% of the total chemisorption typical of that temperature and about 30% of the maximum value. At 550 °C, chemisorption is totally reversible and constitutes 80% of the maximum value. These results indicate the energetic heterogeneity of the rhenium surface under study.

The results obtained in this work on γ-alumina-supported rhenium concerning the general dependence of hydrogen chemisorption on pressure and temperature, as well as its reversible portion at a given temperature, are similar to the respective results established for rhenium powder [2,3]. On the basis of the known surface area of the powder, it was shown that the maximal total amount of hydrogen chemisorbed on the powder at 20 °C with saturation from 400 °C corresponded, with considerable accuracy, to the monoatomic amount calculated by assuming the stoichiometry of chemisorption to be unity (one H atom per one surface Re atom) for the most dense crystallographic plane (001), with the number of surface atoms being 1.53×10^{15} cm^{-2} and the metal site area effectively occupied by one hydrogen atom being 0.065 nm^2 [3]. Thus, it seems reasonable to assume that the maximum total amount of hydrogen chemisorbed on both the catalysts used in the present work at room temperature according to procedure B, i.e. with saturation from 550 °C, also corresponds to the monoatomic layer. This amount was used for calculation of the coverage of rhenium surface with hydrogen, θ, given for the high-percentage catalyst in Fig. 7, as well as for calculating the quantities characterising the dispersion of supported rhenium, given below.

Some results of the present work obtained for chemisorption of hydrogen on γ-alumina-supported rhenium may be compared with the literature data. As already mentioned, the present results do not differ from the previous data obtained volumetrically on rhenium powder [2,3]. They are also consistent with those observed in the previous work on γ-alumina- or silica-supported rhenium (1%) [17]. On both unsupported and supported rhenium, chemisorption of hydrogen appears to be, in a considerable part, slow and thermally activated with a maximum value of the total chemisorption achieved at 300 °C. At room temperature, chemisorption is low, i.e. it does not exceed about 30% of the amount needed to form the monoatomic layer calculated for the most dense crystallographic plane exposed on the rhenium surface. In order to obtain monoatomic coverage of the rhenium surface at that temperature, it is necessary to heat the system above 300 °C. On both unsupported and supported rhenium, at each temperature within the range 20–550 °C, chemisorption of hydrogen is partially or completely reversible, i.e. removable from the rhenium surface by evacuation of the system for 1 h, indicating an energetic heterogeneity of the surface for that chemisorption.

The above results have a parallel in the data reported by other authors. In numerous works using volumetric, gravimetric or pulse-chromatographic methods, no chemisorption of hydrogen was observed on supported rhenium catalysts at room temperature [7,19–26]. Therefore, hydrogen was generally considered an unsuitable adsorbate for estimation of the surface area of rhenium by chemisorption methods. The activated character of chemisorption of hydrogen on rhenium has also been noted by other authors who observed an increase in hydrogen chemisorption on rhenium catalysts at increased temperature [7]. It was also reported that to obtain a high coverage of the rhenium surface with hydrogen at room temperature, the system should be heated over the temperature range 300–500 °C [19–21,25,26]. The present results, as well as those mentioned above, differ from the data of Yates and Sinfelt who found a considerable chemisorption of hydrogen at room temperature on a silica-supported rhenium catalyst cooled in vacuo to the temperature of measurement [18]. Assuming the surface stoichiometry of unity for that chemisorption, they obtained data on rhenium dispersion consistent with those resulting from the broadening of the X-ray diffraction lines. The energetic heterogeneity of the rhenium surface for hydrogen chemisorption, indicated in this work by a partial reversibility of chemisorption which increases at increased temperature, is also the conclusion drawn from the data of other authors obtained on various forms of rhenium. The investigations of the thermal desorption of hydrogen from rhenium powder [26], filaments [48], ribbons [49] or single crystals [50] demonstrated the occurrence of at least two forms of chemisorbed hydrogen on rhenium, differing in desorption temperature and, hence, in heat of chemisorption.

Dispersion of rhenium

Table 1 contains the dispersion data for rhenium, at both concentrations in the catalysts, determined from the chemisorption of hydrogen, i.e. the amount of hydrogen atoms chemisorbed in the monolayer n_m determined in the manner described above, the surface area A_s, calculated per 1 g of the catalyst (m^2 (g cat.)$^{-1}$) and a_s, calculated per 1 g of rhenium (m^2(g Re)$^{-1}$), the average particle diameter, l_{av} and the dispersion D. In calculating the values of A_s and a_s, it was assumed that the metal site area occupied by one hydrogen atom in the monolayer was 0.065 nm^2, as on Re powder [3]. The average particle size was calculated by using the relation

$$l_{av} = \frac{6 \times 10^7}{a_s d} \qquad (d = 21.04 \text{ g cm}^{-3})$$

i.e. by assuming that the particles are spherical. The dispersion D was defined as the atomic ratio n_m/n_{Re}, the ratio of the number of hydrogen atoms chemisorbed in the monolayer to the total number of rhenium atoms in the catalyst, i.e. by assuming the surface stoichiometry of unity for hydrogen chemisorption in the monolayer. To show the effect of the presence of the support on the dispersion of rhenium, the table lists the same parameters for rhenium powder, known or calculated from the data presented in ref. 3. The data on the thermal pre-treatment of the adsorbents are also given in Table 1.

As can be seen, the surface area and dispersion of supported rhenium are fairly large and greatly exceed (44 times and 100 times) the respective quantities for rhenium powder in spite of the more drastic thermal pre-treat-

TABLE 1

Dispersion data

Rhenium content (wt.%)	n_m (atoms (g cat.)$^{-1}$)	A_s (m^2 (g cat.)$^{-1}$)	a_s (m^2 (g Re)$^{-1}$)	l_{av} (nm)	D (n_m/n_{Re})
10.4 [a]	1.19×10^{20}	7.7	75	4.0	0.35
1.04 [a]	3.04×10^{19}	2.0	190	1.5	0.90
100 [b]	2.64×10^{19}		1.72	166	0.008

[a] Re/γ-Al_2O_3 catalyst, reduction and outgassing: 400 °C for 120 h, 550 °C for 360 h.

[b] Re powder, reduction and outgassing: 480 °C for 30 h, 400 °C for 30 h [3].

ment of the supported catalysts than of Re powder. In the case of the low-percentage catalyst, they are larger. The ten-fold decrease in the concentration of rhenium in the catalyst is accompanied by a greater than two-fold increase in its surface area and dispersion. The average diameter of the rhenium particles on the support is 4 nm in the high-percentage catalyst and 1.5 nm in the low-percentage catalyst.

Samples of both catalysts were observed in an electron microscope at magnifications of 500 000 and 1 200 000. There were too few visible particles to determine the distribution function with reference to the size of the metal particles. In the case of the high-percentage catalyst, particles up to 5 nm in size were observed. In the case of the low-percentage catalyst, there were particles up to about 1 nm in size. These observations are in rough agreement with the dispersion results obtained from the chemisorption of hydrogen. The results allow us to conclude that the chemisorption of hydrogen is applicable in the determination of the surface area and dispersion of γ-alumina-supported rhenium, provided that it is measured under properly chosen conditions. It follows from the data presented above that formation of a monolayer of chemisorbed hydrogen may be achieved above 100 Torr at room temperature following saturation from temperatures in excess of 300 °C. The accuracy of the determination of the amount of hydrogen chemisorbed in the monolayer n_m was estimated to be 4 μg, i.e. 7% for the high-percentage catalyst and 15% for the low-percentage catalyst. This accuracy in the determination of n_m and, hence, of the surface area and dispersion of supported rhenium seems to be satisfactory.

Finally, it should be noted that, within the above accuracy, the results did not change after the experiments with oxygen, i.e. after heating the catalysts in oxygen at temperatures up to 400 °C [33]. This means that during these experiments the dispersion of rhenium did not undergo any changes. Thus the effect of redispersion of alumina-supported rhenium described by some authors [7,25] was not observed in our work. This effect is the enhancement of the dispersion of rhenium on pre-heating the catalysts in oxygen at 300–500 °C. In these studies, the dispersion of rhenium was determined by the chemisorption capacity for hydrogen, as in the present work, as well as for oxygen and carbon monoxide. It seems necessary to study the effect more thoroughly with the use of other methods, especially electron microscopy, to determine the dispersion of the rhenium. Investigations into rhenium redispersion based only on the chemisorption capacity for gases, may be disturbed by various effects such as volatilisation of rhenium oxides, oxygen penetration into the metal lattice or resistance of oxidised catalysts to reduction by hydrogen and, hence, possible incomplete reduction of the catalysts before the chemisorption measurements and their possible reduction during measurements of hydrogen chemisorption. The above effects may result in apparent changes in the chemisorption capacity and, hence, in the rhenium dispersion.

CONCLUSIONS

The properties of rhenium supported on γ-alumina at concentrations of about 10 wt.% and about 1 wt.% with respect to the chemisorption of hydrogen in the pressure and temperature ranges of 50–250 Torr and 20–550 °C do not differ from those properties known for rhenium powder. On both supported and unsupported rhenium, chemisorption of hydrogen is, in part, slow, thermally activated and, at each temperature in the applied range, partially or totally reversible.

Under properly chosen conditions, the chemisorption of hydrogen may be used in the determination of the surface area and dispersion of supported rhenium. The formation of the monolayer of chemisorbed hydrogen is achieved above 100 Torr at room temperature following saturation from temperatures exceeding 300 °C.

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