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CHEMISORPTION OF HYDROGEN AND OXYGEN ON γ-ALUMINA-SUPPORTED RHENIUM. PART II. CHEMISORPTION OF OXYGEN AND HYDROGEN–OXYGEN TITRATION

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ABSTRACT

The chemisorption of oxygen and hydrogen–oxygen titration on γ-alumina-supported rhenium (10.4 wt.% and 1.04 wt.%) have been investigated gravimetrically using a Cahn RG (HV) electrobalance with respect to time (within 300 h), pressure (50–150 Torr or 50–250 Torr, 1 Torr = 133.3 N m^{-2}) and temperature (20–400 °C or 20–550 °C). The chemisorption of oxygen was found to be slow and occurred on the surface, as well as in the volume of the rhenium. The reaction of hydrogen with surface oxygen or volume oxygen is slow or very slow and occurs only at properly enhanced temperatures. The catalyst of lower rhenium content is more resistant to oxidation and to reduction by hydrogen, indicating a strong metal–support interaction. Because of the low rate and the volume processes, chemisorption of oxygen and hydrogen–oxygen titration are considered unsuitable methods for estimating the surface area and dispersion of rhenium in the applied temperature ranges.

INTRODUCTION

Part I of this work describes the results for the chemisorption of hydrogen on γ-alumina-supported rhenium (10.4 wt.% and 1.04 wt.%) obtained gravimetrically on a Cahn RG (HV) electrobalance [1]. This part of the study presents the results for the chemisorption of oxygen and for the hydrogen–oxygen titration for the same catalysts using the same method. Some results are compared with earlier data obtained volumetrically on rhenium powder [2].

The literature data on the chemisorption of oxygen and on the reaction of hydrogen with chemisorbed oxygen on supported rhenium have mainly been described in connection with the estimation of the metal surface area [3–13]. Most of the data were obtained at room temperature and only some results refer to elevated temperatures (5, 6, 8, 9, 12, 13). There are also a few studies in which the oxidation state of the supported rhenium, under oxidation or reduction conditions, was investigated by various spectroscopic

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techniques (14–19). The present study gives various data on the parameters of oxidation and reduction of γ-alumina-supported rhenium. The results obtained for hydrogen–oxygen titration reveal the possibility of distinguishing gravimetrically between reactions occurring on the surface and within the volume of rhenium. Some data indicating a strong metal–support interaction are also presented. Finally, the inapplicability of these processes for estimating the surface area and dispersion of rhenium in the applied temperature ranges is indicated.

EXPERIMENTAL

The sorption apparatus, as well as the catalyst preparation and thermal pre-treatment, were described in Part I [1]. The procedures used for the sorption of oxygen and for the uptake of hydrogen during titration were, in general, similar to those applied for the sorption of hydrogen, as described in Part I.

The pressure and temperature ranges applied for the sorption of oxygen were 50–150 Torr and 20–400 °C. The respective ranges for hydrogen–oxygen titration were 50–250 Torr and 20–550 °C, as for the sorption of hydrogen. Gradually increasing pressures and temperatures were applied. The total sorption of oxygen was measured only on the catalyst sample cooled in vacuo from 550 °C to the temperature of measurement, i.e. only after procedure A, as described for the sorption of hydrogen. The reversible sorption of oxygen was determined in the usual way following the total sorption and subsequent outgassing of the sample at the temperature of measurement for 1 h. The uptake of hydrogen during titration was measured after repeated outgassing of the sample at the temperature of measurement for 1 h following the total and reversible sorption of oxygen. The change of sample mass during titration was first recorded at the temperature of oxygen sorption. After completion of the measurements at that temperature at the highest pressure of 250 Torr, the sample was heated up to 550 °C at the rate of 5 °C per minute and kept at that temperature in hydrogen for 16 h. Next, the sample was outgassed at the same temperature for 8 h. After introduction of fresh hydrogen, the heating of the sample in hydrogen at 550 °C for 16 h was repeated. Outgassing of the sample at 550 °C for 2 h was the final step in its preparation for the next measurement. This standard cycle of reduction and outgassing at 550 °C over about 40 h was applied prior to each set of the experiments involving the total and reversible sorption of oxygen at a given temperature, and then the titration of irreversibly bound oxygen with hydrogen at the same temperature or above it. Hydrogen for titration was introduced over the oxidised sample at the temperature at which sorption of oxygen had been measured. In the case of titration at a higher temperature, the system was heated to that temperature. The change of sample mass during sorption of oxygen was recorded for 3–72 h. The time of recording during titration varied from 3 to 25 h. In some experiments, it was much longer and even extended to 300 h. Identical conditions were applied during calibration measurements made on samples of metal-free support. The balance sensitivity during the calibration measurements was 1 μg. During oxygen sorption and hydrogen–oxygen titration on catalyst samples, it varied from 0.01 mg to 0.1 mg.

The amount of oxygen chemisorbed by the supported metal, O_{2chem}, or of hydrogen taken up during titration, H_{2titr}, was determined as the corrected mass change of the catalyst sample, Δm_{corr}. The values of Δm_{corr} were calculated in a manner similar to that applied for the chemisorption of hydrogen, i.e. by subtracting the calibration corrections Δm_{cal} from the mass changes determined for the catalyst samples Δm_{cat} according to the relation

$$O_{2chem}\ (H_{2titr}) = \Delta m_{corr} = \Delta m_{cat} - \Delta m_{cal}$$

The calibration corrections for the sorption of oxygen determined on samples of pure support were established within 30–60 min. They were of little or no importance amounting to, at most, 10% of the mass change corresponding to chemisorption by rhenium.

It appeared that the interaction of oxygen with the catalysts consisted of chemisorption on the surface of the rhenium, as well as of oxidation within the volume of the rhenium. In the description of the results, the term ‘chemisorption of oxygen’ or its derivatives is used for both kinds of interaction.

RESULTS AND DISCUSSION

Chemisorption of oxygen

Typical results of the measurement of oxygen chemisorption by both catalysts are presented in Figs. 1 and 2 and in Tables 1 and 2. Figures 1 and 2 show the change in oxygen sorption with time on samples of each catalyst in the form of Elovich plots, Δm_{cat} versus log t, [20–22]. Tables 1 and 2 list the amount of chemisorbed oxygen O_{2chem} in mg per sample and in molecules per 1 g of the catalyst (molecules (g cat.)$^{-1}$) as a function of time and temperature. The corresponding values of the O/H and O/Re ratios are also given in Tables 1 and 2. They denote the ratio of the number of chemisorbed oxygen atoms to the number of hydrogen atoms chemisorbed in the monolayer, see Part I [1], and to the total number of rhenium atoms in the catalyst.

All the results given in Tables 1 and 2 were found to be completely irreversible, independent of pressure. The results show, above all, that the sorption of oxygen by the catalysts is a slowly activated process.

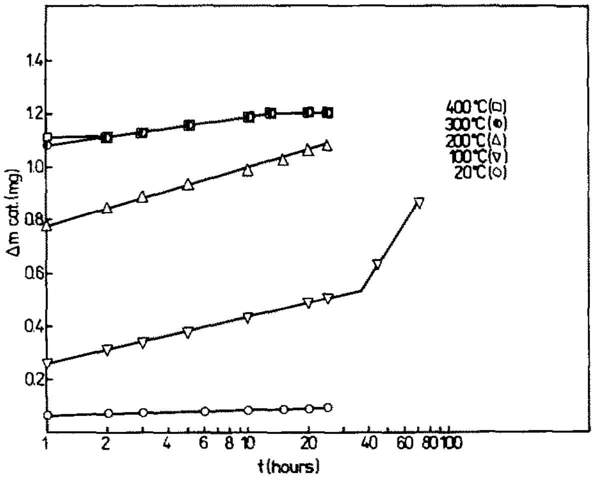

Fig. 1. Elovich plots for sorption of oxygen at 100 Torr on a sample of the 10.4 wt.% Re/γ-Al_2O_3 catalyst (m = 306.6 mg).

For the high-percentage catalyst below 400 ° C, a portion of the oxygen was sorbed rapidly over 1 min; but following that rapid sorption, a much slower mass change was recorded. At 20 ° C and 100 ° C, saturation of the catalyst sample with oxygen was not attained after 25 h or 72 h contact, respectively, of the sample with oxygen. At 200 ° C, the mass increase in

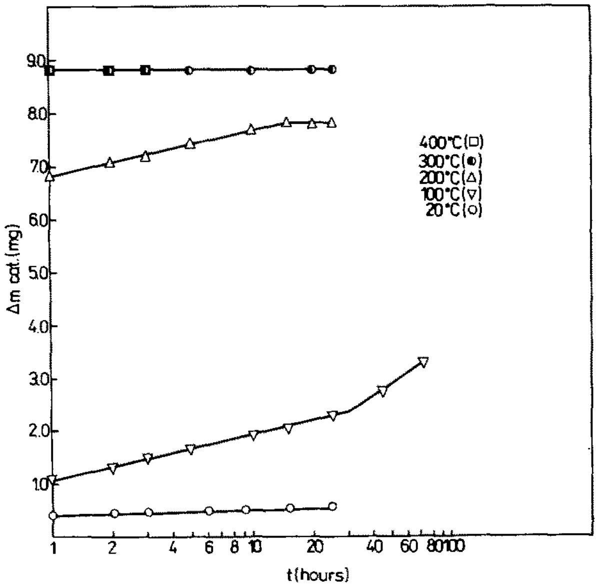

Fig. 2. Elovich plots for sorption of oxygen at 100 Torr on a sample of the 1.04 wt.% Re/γ-Al_2O_3 catalyst (m = 516.4 mg).

TABLE 1

Chemisorption of oxygen on the 10.4 wt% Re/γ-Al_2O_3 catalyst

T (°C)	t (h)	O_{2chem} (mg)	O_{2chem} (molecules (g cat.)$^{-1}$ $\times 10^{-20}$)	O/H	O/Re
20	1/60	0.25	0.15	0.26	0.09
	1/4	0.30	0.18	0.31	0.11
	1/2	0.35	0.22	0.36	0.13
	1	0.40	0.24	0.41	0.15
	3	0.42	0.26	0.43	0.15
	6	0.50	0.31	0.52	0.18
	9	0.51	0.31	0.53	0.19
	25	0.55	0.34	0.56	0.20
100	1/60	0.80	0.49	0.83	0.30
	1/4	1.05	0.64	1.08	0.38
	1/2	1.10	0.68	1.14	0.40
	1	1.20	0.74	1.24	0.44
	2	1.30	0.80	1.34	0.47
	5	1.55	0.95	1.60	0.57
	10	1.90	1.17	1.96	0.70
	15	2.05	1.26	2.12	0.75
	20	2.20	1.35	2.27	0.80
	25	2.30	1.41	2.38	0.84
	45	2.74	1.68	2.83	1.00
	72	3.34	2.05	3.45	1.22
200	1/60	4.4	2.70	4.55	1.61
	1/4	6.0	3.68	6.20	2.20
	1/2	6.55	4.02	6.77	2.0
	1	6.8	4.18	7.03	2.48
	3	7.2	4.42	7.44	2.63
	5	7.4	4.54	7.64	2.70
	10	7.7	4.72	7.96	2.81
	15	7.8	4.79	8.06	2.85
	20	7.8	4.79	8.06	2.85
	25	7.8	4.79	8.06	2.85
300	1/60	8.4	5.16	8.68	3.07
	1/4	8.55	5.25	8.83	3.12
	1/2	8.8	5.40	9.10	3.22
	1	8.8	5.40	9.10	3.22
	–	–	–	–	–
	–	–	–	–	–
	–	–	–	–	–
	25	8.8	5.40	9.10	3.22
400 [a]	1/60	8.8	5.40	9.10	3.22
	1/4	8.8	5.40	9.10	3.22
	1/2	8.8	5.40	9.10	3.22
	1	8.8	5.40	9.10	3.22
	2	8.8	5.40	9.10	3.22
	3	8.8	5.40	9.10	3.22

[a] Because of the observed Re_2O_7 volatilisation, measurements were made for 3 h only.

TABLE 2

Chemisorption of oxygen on the 1.04 wt.% Re/γ-Al_2O_3 catalyst

T (°C)	t (h)	O_{2chem} (mg)	O_{2chem} (molecules (g cat.)$^{-1}$ $\times 10^{-19}$)	O/H	O/Re
20	1/60	0.070	0.26	0.17	0.15
	1/4	0.075	0.27	0.18	0.16
	1/2	0.080	0.29	0.19	0.17
	1	0.110	0.39	0.26	0.24
	3	0.115	0.43	0.28	0.25
	6	0.120	0.44	0.29	0.26
	10	0.125	0.46	0.30	0.27
	20	0.130	0.47	0.31	0.28
	25	0.140	0.52	0.34	0.30
100	1/60	0.25	0.91	0.60	0.54
	1/4	0.28	1.02	0.67	0.61
	1/2	0.32	1.17	0.77	0.69
	1	0.35	1.28	0.84	0.76
	3	0.42	1.54	1.01	0.91
	5	0.45	1.64	1.08	0.97
	10	0.50	1.82	1.20	1.08
	15	0.55	2.00	1.32	1.19
	20	0.58	2.11	1.39	1.25
	25	0.61	2.23	1.47	1.32
	45	0.72	2.63	1.73	1.56
	72	0.96	3.51	2.31	2.08
200	1/60	0.65	2.37	1.56	1.41
	1/4	0.75	2.74	1.80	1.62
	1/2	0.80	2.92	1.92	1.73
	1	0.88	3.22	2.12	1.90
	3	0.99	3.62	2.38	2.14
	5	1.03	3.77	2.48	2.23
	10	1.08	3.96	2.60	2.34
	15	1.12	4.09	2.69	2.42
	20	1.16	4.24	2.79	2.51
	25	1.20	4.38	2.88	2.60
300	1/60	1.08	3.95	2.60	2.34
	1/4	1.13	4.13	2.72	2.44
	1/2	1.15	4.20	2.76	2.49
	1	1.18	4.32	2.84	2.55
	3	1.23	4.50	2.96	2.66
	5	1.24	4.53	2.98	2.68
	10	1.28	4.68	3.08	2.77
	13	1.30	4.74	3.12	2.81
	25	1.30	4.74	3.12	2.81

TABLE 2 (continued)

T (° C)	t (h)	O_{2chem} (mg)	O_{2chem} (molecules (g cat.)$^{-1}$ ×10^{-19})	O/H	O/Re
400	1/60	1.20	4.38	2.88	2.60
	1/2	1.20	4.38	2.88	2.60
	1	1.21	4.42	2.91	2.62
	3	1.23	4.50	2.96	2.66
	5	1.24	4.53	2.98	2.68
	13	1.30	4.74	3.12	2.81
	25	1.30	4.74	3.12	2.81

oxygen was established only after several hours; but at 300 ° C, within 30 min and at 400 ° C, after 1 min.

The irreversibility, as well as the presence of a slowly activated component of the sorption, suggest that the interaction of oxygen with the catalyst consists not only of chemisorption on the surface of the rhenium but also of oxidation of the bulk rhenium. This is confirmed by the values of the O/H and O/Re ratios given in Table 1.

At room temperature, the maximum coverage of the rhenium surface with oxygen obtained after 25 h amounts to 0.56. At 100 ° C, the maximum coverage attained after 72 h amounts to 3.45 and considerably exceeds the monoatomic value of unity. At increased temperatures, the O/H ratio increases. At 300 ° C and 400 ° C, it attains the high value of 9.10, indicating considerable oxidation of the bulk rhenium. At these temperatures, the O/Re ratio reaches 3.22 which is only 8% lower than that of 3.5 corresponding to the complete oxidation of rhenium to rhenium heptoxide Re_2O_7. It should be added that the above result, i.e. the O/Re ratio of 3.22 at 400 ° C, may be underestimated because of the possibility of volatilisation of the rhenium heptoxide formed as a product of rhenium oxidation [23]. In our experiments, this was indicated by the appearance of a grey deposit on the inner wall of the hangdown tube above the sample bulb during heating of the sample of high-percentage catalyst in oxygen at 400 ° C.

The results obtained on the low-percentage catalyst are similar and also indicate surface chemisorption of oxygen, as well as oxidation of the bulk rhenium. The differences in the behaviour of the catalysts are that both the rate and extent of chemisorption are smaller in the low-percentage catalyst.

Below 300 ° C, the uptake of oxygen by the low-percentage catalyst was very slow and after 25 h was still far from saturation. At 300 ° C and 400 ° C, the mass change of that catalyst in oxygen was established after several hours, while for the high-percentage catalyst this change took only 30 min or 1 min, respectively.

The maximum chemisorption of oxygen observed on the low-percentage catalyst at room temperature corresponds to the O/H ratio of 0.34, 40% lower than the ratio of 0.56 found on the high-percentage catalyst. At 100 ° C, the O/H ratio after 72 h is 2.31, over 30% lower than the value of 3.45 attained on the high-percentage catalyst. At 300 and 400 ° C, the maximum chemisorption corresponds to an O/Re ratio of 2.81, 13% lower than that of 3.22 found for the high-percentage catalyst, and 20% lower than the value of 3.5 expected at oxidation of rhenium to the heptoxide Re_2O_7. The volatilisation of rhenium heptoxide during heating of the low-percentage catalyst in oxygen at 300 ° C or 400 ° C was not noticed and could not be responsible for the underestimation of the O/Re ratio.

The data given in Figs. 1 and 2 indicate that the sorption of oxygen by both catalysts obeys Elovich kinetics, resulting in a linear dependence of the amount sorbed, Δm_{cat}, on log t. At 100 ° C, the plots bend after about 30 h or 40 h. Above the bending point, the slope of the straight lines increases. Changes in the mass of oxygen in the support were too small and too fast to have any influence on the kinetics of the mass changes in the catalysts and the latter must be connected with chemisorption by the metal. The bending of the Elovich plots indicates that chemisorption of oxygen at 100 ° C proceeds in two stages. The point of bending occurs at 2.4 mg of chemisorbed oxygen for the high-percentage catalyst, and at 0.61 mg for the low-percentage catalyst. This corresponds to an O/H ratio of 2.5 and 1.5, respectively. Thus, it is possible that the first stage of the process is the oxidation of 2–3 surface layers of rhenium whereas the second stage represents the slow diffusion of oxygen deep into the metal lattice and the volume oxidation of the metal. At 300 ° C and 400 ° C, the Elovich plots show a final convex part or a flat plateau indicating saturated oxidation in the volume of the metal. The Elovich plots in Figs. 1 and 2 would seem to be related to the S-shaped plots discussed by Aharoni [22].

The results presented above show that the interaction of oxygen with γ-alumina-supported rhenium in the temperature range 20–400 ° C consists of chemisorption on the surface, as well as in-volume oxidation of rhenium.

At room temperature, the interaction of oxygen with the catalysts is confined to chemisorption on the surface of the rhenium. The maximum coverage of the rhenium surface with oxygen at 20 ° C, equal to 0.56 or 0.34, is comparable with the coverage of 0.5 established for rhenium powder [2]. It does not differ essentially from the data of other researchers who found average fractional coverages of 0.63 for rhenium powder and for rhenium in the 0.1–1.43% Re/alumina catalysts [4], or of 0.29 for rhenium powder [9]. A surface coverage with oxygen of close to half a monoatomic layer at room temperature is also characteristic of single crystals of rhenium in which the most dense crystallographic plane (001) is exposed [24]. From the results obtained in this work, it follows that the chemisorption of oxygen on rhenium is a slowly activated process. Hence the attainment of monoatomic coverage of the rhenium surface with oxygen at room temperature probably requires a very long time and is not possible in practice. However, some reports have obtained or assumed coverages close to unity [5–7,11,12] and slightly higher than unity [5]. The coverages exceeding unity were explained by the authors as being due to partial chemisorption of oxygen in the molecular form. In our work, there was no indication of molecular chemisorption of oxygen. Coverages of the rhenium surface larger than unity were only found at elevated temperatures. The low rate and irreversibility of that chemisorption, as well as the results of hydrogen–oxygen titration described below, testify to volume oxidation of rhenium and not to non-dissociative surface chemisorption of oxygen.

The difficulties in attaining the saturation of the catalysts with oxygen at 20 °C may be indicative of some penetration of oxygen into the rhenium lattice even at room temperature. Certainly, it is not a deep oxidation because, under the applied conditions, the extent of oxygen chemisorption does not attain the monoatomic amount and the maximum value of the O/Re ratio amounts to only 0.2 or 0.3. Thus the volume oxidation at room temperature, if any, refers to only a few sub-surface layers of rhenium.

Above room temperature, oxidation of bulk rhenium occurs. A distinct bulk oxidation is already observable at 100 °C. The extent of oxidation increases at increased temperature and attains a maximum level at 300 and 400 °C. The present results on the temperature dependence of the interaction of oxygen with γ-alumina-supported rhenium have a parallel in the data of other researchers, who found oxidation of bulk rhenium when Re/alumina catalysts were exposed to oxygen at 500 °C [5] or at 150–500 °C [9].

The O/Re ratio values of 3.22 or 2.81 at temperatures of 300 and 400 °C are comparable with those of close to 3.5 found at 500 °C for Re/alumina catalysts containing over 7% of the metal [5], or of approximating 3.0 (2.51–2.86) found at 400 and 500 °C for the 0.5–10.0% Re/alumina catalysts [9]. Thus, it may be concluded that at 300 °C and above rhenium heptoxide is the main product of the oxidation of rhenium supported on alumina, as in the case of oxidation of rhenium powder [23]. Various effects may be responsible for some deviations of the observed O/Re ratio from the expected value of 3.5. The rather small 8% deviation found for the high-percentage catalyst is probably mainly due to volatilisation of rhenium heptoxide observed during the heating of that catalyst in oxygen at 400 °C. The rather large 20% deviation found for the low percentage catalyst should probably be considered as being mainly due to a strong metal–support interaction as discussed below.

Hydrogen–oxygen titration

The hydrogen–oxygen titrations indicate that the reaction of hydrogen with chemisorbed oxygen is only possible at elevated temperatures. It is accompanied by an increase in the mass of the catalyst at slightly elevated

TABLE 3

Hydrogen–oxygen titration on a sample of the 10.4 wt.% Re/γ-Al_2O_3 catalyst ($m = 306.6$ mg)

T_{chem} (°C)	t_{chem} (h)	O_{2chem}		T_{titr} (°C)	$H_{2titr,exp}$		$H_{2titr,calc}$ (molecules (g cat.)$^{-1}$ $\times 10^{-19}$)
		(mg)	(molecules (g cat.)$^{-1}$ $\times 10^{-19}$)		(mg)	(molecules (g cat.)$^{-1}$ $\times 10^{-19}$	
20	3	0.42	2.58	20	0.00	0	7.0
20		0.42	2.58	100	0.055	5.4	8.4
20		0.42	2.58	165	0.09	8.9	8.7
20	6	0.50	3.07	20	0.00	0	8.0
20		0.50	3.07	100	0.055	5.4	9.4
20		0.50	3.07	165	0.10	9.8	9.6
20	9	0.51	3.13	20	0.00	0	8.1
20		0.51	3.13	100	0.055	5.4	9.5
20		0.51	3.13	165	0.10	9.8	9.8
20	25	0.55	3.38	20	0.00	0	8.6
20		0.55	3.38	100	0.055	5.4	10.0
20		0.55	3.38	165	0.11	10.8	10.3
100	25	2.30	14.1	100	0.14	13.7	31.5
100		2.30	14.1	165	0.16	15.7	31.7
100	45	2.74	16.8	100	0.14	13.7	36.9
100		2.74	16.8	165	0.18	17.7	37.1

T_{chem} and t_{chem}, Temperature and time of oxygen chemisorption; O_{2chem}, amount of chemisorbed oxygen; T_{titr}, temperature of hydrogen–oxygen titration; $H_{2titr,exp}$, experimental amount of hydrogen taken up during titration for 3 h; and $H_{2titr,calc}$, $O_{2chem} \times 2 + H_{2chem}$, total calculated amount of hydrogen required during titration.

temperatures and by a decrease in the catalyst mass at sufficiently high temperatures. During rapid heating in hydrogen up to 550 °C, samples of the catalysts oxidised at 20 °C initially increased in mass. The mass increase attained a maximum at 165 °C for the high-percentage catalyst and at 350–460 °C for the low-percentage catalyst. Above these temperatures, the mass of hydrogen in the sample decreased. Tables 3 and 4 list the results of titrations obtained under isothermal conditions over the temperature range of 20–165 °C for the 10.4 wt.% Re/γ-Al_2O_3 catalyst and of 20–400 °C for the 1.04 wt.% Re/γ-Al_2O_3 catalyst.

For a sample of the high-percentage catalyst oxidised at 20 °C over 3, 6, 9 or 25 h, the maximum mass increase in hydrogen observed at 165 °C is consistent with the calculated amount of hydrogen necessary to react with chemisorbed oxygen and for chemisorption on the bare rhenium surface. At 100 °C, the experimental titration result is 40% lower than the calculated value. At 20 °C, the titration result is zero, i.e. no mass change in hydrogen

TABLE 4

Hydrogen–oxygen titration on a sample of the 1.04 wt.% Re/γ-Al_2O_3 catalyst ($m = 516.4$ mg)

T_{chem} (° C)	t_{chem} (h)	O_{2chem}		T_{titr} (° C)	$H_{2,titr,exp}$		$H_{2titr,calc}$ (molecules (g cat.)$^{-1}$ $\times 10^{-19}$)
		(mg)	(molecules (g cat.)$^{-1}$ $\times 10^{-19}$)		(mg)	(molecules (g cat.)$^{-1}$ $\times 10^{-19}$)	
20	3	0.115	0.42	20	0.00	0	1.2
20		0.115	0.42	100	0.01	0.6	1.7
20		0.115	0.42	200	0.015	0.9	1.8
20		0.115	0.42	300	0.02	1.2	1.9
20		0.115	0.42	400	0.03	1.7	1.5
20	6	0.12	0.44	20	0.00	0	1.2
20		0.12	0.44	100	0.01	0.6	1.7
20		0.12	0.44	200	0.015	0.9	1.9
20		0.12	0.44	300	0.02	1.2	1.9
20		0.12	0.44	400	0.03	1.7	1.6
20	25	0.14	0.51	20	0.00	0	1.4
20		0.14	0.51	100	0.01	0.6	1.8
20		0.14	0.51	200	0.015	0.9	2.0
20		0.14	0.51	300	0.02	1.2	2.0
20		0.14	0.51	400	0.03	1.7	1.7
100	3	0.42	1.53	100	0.01	0.6	3.9
100		0.42	1.53	200	0.05	2.9	4.0
100		0.42	1.53	300	0.06	3.5	4.1
100		0.42	1.53	400	0.07	4.1	3.8
100	13	0.53	1.93	100	0.01	0.6	4.7
100		0.53	1.93	200	0.05	2.9	4.8
100		0.53	1.93	300	0.06	3.5	4.9
100		0.53	1.93	400	0.07	4.1	4.6
100	25	0.61	2.22	100	0.01	0.6	5.3
100		0.61	2.22	200	0.05	2.9	5.4
100		0.61	2.22	300	0.07	4.1	5.5
100		0.61	2.22	400	0.09	5.2	5.2
200	25	1.20	4.37	200	0.10	5.8	9.7
200		1.20	4.37	300	0.12	7.0	9.8
200		1.20	4.37	400	0.16	9.3	9.5
300	25	1.30	4.74	300	0.12	7.0	10.5
300		1.30	4.74	400	0.17	9.9	10.2
400	25	1.30	4.74	400	0.17	9.9	10.2

For symbols, see footnotes to Table 3.

was observed for the catalyst sample oxidised at the same temperature. The titration result at 165 ° C for the sample oxidised at 100 ° C for 25 h or 45 h is much lower than the calculated value.

It may be concluded that, in the case of the high-percentage catalyst at 165 ° C, all the oxygen chemisorbed at 20 ° C reacts with hydrogen. Water resulting from the reaction is desorbed from the surface of rhenium and now chemisorption of hydrogen typical of a bare surface of rhenium takes place. The water is trapped by the support but is not desorbed over the 3 h period of the experiment. Oxygen chemisorbed at 100 ° C only partially reacts with hydrogen at 165 ° C. At 100 ° C, it is not possible for oxygen chemisorbed at 20 or 100 ° C to react completely with hydrogen. At 20 ° C, hydrogen does not react or reacts very slowly with chemisorbed oxygen. At that temperature, chemisorption of hydrogen on the rhenium surface covered with oxygen in amounts corresponding to 43–56% of the monoatomic layer does not occur or is exceedingly slow.

For the low-percentage catalyst sample oxidised at 20 ° C over 3–25 h, the maximum mass increment in hydrogen at 400 ° C is also consistent with the calculated amount necessary to react with oxygen and for chemisorption. At lower temperatures, 100 ° C, 200 ° C and 300 ° C, the amount of hydrogen taken up during titration is smaller than the calculated value. At 20 ° C, as in the case of the high-percentage catalyst, the titration result is zero. The titration results at 400 ° C obtained on the catalysts oxidised at elevated temperatures in the range 100–400 ° C are similar, i.e. they correspond to the complete reaction of chemisorbed oxygen with hydrogen. Thus, 400 ° C is high enough for the oxygen chemisorbed at elevated temperatures to react with hydrogen. Water formed during the reaction is desorbed from the rhenium surface but trapped by the support and cannot be desorbed during the 3 h experiment. At 20 ° C, hydrogen does not react with chemisorbed oxygen and is not chemisorbed on the rhenium surface covered with oxygen in amounts corresponding to 28–34% of the monoatomic layer, or these processes are too slow to be recorded.

A decrease in mass of the oxidised samples in hydrogen, observed above 165 ° C for the high-percentage catalyst and above 400 ° C for the low-percentage catalyst, must be due to reduction of the catalysts and removal of oxygen from them in the form of water generated during the reduction by hydrogen of the supported rhenium oxides. The complete reduction of the oxides should be matched by a decrease in the mass of the catalyst to its initial value, recorded after reduction and outgassing at 550 ° C and prior to sorption of oxygen. In the case of both the catalysts, such results were obtained only at 550 ° C for all the applied temperatures of oxidation.

After oxidation of the high-percentage catalyst sample at 400 ° C, its complete reduction in the above conditions was guaranteed by a standard cycle of reduction and outgassing at 550 ° C, including jointly heating in hydrogen for 32 h and in vacuo for 10 h. After oxidation of this catalyst at lower temperatures, the time of heating in hydrogen at 550 ° C could be shortened to 11–13 h to obtain once again the initial mass of the catalyst sample. In the case of the low-percentage catalyst, the standard cycle of reduction and outgassing at 550 ° C made it possible to remove about 85% of the oxygen from the sample. Complete reduction of the sample required five additional standard cycles of reduction and outgassing. Below 550 ° C, the mass decrease in hydrogen of oxidised samples of both the catalysts was very slow. After oxidation of the 10.4 wt.% Re/γ-Al_2O_3 catalyst sample at 400 ° C, the decrease of its mass in hydrogen at the same temperature over 25 h corresponded to removal of about 85% of the oxygen. A decrease in the mass of this sample was recorded even after a week of its heating in hydrogen at 400 ° C.

From the results presented above, it follows that the reaction of hydrogen with oxygen chemisorbed on the surface or bound in the volume of rhenium occurs only at properly enhanced temperatures. At slightly elevated temperatures, the reaction is probably confined to oxygen chemisorbed on the rhenium surface. Reduction of the volume rhenium oxides is conditioned by desorption of the water formed as a product of the reduction, not only from the rhenium but also from the support, and is possible only at sufficiently high temperatures. The former process is rather fast and brings about an increase in mass of the catalyst sample, at least during a 3 h experiment. The rate of the latter process is probably determined by the rate of desorption of water from the support and is slow or very slow, accompanied by a decrease in the sample mass. Thus, the application of the gravimetric method to hydrogen–oxygen titration on Re/γ-alumina catalysts enables us to distinguish between the reactions occurring on the surface and in the body of the metallic phase. The necessity of using elevated temperatures for the reaction of hydrogen with chemisorbed oxygen was also found on rhenium powder [2] and by some authors on rhenium supported on alumina [3,6,7,12,13].

It should be noted that the presence of even a small amount of oxygen on the surface of the rhenium is of great importance as it affects its chemisorptive properties for hydrogen at room temperature. According to the data obtained in this work, the presence of about 30% of the monoatomic amount of oxygen on the surface of the rhenium is sufficient to inhibit the chemisorption of hydrogen on this surface at 20 ° C. A similar behaviour was reported for the surface of rhenium ribbons for which one simple oxygen atom on the surface was found to prevent adsorption of six hydrogen atoms [25].

The investigations revealed differences in the susceptibilities of the catalysts to oxidation and, after oxidation, to reduction by hydrogen. The higher resistance of the low-percentage catalyst to the above processes may be indicative of a strong metal–support interaction resulting in the fact that a considerable part of the supported rhenium, at low concentration and high dispersion, as established in Part I [1], is bound to the alumina support, probably mainly in the tetravalent state, in the form of stable oxide complexes which are resistant to oxidation, as well as to reduction by hydrogen. The lack of volatilisation of rhenium heptoxide during the heating of the low-percentage catalyst in oxygen, mentioned above, is an additional indication of the stabilisation of rhenium oxides by the alumina support. Examples of such oxide complexes are known in the literature [5,14–19,26]. The importance of the stabilisation of rhenium oxides by the alumina support for the properties of Re/alumina catalysts has been discussed by Yao and Shelef [5].

Because of the low rates and the presence of volume processes, the chemisorption of oxygen and hydrogen–oxygen titration appear to be rather unsuitable methods for the determination of the surface area and dispersion of γ-alumina-supported rhenium, at least in the temperature ranges applied in this work.

CONCLUSIONS

The chemisorption of oxygen at 20–400 °C by γ-alumina-supported rhenium (10.4 wt.% and 1.04 wt.%) is a slowly activated process and, above room temperature, it occurs on the surface as well as in the body of the rhenium. Application of the gravimetric method to hydrogen–oxygen titration at 20–550 °C, enables one to distinguish between the reactions of hydrogen with chemisorbed oxygen occurring on the surface and in the body of rhenium. The reactions are slow or very slow and occur only at properly enhanced temperatures.

The catalyst with lower rhenium content is more resistant to oxidation and to reduction by hydrogen, indicating a strong metal–support interaction.

Because of the low rate and the presence of volume processes, the chemisorption of oxygen and hydrogen–oxygen titration are considered to be rather unsuitable methods for determination of the surface area and dispersion of γ-alumina-supported rhenium in the temperature ranges applied.

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