JOURNAL OF CATALYSIS 59, 176–187 (1979)

The Hydrogen–Oxygen Reaction on Lanthanide Oxides

VIII. The Hydrogen–Oxygen Reaction on Gadolinium Oxide

JOHN F. READ, ANDERSON R. MAXWELL, VEDA C. STOREY, AND GILLIAN A. WALLACE

Department of Chemistry, Mount Allison University, Sackville, New Brunswick, Canada, EOA 3CO

Received August 24, 1978; revised February 1, 1979

The stoichiometric hydrogen–oxygen reaction has been studied over gadolinium oxide at an approximately constant initial hydrogen pressure of 220 N m^{-2} over the temperature range 328 to 621 K, and at varying initial pressures at 496, 522, 548, 574, 598, and 623 K. The nonstoichiometric reaction has been studied at hydrogen–oxygen ratios from 0.11 to 9.0, at initial hydrogen pressures up to about 1×10^3 N m^{-2}, and at 443, 496, 546, and 623 K. After detailed kinetic analysis it is shown that the results best fit an equation of the form:

$$-\frac{dP_T}{dt} = \frac{kb_{H_2}{}^2P_{H_2}{}^2b_{O_2}P_{O_2}}{(1 + b_{H_2}P_{H_2} + b_{O_2}P_{O_2})^3},$$

where k is a proportionality constant, b_{H_2} and b_{O_2} are the adsorption coefficients for hydrogen and oxygen, respectively, P_T is the total pressure of hydrogen plus oxygen, and P_{H_2} and P_{O_2} are the partial pressures for hydrogen and oxygen, respectively. The most likely mechanism is one involving the competitive adsorption of molecular hydrogen and oxygen, with the rate-determining step involving the interaction between H_2O_2(ads) and H_2(ads).

INTRODUCTION

Gadolinium oxide has very similar catalytic properties to those of samarium oxide which were recently summarized (*1*). Gadolinium oxide has a very stable +3 valence and a more stable structure than samarium oxide, and, therefore, many of the differences, especially pretreatment effects, are attributed to these facts.

The oxygen exchange reaction has been studied under various conditions. The activation energy is reported as 50 kJ mol^{-1} (*2*) or 40 kJ mol^{-1} (*3*) on an oxygen pretreated sample; and 90 kJ mol^{-1} (*4*) or 80 kJ mol^{-1} (*5*) on a sample heated in air and then *in vacuo*. Heating *in vacuo* and then cooling below 500 K leads to a high activity, with an activation energy of 20 kJ mol^{-1} in the temperature range 250 to 500 K (*6*). Above 500 K, the catalyst is deactivated by oxygen, giving an activation energy of 40 kJ mol^{-1} above 500 K but resulting in complete deactivation below this temperature. Boreskov (*3*) explains this by stating that there is homogeneous, but not heterogeneous, exchange below 500 K, and that the sites for the homogeneous exchange are blocked by high temperature oxygen pretreatment. Therefore, the homogeneous exchange below 500 K does not involve surface oxygen but occurs on very active sites

0021-9517/79/110176-12$02.00/0

produced by partial loss of oxygen from the oxide surface. Above 500 K, both homogeneous and heterogeneous exchange occur, both involving surface oxygen. Boreskov records a second type of site on aluminum oxide, formed both by treatment *in vacuo* and by high temperature pretreatment with oxygen, resulting from the removal of hydroxyl groups. There is some evidence that these sites also occur on gadolinium oxide, but, if this is so, some activity would be expected below 500 K after oxygen pretreatment. However, this activity may be sufficiently low as to be immeasurable. The retarding effect of oxygen is also noticed with nitric oxide decomposition, where added oxygen up to a pressure of 400 N m^{-2} retards the reaction over gadolinium oxide to a much greater extent than over samarium oxide (*7*).

The activity of gadolinium oxide toward the hydrogen–oxygen reaction has been determined only for the stoichiometric mixture at low pressures, and the results are similar to those for samarium oxide (*8*). The parahydrogen conversion reaction and the hydrogen–deuterium equilibration reaction have been studied extensively over the temperature range 77 to 657 K (*9*). Both reactions occur above 400 K with identical rates, and, presumably, with similar mechanisms. Below 400 K, the parahydrogen conversion predominates, probably utilizing a paramagnetic mechanism, with two maxima for the activity at 300 and 90 K, and a minimum at 130 K. There is no decrease in activity in a weak magnetic field (*10*). The adsorption of hydrogen was studied in the range 77 to 98 K, giving results similar to samarium oxide (*11*).

EXPERIMENTAL METHODS

The apparatus, experimental procedure, catalyst conditioning, method of analysis, and identification system for reactions were identical to those described in previous papers in this series [for example, (*12*)]. Specpure grade gadolinium oxide was used with a surface area of 1.5×10^3 m^2 kg^{-1} and a total weight of 1.106×10^{-3} kg.

Twenty-eight groups of experiments were conducted. Groups 1 to 15 contain stoichiometric reactions at various temperatures in the range 328 to 621 K at an approximately constant initial hydrogen pressure of 220 N m^{-2}, two or three identical reactions being conducted in each group; groups 16 to 21 contain stoichiometric reactions at 496, 522, 548, 574, 598, and 623 K, respectively, each group comprising nine different reactions at various initial hydrogen pressures in the range 40 to 800 N m^{-2}; groups 22 to 25 contain nonstoichiometric and standard stoichiometric reactions; group 26 contains stoichiometric reactions at approximately 800 K after hydrogen pretreatment (12 hr at 200 N m^{-2}); group 27 contains stoichiometric reactions at 549 K; and group 28 contains stoichiometric reactions at 549 K after oxygen pretreatment (12 hr at 200 N m^{-2}).

RESULTS

Structure of Gadolinium Oxide

As for samarium oxide (*1*), gadolinium oxide can exist in forms other than the C-type at high temperatures. However, under the conditions prevailing in the present experiments, a stable C-type would be expected [for example, (*13*)]. X-Ray and ir analysis confirmed this structure and the absence of surface water and hydroxyl groups.

Analysis of Data

The data were analyzed as before [for example, (*12*, *1*)] and are summarized below and in the tables. The reaction types are as illustrated in Fig. 1 in (*1*). Types "a" and "b" show three distinct

TABLE 1

Summary of the Experiments and Results for the Stoichiometric Hydrogen–Oxygen Reaction on Gadolinium Oxide

Group, sets, and runs	Average temperature (K)	Initial hydrogen pressure range ($N\ m^{-2}$)	Gas in stoichiometric excess immediately prior to reaction	Overall order with respect to time	Initial rate ($N\ m^{-2}\ s^{-1}$)	Reaction type
01A1-6	445	220 ± 7		0.2 ± 0.2	3.6 → 1.0	a
02A1-3	407	220 ± 3		0.4 → 0.1	1.0 ± 0.4	a
03A1-3	367	220 ± 7		0.1 → 0.2	1.1 ± 0.1	a
04A1-2	328	220 ± 2		0.2	0.03	a, c
05A1-3	380	220 ± 3		0.1 → 0.2	0.4 → 1.0	a
06A1-2	471	220 ± 4		0.2 → 0.1	1.5 → 1.1	a
07A1-2	497	220 ± 2		0.2	1.8	a, b
08A1-3	522	220 ± 5		0.2 → 0.5	1.9 → 1.5	a
09A1-3	549	220 ± 4		0	1.9 → 1.6	a
10A1-3	572	220 ± 15		0	2.3 → 1.9	a
11A1-3	596	220 ± 3		0.1	2.0 ± 0.1	a
12A1-2	621	220 ± 1		0.2, 0.1	2.0, 1.8	a
13A1-3	572	220 ± 1		0.1 → 0	1.6 ± 0.1	a
14A1-2	497	220 ± 5		0	1.7, 1.2	a
15A1-2	445	220 ± 3		0	1.3, 0.6	a
16A1-9	496	800–50		0.2 ± 0.1	1.4 ± 0.6	a → c
17A1-9	522	770–40		0.2 ± 0.2	2.8 → 0.6	a → c
18A1-9	548	770–50		0.1 → 0.3	2.9 → 0.9	a → b
19A1-9	574	780–30		0.3 ± 0.1	2.3 → 0.7	a → b
20A1-9	598	780–40		0.2	2.2 → 0.7	a → c
21A1-9	623	780–50		0.3 ± 0.3	2.9 → 0.5	a → b
22B1-3	496	230 ± 114		0.1 ± 0.1	1.9 → 0.5	a
22D1		220	H_2	0.2	0.4	a
22F1		220	O_2	—	0.8	—
22H1		220	H_2	0	1.3	a
22J1		220	O_2	0	1.1	a
22L1		220	O_2	0.1	1.2	a
22N1		210	O_2	0.1	0.1	a
22P1		190	O_2	0	1.4	a
22R1		220	H_2	0	2.3	a
22T1		220	O_2	0.2	1.2	a
22V1		220	H_2	0	0.3	a
22X1		210	O_2	—	0.3	—
22Z1		210	H_2	0	0.5	a
23A1-3	623	240 ± 90		0	1.5 ± 0.1	a
23C1		210	H_2	0.2	1.4	a
23E1		220	O_2	0.4	1.4	a
23G1		220	H_2	0.2	1.2	a
23I1		220	O_2	0	1.5	a
23K1		220	O_2	0.3	1.4	a
23M1		210	O_2	0	1.1	a
23O1		220	O_2	0.1	1.5	a
23Q1		220	H_2	0	1.4	a
23S1		220	O_2	0.2	1.4	a
23U1		210	H_2	0.2	1.3	a
23W1		220	O_2	0	1.4	a

TABLE 1—*Continued*

Group, sets, and runs	Average temperature (K)	Initial hydrogen pressure range (N m^{-2})	Gas in stoichiometric excess immediately prior to reaction	Overall order with respect to time	Initial rate (N m^{-2} s^{-1})	Reaction type
23Y1		150	H_2	0.4	1.4	a
24A1-3	443	250 ± 125		0.2 → 0	1.6 → 0.8	a
24C1		220	H_2	0	1.0	c
24E1		220	O_2	0	0.6	a
24G1		220	H_2	0.2	0.8	a
24I1		210	O_2	0.2	0.8	a
24K1		220	O_2	0	1.0	a
24M1		220	O_2	0.1	0.9	a
24O1		220	O_2	0.2	0.8	a
24Q1		220	H_2	0	1.0	a
24R1-2		200 ± 10	O_2	0, 0.1	0.5, 0.7	a
24S1-2		190 ± 30	O_2	0	1.1, 0.7	a → c
25A1-3	546	250 ± 85		0.4 → 0	1.2 ± 0.2	a
25C1		220	H_2	0	1.1	a
25G1		220	H_2	0	1.0	a
25I1		220	O_2	0	1.0	a
25M1		320	O_2	0.2	0.9	a
25O1		210	O_2	0	2.2	a
25Q1		220	H_2	0.1	1.1	a
25S1		210	O_2	0.2	0.8	a
25U1		210	H_2	0	0.6	a
25W1		210	O_2	0	1.0	a
25Y1		170	H_2	0.1	1.0	a
26A1-3	821, 799, 773	106	Hydrogen pretreatment	0.6 → 0.4	0.8 → 1.0	b → c
27A1-5	549	160 ± 60		0.5 → 0.1	1.0 → 1.2	b → a
28A1-3	549	160 ± 60	Oxygen pretreatment	—	0.1	—

regions: an initial section of short duration with a slope which is either greater than the second section (type "a") or less than the second section (type "b"); a second linear section lasting for most of the reaction (the quoted orders with respect to time are calculated from this slope); and a third section with rapidly increasing slope. Type "c" does not show the "initial" section.

Summary of the Results for the Stoichiometric Reactions

Some of the results are summarized in Table 1. Missing letters within the groups indicate the presence of nonstoichiometric reactions.

Reaction type. Most of the reactions were of type "a," particularly at initial oxygen pressure > 90 N m^{-2}. Type "b" occurred only a few times, usually at low initial oxygen pressures in the range 15 to 25 N m^{-2} (for example, runs 07A2, 17A9, 18A9, 19A9, 21A8, and 21A9); coincidentally, these runs were often the last runs in the set. This type also occurred immediately after hydrogen pretreatment. Type "c" occurred at most temperatures, usually at initial oxygen pressures in the range 25 to 50 N m^{-2} (for example runs 16A8–9, 17A8, 19A8, 20A8–9, 23I1, and 26A3). The most consistent results were obtained before the nonstoichiometric reactions were conducted. From group 22 onward the stoichiometric reactions showed some irregularity, particularly after pretreatment by oxygen or hydrogen.

Catalyst activity. The initial rates are given in Table 1. The rate increases from 1 to 2 N m^{-2} s^{-1} as the temperature increases within groups 1 to 15, except for an abnormally high rate for the first run in group 1, and an abnormally low rate at the lowest temperature of 328 K. For groups 16 to 21 there was little temperature effect but the rates did decrease with pressure from approximately 2.8 N m^{-2} s^{-1} at initial hydrogen pressures of about 800 N m^{-2} to 0.5 N m^{-2} s^{-1} at pressures of 50 N m^{-2}. For the standard runs in groups 22 to 25, excess of either hydrogen or oxygen prior to the reaction lowered the initial rates slightly, with hydrogen having the greater effect at the higher temperatures and oxygen having the greater effect at the lowest temperature (443 K). Hydrogen pretreatment (groups 26 and 27) did not appear to affect the initial rate but oxygen pretreatment (group 28 at 549 K) reduced the initial rate considerably.

The rate of the central linear portion is consistently between 0.5 and 0.6 N m^{-2} s^{-1}, with no noticeable temperature effect but with a tendency to increase with increasing pressure. Prior excess of, or pretreatment with, hydrogen or oxygen had no observable effect on this rate.

The time taken for the reactions to go to completion is fairly consistent at 500 to 700 s for reactions at an initial hydrogen pressure of about 200 N m^{-2}. This changes from 200 to 2000 s as the initial pressure increases from 50 to 800 N m^{-2}.

Orders with respect to time. The orders with respect to time, calculated from the central, linear, portion of each plot, are shown in Table 1. For groups 1 to 15 most orders vary somewhat erratically between 0 and 0.2 with no obvious temperature dependence. In groups 16, 17, 18, and 19 the order increases from about 0.1 at an initial hydrogen pressure of 800 N m^{-2} to about 0.8 at 50 N m^{-2}. This trend is less obvious in groups 20 and 21 at the highest temperatures of 598 and 623 K, respectively. In groups 22 to 25 there is no overall effect of prior exposure to excess hydrogen or oxygen, although some orders in group 23 (at the highest temperature of 623 K) are slightly higher than the norm. This is also reflected in group 26 at 800 K.

Orders with respect to concentration. These orders are calculated from the six pressure-dependent groups 16 to 21. The plots were good, giving orders of 0.3, 0.5, 0.5, 0.6, 0.3, and 0.5 at 496, 522, 548, 574, 598, and 623 K, respectively. The average order is 0.5, with no uniform change with temperature.

Temperature effects. The Arrhenius plot, drawn assuming zero-order kinetics, is shown in Fig. 1. The activation energy has an average value of 1 to 2 kJ mol^{-1} over the entire temperature range, with an indication of a slight increase below about 380 K.

Summary of the Results for the Nonstoichiometric Reactions

Some of the results are summarized in Table 2 for groups 22 to 25. Missing letters within these groups indicate the presence of standard stoichiometric reactions.

Reaction type. Most reactions are type "a." In excess oxygen, all runs at 496 and 623 K are type "a." At 443 K (group 24) type "c" occurs for ratios in the range 1.00 to 1.75, with type "a" appearing at ratios of 0.50 and 2.00. At 546 K (group 25) type "c" occurs for ratios in the range 1.00 to 1.25, with type "a" appearing at higher and lower ratios. There are no type "b" reactions. In excess hydrogen, type "c" appears at high ratios at 443, 497, and 546 K, whereas at 623 K, type "b" appears at the highest ratios.

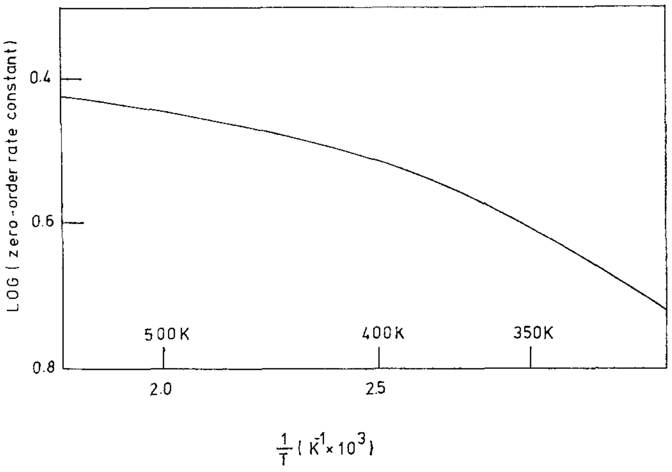

Fig. 1. Arrhenius plot from the results of groups 01 to 15.

Catalyst activity. The initial rate decreases as the hydrogen–oxygen ratio becomes more extreme, down to about 0.1 N m^{-2} s^{-1}, with the rate usually being higher in oxygen excess than in hydrogen excess. There appears to be a slight increase in rate with temperature.

The average rates for the major portion of the reaction are summarized in Table 3 for groups 22 to 25. As the ratio deviates slightly from stoichiometry, the rate decreases in excess hydrogen and increases in excess oxygen. This pattern continues for the rate in excess hydrogen with a low value of approximately 0.1 N m^{-2} s^{-1} at ratios of 9.00 or 0.11. In excess oxygen the rate increases for ratios of 2.50 or 1.50, and for a ratio of 1.25 at the lowest two temperatures. However, as the mixtures get further from stoichiometry the rate in excess oxygen begins to decrease, with the rate in excess oxygen now being lower than the rate in excess hydrogen. There does not appear to be any consistent temperature effect.

In general, reactions in excess oxygen go to completion in less time than those in excess hydrogen, but they also have the greatest variation with respect to ratio and temperature. Reactions in excess hydrogen are fairly consistent, except that when more than one identical reaction is performed under the same conditions, the second reaction is much faster than the first.

Orders with respect to time. The orders as summarized in Table 2 are somewhat erratic but tend to increase as the ratio deviates from stoichiometry and as the temperature increases. Close to stoichiometry, the hydrogen order is zero whereas the oxygen order is slightly higher. Further from stoichiometry the order increases to about 2, with a few orders being higher than this, and with the oxygen orders tending to be lower than the hydrogen orders.

Isobars. For all four nonstoichiometric groups the hydrogen and oxygen isobars exhibit maxima similar to those observed in previous work [for example, (*1*)]. The results are summarized in Table 4.

The ratio at the maxima of the isobars decreases with increasing oxygen pressure and increases with increasing hydrogen pressure. The ratios for the oxygen isobars are slightly higher than for the hydrogen isobars.

The average slopes on either side of the isobar are given in Table 4. A few anomalous results are not included and no average is given for the high pressure

TABLE 2

Summary of the Experiments and Results for the Nonstoichiometric Hydrogen–Oxygen Reaction on Gadolinium Oxide

Group, sets, and runs	Average temperature (K)	Initial H_2 pressure range (N m^{-2})	Initial H_2–O_2 ratio	Average order with respect to time		Reaction type
				O_2	H_2	
22E1-2	496	295, 163	1.75		0	a
22G1-2		410, 161	2.50	0.36, 0.32		a
22I1-2		240, 148	1.50		0, 0.4	a
22K1		157	1.00		1.3	a
22M1-2		200, 116	1.25		1.3, 0	c, a
22O1-2		160, 78	0.50		2.2, 1.8	a
22Q1-2		662, 162	4.00	0.9, 1.1		a
22S1-2		165, 42	0.25		—, 1.2	—, a
22U1-2		974, 132	9.00	—, 1.5		—, c
22W1-2		106, 18	0.11		—, —	—
22Y1		167	7.00	1.8		c
23B1-2	623	381, 163	2.25	0.5, 0.3		a
23D1-2		308, 168	1.75		0, 0	a
23F1-2		422, 167	2.50	0.5, 0.4		a
23H1-2		246, 156	1.50		0, 1.5	a
23J1		158	1.00		1.4	a
23L1-2		196, 143	1.25		1.4, 1.2	a
23N1-2		169, 83	0.50		1.4, 1.4	a
23P1-2		662, 167	4.00	0.4, 1.1		a
23R1-2		164, 42	0.25		1.8, 1.8	a
23T1-2		975, 170	9.00	2.5, 1.8		—, b
23V1-2		106, 18	0.11		—, 1.6	—, a
23X1-2		—, 163	7.00	—, 1.2		—, b
23Z1-2		—, 23	0.14		—, 2.8	—, a
24B1-2	443	373, 162	2.25	0.4, 0		a
24D1-2		289, 159	1.75		—, 0	a, c
24F1-2		417, 168	2.50	0.6, 0.4		c, a
24H1-2		242, 166	1.50		0, 0	c
24J1		167	1.00		0	c
24L1-2		200, 155	1.25		0, 0	c
24N1-2		163, 80	0.50		1.9, 2.0	a
24P1-2		579, 161	4.00	0.7, 1.0		a
25B1-2	546	370, 161	2.25	0, 0.3		a
25D1-2		287, 166	1.75		0, —	a, —
25F1-2		417, 164	2.50	0.6, 0.4		a
25H1-2		246, 164	1.50		0.2, 0	a
25J1		152	1.00		1.8	c
25L1-2		202, 152	1.25		1.4, 1.6	c
25P1-2		647, 167	4.00	1.1, 0.9		c, a
25R1-2		159, 39	0.25		3.0, 1.6	a
25T1-2		945, 165	9.00	2.5, 1.7		a, c
25X1-2		—, 164	7.00	—, 0.7		—, c
25Z1		22	0.14		2.4	a

side of the oxygen isobar at 546 K because of limited data. The only consistent pressure effect is for the high pressure side of the hydrogen isobars where the slope is always highest at the lowest pressure, giving an average value over the four

TABLE 3

Summary of the Average Reaction Rates (N m^{-2} s^{-1}) for the Nonstoichiometric Groups 22, 23, 24, and 25

Initial hydrogen–oxygen ratio	Group 24 (443 K)		Group 22 (496 K)		Group 25 (546 K)		Group 23 (623 K)	
	Excess of hydrogen	Excess of oxygen	Excess of hydrogen	Excess of oxygen	Excess of hydrogen	Excess of oxygen	Excess of hydrogen	Excess of oxygen
2.25 or 1.75	0.44 B[a]	0.64 D		0.78 E	0.42 B	0.78 D	0.44 B	0.79 D
2.50 or 1.50	0.36 F	0.80 H	0.48 G	0.94 I	0.36 F	0.86 H	0.38 F	0.89 H
1.25		0.88 L		1.00 M		0.77 L		0.72 L
1.00		0.17 J		0.45 K		0.50 J		0.55 J
0.50		0.16 N		0.39 O		0.15 N		0.14 N
4.00 or 0.25	0.22 P		0.24 Q	0.18 S	0.24 P	0.08 R	0.19 P	0.08 R
7.00 or 0.14			0.48 Y	0.02 l	0.05 X	0.02 Z	0.11 X	0.02 Z
9.00 or 0.11			0.12 U	0.05 W	0.09 T	0.03 V	0.08 T	0.02 V

[a] Indicates set from which rates are taken.

temperatures of 2.0. There may be a slight increase in the average slopes with temperature, but the error is too large to be definitive on this point.

The average value, using absolute numbers, from the low pressure side of the hydrogen isobar and the high pressure side of the oxygen isobar is 1.0, and the average value of the opposite slopes is 1.5.

DISCUSSION

The overall results fit the general pattern described previously [for example,

TABLE 4

Average Slopes and Maxima from the Isobars

Isobar	Group	Temperature (K)	H_2–O_2 ratio at max of isobar	Slope of isobar	
				Low pressure side of max	High pressure side of max
Hydrogen	24	443	1.1 ± 0.1	1.0 ± 0.2	−1.4 ± 0.4
Hydrogen	22	496	1.1 ± 0.2	1.0 ± 0.2	−1.6 ± 0.5
Hydrogen	25	546	1.2 ± 0.1	1.1 ± 0.2	−1.5 ± 0.5
Hydrogen	23	623	1.1 ± 0.1	1.1 ± 0.2	−1.2 ± 0.2
Oxygen	24	443	1.3 ± 0.3	1.4 ± 0.3	−0.8 ± 0.2
Oxygen	22	496	1.3 ± 0.1	1.7 ± 0.7	−0.8 ± 0.3
Oxygen	25	546	1.4 ± 0.1	1.7 ± 0.4	—
Oxygen	23	623	1.4 ± 0.2	1.7 ± 0.5	−0.9 ± 0.4

(*14*)] and so they will be discussed on the same basis as before [for example, (*1*)].

General Characteristics

Reaction type. Most of the reactions are of type "a," involving a rapid, reversible deactivation of the most active surface sites. An initial oxygen pressure of approximately 90 N m^{-2} is necessary for significant reaction to take place on these sites. At slightly lower initial pressures type "c" appears, and at pressures below about 50 N m^{-2} these sites are not readily available and the reaction starts slowly. This initially slow, type "b" reaction also occurs when the sites are occupied by hydrogen as a result of hydrogen pretreatment, and at high temperatures and high ratios with hydrogen excess. Conversely, excess oxygen produces more type "a" reactions with a tendency toward type "a" as the ratio approaches the stoichiometric composition. Therefore, it appears as if hydrogen blocks the most active sites whereas oxygen regenerates these sites. Unfortunately, the results after oxygen pretreatment are too erratic to confirm this suggestion, and it is possible that deactivation is by oxygen, and that at low oxygen pressures these sites are never fully deactivated.

Catalyst activity. The initial rate tends to increase with temperature and pressure. It decreases as the ratio of the nonstoichiometric reaction becomes more extreme and the availability of the alternate gas is decreased. The rate is slightly higher in oxygen excess than in hydrogen excess tending to confirm the suggestion above that hydrogen blocks some of the active sites. The effect of pretreatment, or nonstoichiometric reactions, on the initial rate of subsequent stoichiometric reactions is not clear, although there appears to be a temperature effect, with oxygen tending to increase the rate at low temperatures but with hydrogen tending to increase the rate at high temperatures.

The rate of the central, linear, portion decreases steadily as the nonstoichiometric ratio becomes more extreme in excess hydrogen probably due to the increasing scarcity of the alternate gas on the catalyst surface. The same pattern occurs in excess oxygen after an initial increase in rate as the ratio deviates slightly from stoichiometry. The rate in excess oxygen not only increases as the ratio increases but it is also higher than the rate in excess hydrogen. However, as the ratio becomes more extreme, oxygen has a greater retarding effect on the reaction and at the highest and lowest ratios of 9.00 or 0.11 the rate in excess oxygen is significantly lower than the rate in excess hydrogen. This suggests that, although initially the rate of reaction is enhanced by oxygen, the active sites are more susceptible to deactivation by oxygen than by hydrogen.

There is little change in activity with temperature, illustrated by the Arrhenius plot shown in Fig. 1, and the results as summarized in Table 3.

Active sites. At least two sets of active sites have been described: a hyperactive set, characterized by the reaction type, the initial rates, and the orders with respect to concentration, and a less active set, characterized by the rate of the central portion of the plots, and the orders with respect to time.

From the introduction it can be seen that at least two types of sites have been identified. One results from the loss of surface oxygen during conditioning. These sites are assumed to be the ones responsible for oxygen exchange below 500 K. Heating *in vacuo* increases the number of these sites, but they are readily reversibly deactivated by oxygen, particularly above 500 K. The other type of site results from the removal of hydroxyl groups. Heating in oxygen or *in vacuo* increases the number of these sites, whereas hydrogen pretreatment will deactivate these sites. For the oxygen exchange results it appears as if these sites are less abundant than the anion vacancy sites.

The results obtained in the present work are consistent with the assumption that the hyperactive set of sites results from the loss of hydroxyl groups and the other set of sites results from the loss of surface oxygen.

The hyperactive set of sites is more evident for stoichiometric reactions at initial oxygen pressures above 90 N m^{-2}, and after nonstoichiometric reactions with oxygen excess. Also, nonstoichiometric reactions with oxygen excess tend to have a faster initial rate than reactions with hydrogen excess. All of these conditions would be expected to increase the number of sites produced by the loss of hydroxyl groups. Conversely, some or all of these sites are deactivated after pretreatment with hydrogen or after reactions with hydrogen excess, due to the reformation of hydroxyl groups. The orders with respect to concentration indicate that there may be some dissociative adsorption occurring on these sites, a fact that is not surprising if these sites are produced by loss of hydroxyl groups from adjacent sites.

The major part of the reaction occurs on the second set of sites resulting from the loss of surface oxygen. These sites are not particularly susceptible to deactivation and are not affected by mild pretreatment. However, nonstoichiometric reactions with a large excess of oxygen are slower than those with a large excess of hydrogen, indicating some deactivating effect under these conditions. In the introduction, it has been suggested that surface oxygen is involved in oxygen exchange above 500 K. This may explain the slight decrease in activation energy with increasing temperatures but the effect does not appear to be significant and it is most probable that only one type of site is being utilized for the reaction.

Kinetic Expression

The major part of the reaction can be considered as following the same kinetic expression as proposed for samarium oxide (*1*), namely,

$$-\frac{dP_{\mathrm{T}}}{dt} = \frac{k(b_{\mathrm{H_2}}P_{\mathrm{H_2}})^x(b_{\mathrm{O_2}}P_{\mathrm{O_2}})^y}{(1 + b_{\mathrm{H_2}}P_{\mathrm{H_2}} + b_{\mathrm{O_2}}P_{\mathrm{O_2}})^{x+y}}, \quad (1)$$

where k is a proportionality constant, $b_{\mathrm{H_2}}$ and $b_{\mathrm{O_2}}$ are the adsorption coefficients for hydrogen and oxygen, respectively, and x and y are integers. The results will now be discussed in terms of this relationship.

Orders with respect to time. Most of the orders for the stoichiometric reactions are close to zero with little temperature dependence. However, the orders do increase with decreasing pressure, giving an overall order of about 0.8 at a total pressure less than 75 N m^{-2}. This indicates that $[(2b_{\mathrm{H_2}} + b_{\mathrm{O_2}})/3] \times 75$ is not significantly different from unity.

The orders obtained from the nonstoichiometric reactions for oxygen (in excess hydrogen) and hydrogen (in excess oxygen) are necessarily inaccurate. Maximum accuracy would be expected at intermediate stoichiometries where one gas is sufficiently in excess to be considered constant, but where it is not so much in excess as to affect the kinetics because of the scarcity of the alternate gas. Using this criterion it can be seen that there is a tendency for the order in hydrogen to increase to about 2 (only considering ratios above about 0.25), whereas the order in oxygen increases to about 1 (only considering ratios below about 7).

Isobars. All the isobars have a maximum, as would be expected from a kinetic expression of the form shown in Eq. (1). From the slopes of the isobars on either side of the maximum, it appears as if the order for oxygen is 1 and that the order for hydrogen is higher and in the vicinity of 1.5. Using the fact that the slopes on the low pressure side of the maximum are

TABLE 5

Average Values for the Adsorption Coefficients Calculated at Constant Hydrogen Partial Pressure, with $y = 1$ and $x = 1$ or 2

Group number	Temperature (K)	Oxygen pressure range ($N\ m^{-2}$)	x	$b_{O_2} \times 10^2$ ($N^{-1}\ m^2$)	$b_{H_2} \times 10_2$ ($N^{-1}\ m^2$)
24	443	47–107	1	0.1	—
			2	0.05	—
22	496	50–129	1	2.0	1.0
			2	1.0	1.0
25	546	44–117	1	2.0	0.6
			2	1.0	0.6
23	623	36–107	1	3.0	0.6
			2	2.0	2.0

likely to be more accurate than the opposite slopes, the accuracy for the oxygen order is very high, and the hydrogen order is closer to 2 than to 1.

The hydrogen–oxygen ratio at the maximum of the isobars changes with pressure in the same manner as observed over samarium oxide (*1*). This indicates that both the hydrogen and the oxygen adsorption coefficients decrease with increasing pressure. Values for the adsorption coefficients can be calculated and average values are shown in Table 5, using $y = 1$ and $x = 1$ or 2 in Eq. (1). Generally, b_{O_2} shows a slight increase with temperature and is larger than b_{H_2}. Both of these facts are consistent with the previous suggestion that reaction is occurring on anion vacancies. In addition, the values obtained are of the correct order of magnitude to give the observed change in order with respect to time as the pressure varies. The values for b_{O_2} are lower when $x = 2$, than when $x = 1$, but there is no evidence from these values to help ascertain the exact order in hydrogen. The values for the adsorption coefficients are similar to those obtained for samarium oxide (*1*), a fact that is to be expected in view of the similarities between these oxides, and the similar values obtained at much lower temperatures for the heats of adsorption for hydrogen over these two oxides (*11*).

A value for the proportionality constant, k, has been calculated using the average values for b_{O_2} and b_{H_2} of $1.0 \times 10^{-2}\ N^{-1}\ m^2$. Over the temperature range 380 to 500 K there is a slight increase in the value of k with temperature, from 4 to 6 $N\ m^{-2}\ s^{-1}$ with $x = 1$, $y = 1$, and from 11 to 12 $N\ m^{-2}\ s^{-1}$ with $x = 2$, $y = 1$. Again, although these values are consistent with the general kinetic model, they do not help distinguish between the possible values for x.

From a consideration of all the kinetic data, the evidence is fairly conclusive that an expression of the form shown in Eq. (1) is correct and that $y = 1$. The evidence is less compelling for the order in hydrogen although it would appear most likely that $x = 2$.

Mechanism

Most of the evidence in the literature and in the present work indicates that gadolinium oxide behaves in a manner very similar to samarium oxide except for the slight difference in ability to form hydrates and the mobility of surface oxygen [for example (*8, 13*)]. Gadolinium oxide tends to give more consistent results than samarium oxide and the data in the present paper illustrate this fact. In view of this the same mechanism is proposed as was suggested for samarium oxide (*1*), namely:

$$H_2(g) \rightleftarrows H_2(ads) \qquad (i)$$

$$O_2(g) \rightleftarrows O_2(ads) \qquad (ii)$$

$$H_2(ads) + O_2(ads) \rightleftarrows H_2O_2(ads) \qquad (iii)$$

$$H_2O_2(ads) + H_2(ads) \rightarrow 2H_2O(ads) \qquad (iv)$$

$$H_2O(ads) \rightleftarrows H_2O(g) \qquad (v)$$

This mechanism will give rise to the kinetic expression shown in Eq. (1), with $x = 2$ and $y = 1$.

ACKNOWLEDGMENT

The authors express their appreciation to the National Research Council and Shell (Canada) Ltd. for the financial support of this project.

REFERENCES

1. Read, J. F., Chan, Y. T., and Conrad, R. E., *J. Catal.* **55**, 166 (1978).
2. Winter, E. R. S., *J. Chem. Soc. A*, 1832 (1969).
3. Boreskov, G. K., *Discuss. Faraday Soc.* **41**, 263 (1966).
4. Minachev, Kh. M., and Antoshin, G. V., *Dokl. Akad. Nauk. SSSR* **161**, 122 (1965).
5. Antoshin, G. V., Minachev, Kh. M., and Dmitriev, R. V., *Izvest. Akad. Nauk. SSSR, Ser. Khim.* 1864 (1967).
6. Sazonov, L. A., Sokolovskii, V. D., and Boreskov, G. K., *Kinet. Katal.* **7**, 284 (1966).
7. Winter, E. R. S., *J. Catal.* **34**, 440 (1974).
8. Minachev, Kh. M., *Int. Congr. Catal. 5th* **1**, 219 (1973).
9. Ashmead, D. R., Eley, D. D., and Rudham, R., *J. Catal.* **3**, 280 (1964).
10. Selwood, P. W., *J. Catal.* **22**, 123 (1971).
11. Read, J. F., *Canad. J. Chem.* **50**, 490 (1972).
12. Read, J. F., Dunfield, L. G., Shreve, R. M., and Spinney, E. A., *J. Catal.* **33**, 335 (1974).
13. Bloor, D., and Dean, J. R., *J. Phys. C.* **5**, 1237 (1972).
14. Read, J. F., and Perkins, E. W., *J. Catal.* **42**, 443 (1976).