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The Hydrogen–Oxygen Reaction on Lanthanide Oxides

III. The Hydrogen–Oxygen Reaction on Neodymium Oxide

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The hydrogen–oxygen reaction has been studied over a neodymium oxide catalyst at hydrogen:oxygen ratios from 10:1 to 1:10, at pressures of hydrogen up to 4 Torr and oxygen up to 5 Torr, and at temperatures in the range 270°–450°C. The effect of various pretreatments by hydrogen and oxygen was observed. The kinetic results can be explained in terms of an equation of the form

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

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 probable mechanism is one in which the rate-determining step involves adsorbed hydroxyl groups.

INTRODUCTION

The catalytic effect of neodymium oxide has been recognized since 1929 when Cremer (*1*) compared the rate of dehydration to the rate of dehydrogenation of ethyl alcohol. Since that time, this catalyst has been used for many simple reactions; for example, the dehydrogenation of hydrocarbons (*2–4*), the dehydration and dehydrogenation of alcohols (*1, 2, 5, 6*), the oxidation of carbon monoxide (*7*), and the decomposition of nitrous oxide (*8, 9*).

Reaction and adsorption studies involving hydrogen or oxygen indicate that both these gases are readily adsorbed on neodymium oxide. Parallel temperature dependencies have been noted for hydrogen adsorption (*10*), the parahydrogen conversion, and the hydrogen–deuterium equilibration reaction (*11*) over the temperature range 77°–771°K at pressures of approximately 6 Torr. Isotopic oxygen exchange reactions have been studied by several workers. Minachev and Antoshin (*12*), and Antoshin *et al.* (*13*) stated that the rate of exchange was dependent upon the mobility of the oxygen of the oxide surface, and they recorded an activity for neodymium oxide intermediate between that of the other lanthanide oxides; Sazonov *et al.* (*14*) found that there was a fast first-order exchange reaction that was decreased by oxygen pretreatment but unaffected by the crystalline form of the oxide; and Winter (*15*) determined that the activity was dependent on pretreatment and that the rate-determining step was the desorption of oxygen.

Several preliminary studies have been made of the hydrogen–oxygen reaction over neodymium oxide but no detailed kinetic analysis has been attempted. Bakumenko (*16*) studied the reaction in the temperature range 300°–500°C at total pressures of 550 Torr for two reaction mixtures (1% oxygen in hydrogen and 2% hydrogen in oxygen), and noted a loss of activity in excess oxygen and a considerable decrease in activity in excess hydrogen after several reactions. Bakumenko and Chashechnikova

TABLE 1

Summary of the Experimental Conditions for the Hydrogen-Oxygen Reaction on Neodymium Oxide

Pretreatment before the group of reactions	Group	Set and run	Temperature (°C)	Initial hydrogen: oxygen ratio	Initial hydrogen pressure (Torr)	Initial rate (Torr min^{-1})
6 days at 500°C and $<10^{-6}$ Torr	1	A1-3*	398	10.0	2.1, 1.5, 0.7	0.11, 0.19, 0.11
		B1-3	397	0.12	0.2, 0.1, 0.1	0.10, 0.072, 0.063
		C1-3	397	2.0	2.1, 1.1, 0.4	1.5, 1.1, 1.2
		D1-3	398	10.6	2.0, 1.0, 0.4	0.18, 0.12, 0.10
		E1-3	400	0.10	0.2, 0.1, 0.05	0.12, 0.064, 0.034
12 hr at 330°C and $<10^{-6}$ Torr	2	A1-3	334	10.2	2.9, 1.3, 0.6	0.25, 0.11, 0.090
		B1-3	334	0.11	0.2, 0.1, 0.05	0.11, 0.038, 0.027
		C1-4	333	2.0	1.9, 1.1, 0.3, 0.2	1.3, 0.92, 0.41, 0.25
		D1-3	333	8.1	1.9, 0.9, 0.6	0.25, 0.090, 0.075
		E1-3	333	0.098	0.2, 0.1, 0.04	0.096, 0.037, 0.019
12 hr at 270°C and $<10^{-6}$ Torr	3	A1-3	268	9.5	3.6, 1.7, 0.8	0.22, 0.13, 0.098
		B1-3	268	0.13	0.6, 0.2, 0.05	0.45, 0.060, 0.024
		C1-3	268	2.0	2.3, 1.3, 0.5	1.6, 1.6, 0.76
		D1-3	266	8.0	2.2, 0.9, 0.5	0.33, 0.085, 0.062
		E1-3	266	0.097	0.1, 0.1, 0.06	0.055, 0.037, 0.034
12 hr at 450°C and $<10^{-6}$ Torr	4	A1-3	452	10.9	1.6, 0.8, 0.6	0.16, 0.069, 0.080
		B1-3	453	0.12	0.2, 0.1, 0.1	0.099, 0.058, 0.060
		C1-3	453	2.0	2.0, 0.9, 0.9	1.7, 1.1, 0.49
		D1-3	453	8.2	2.0, 0.8, 0.5	0.31, 0.11, 0.12
		E1-3	452	0.10	0.2, 0.1, 0.04	0.13, 0.076, 0.046
12 hr at 390°C and $<10^{-6}$ Torr	5	A1-2	394	10.1	1.7, 0.8	0.12, 0.15
		B1-2	394	2.0	1.6, 0.8	1.4, 0.91

10 hr at 330°C and $<10^{-6}$ Torr + 11 hr at 330°C in 3.6 Torr oxygen	6	A1–3	332	2.0	1.5, 0.7, 0.4	3.2, 0.98, 0.86
		B1–2	332	1.0	1.1, 0.7	1.1, 0.82
		C1–3	333	0.50	0.9, 0.3, 0.2	0.91, 0.25, 0.18
		D1–3	332	6.4	2.1, 0.1, 0.6	0.34, 0.12, 0.091
		E1–3	332	0.17	0.3, 0.1, 0.05	0.17, 0.080, 0.051
		F1–2	332	2.0	1.6, 0.5	1.3, 0.20
3 hr at 330°C and $<10^{-6}$ Torr + 12 hr at 330°C in 3.6 Torr oxygen	7	A1–3	331	2.0	1.7, 0.6, 0.5	1.3, 0.78, 0.82
		B1–3	331	3.0	1.4, 0.7, 0.7	0.27, 0.32, 0.36
		C1–3	331	0.33	0.6, 0.3, 0.05	0.57, 0.34, 0.060
		D1–3	332	7.5	2.8, 1.2, 0.6	0.35, 0.12, 0.10
		E1–3	333	0.093	0.1, 0.1, 0.04	0.044, 0.022, 0.029
		F1–3	332	2.0	1.6, 1.6, 2.0	0.75, 0.90, 0.20
40 hr at 330°C and $<10^{-6}$ Torr	8	A1–3	331	2.0	1.4, 0.7, 0.3	2.8, 0.97, 0.81
		B1–3	331	1.0	1.8, 0.7, 0.3	0.63, 0.95, 0.63
		C1–3	331	0.48	1.6, 0.8, 0.3	1.5, 0.39, 0.21
24 hr at 330°C and $<10^{-6}$ Torr + 12 hr at 330°C in 3.6 Torr hydrogen	9	A1–3	331	2.0	2.9, 1.4, 0.7	1.9, 1.5, 0.92
		B1–3	331	1.0	1.2, 0.7, 0.3	0.69, 1.1, 0.77
		C1–3	331	3.0	2.9, 1.5, 0.7	0.31, 0.55, 0.40
		D1–3	331	0.51	1.3, 0.6, 0.5	1.9, 0.56, 0.28
		E1–3	331	0.34	0.5, 0.2, 0.1	0.41, 0.20, 0.19
		F1–3	331	5.8	3.0, 1.3, 0.6	0.30, 0.16, 0.12
		G1–2	331	2.0	2.8, 0.6	1.9, 0.10
See Note 1	10	A1–5	329	2.0	1.2, 1.0, 1.2, 1.2, 1.1	0.39, 1.2, 0.98, 0.88, 1.0
		B1–5	329	2.0	2.0, 2.1, 1.2, 1.9, 1.2	1.5, 2.2, 0.78, 1.4, 0.88
		C1–5	329	2.0	1.1, 1.2, 0.9, 1.1, 1.2	0.77, 0.99, 0.63, 1.0, 1.0
See Note 2	11	A1–2	330	2.0	1.2, 1.2	1.8, 2.2
		B1–5	330	2.0	2.0, 1.9, 2.0, 2.0, 2.0	2.1, 1.9, 1.6, 1.9, 1.2
		C1–5	330	2.0	1.1, 1.2, 1.1, 1.1, 1.2	1.1, 1.0, 0.90, 1.1, 0.81

(Continued)

TABLE 1 (*Continued*)

Pretreatment before the group of reactions	Group	Set and run	Temperature (°C)	Initial hydrogen: oxygen ratio	Initial hydrogen pressure (Torr)	Initial rate (Torr min^{-1})
See Note 3	12	A1-3	331	2.0	1.2, 1.3, 1.2	1.5, 2.1, 1.6
		B1-5	331	2.0	2.0, 2.1, 2.0, 2.0, 1.3	3.0, 1.8, 2.0, 1.6, 1.3
		C1-5	330	2.0	1.1, 1.1, 1.1, 1.2, 1.2	1.1, 0.86, 0.69, 1.3, 0.98
See Note 4	13	A1-3	330	2.0	1.3, 1.3, 1.2	1.7, 2.1, 2.0
		B1-5	330	2.0	2.1, 2.0, 2.1, 2.0, 1.2	1.6, 1.7, 2.6, 2.0, 1.2
		C1-4	329	2.0	1.1, 1.1, 1.2, 1.3	1.9, 1.0, 1.6, 0.86
29 hr at 330°C and $<10^{-6}$ Torr	14	A	329	2.0	1.3	1.6

* 1A1-3 signifies the three runs 1A1, 1A2, and 1A3.

Note: 1 Torr = 133.3 $N\ \text{m}^{-2}$.

Note 1: Pretreatment was 6 days evacuation at 500°C and $<10^{-6}$ Torr (conditioning for catalyst sample No. 2), plus initial oxygen pretreatment for 26 hr at 330°C and 3.5 Torr, plus immediate oxygen pretreatment for sets B and C for successively longer contact times (between 2 and 15 min) within each set at approximately 3 Torr.

Note 2: Pretreatment was 3 hr evacuation at 330°C and $<10^{-6}$ Torr, plus initial oxygen pretreatment for 12 hr at 330°C and 2.5 Torr, plus immediate oxygen pretreatment for sets B and C for successively longer contact times (between 2 and 15 min) within each set at 2.4 Torr.

Note 3: Pretreatment was 28 hr evacuation at 330°C and $<10^{-6}$ Torr, plus initial hydrogen pretreatment for 12 hr at 330°C and 3.5 Torr, plus immediate hydrogen pretreatment for sets B and C for successively longer contact times (between 2 and 15 min) within each set at 3.7 Torr.

Note 4: Pretreatment was 5 hr evacuation at 330°C and $<10^{-6}$ Torr, plus initial hydrogen pretreatment for 12 hr at 330°C and 2.1 Torr, plus immediate hydrogen pretreatment for sets B and C for successively longer contact times (between 2 and 15 min) within each set at 2.3 Torr.

(*17*) studied the stoichiometric reaction with excess argon, and the non-stoichiometric reaction with excess hydrogen and found the activity of neodymium oxide to be intermediate between that of the other lanthanide oxides, with a pressure dependence of unity with respect to hydrogen. The high activity of the oxides of cerium, praseodymium, and terbium is correlated with the variable valencies of these oxides, and the intermediate activity of neodymium (III) oxide was attributed to a slight tendency of this oxide to form neodymium (V) oxide. Antoshin *et al.* (*18*) observed a similarity between the rate of exchange of isotopic oxygen and the rate of the hydrogen–oxygen reaction.

In the previous article in this series, Read and Conrad (*19*) studied the stoichiometric hydrogen–oxygen reaction over the temperature range 68°–150°C and the pressure range 1–14 Torr. The results were explained in terms of a general kinetic expression based on the Langmuir isotherm, namely,

$$-\frac{dP_T}{dt} = \frac{(A_m P_T)^m}{(1 + BP_T)^m}, \qquad [1]$$

where A_m and B are temperature-dependent constants, P_T is the total pressure of hydrogen plus oxygen, and m is an integer of value 1 to 3. The present contribution extends this work to include non-stoichiometric reactions and the effect of catalyst pretreatment.

EXPERIMENTAL METHODS

The apparatus comprised a conventional high-vacuum system. Traps, surrounded by liquid nitrogen, protected the catalyst from contamination and allowed the water produced in the reaction to be condensed. The reaction was followed by continuously monitoring the total pressure in the closed reaction chamber with a capacitance manometer (Granville Phillips, Model #03, Series 212). Gas samples were removed from the reaction chamber via an adjustable leak and analysed by a mass spectrometer (AE1, Model MS10). Reactions were usually followed to about 90% completion and a typical run lasted 20 min. The results were reproducible. Variations in the measuring procedure, the amount and distribution of the catalyst, and in the apparatus itself, together with a comparison of results obtained in the present work and a previous study (*19*) using a completely different apparatus, assured that the pressure readings were valid and that there were no problems associated with the mass transport of the reactants and products. Thermal transpiration calculations, and experiments using nitrogen or argon together with the hydrogen and oxygen, indicated that there was no problem associated with heat transfer.

Spectral-analysed hydrogen and oxygen (Airco and Lindé) were used; the pressure and ratio being determined before the gases were admitted to the reaction chamber. The catalyst was "Specpure" grade neodymium oxide (Johnson Matthey) with a surface area of 10 m^2 g^{-1} as measured by the BET method using krypton.

Fourteen groups of experiments were conducted using two different catalyst samples. Within each group of experiments, several sets of reactions were performed, each set being designated by a different letter. In groups 1–9, a new set of reactions indicates a change in the initial hydrogen:oxygen ratio, whereas in groups 10–13 a new set indicates a change in the catalyst conditioning. Each set of reactions comprises several separate runs, each run within a set having a different total initial pressure or a different pretreatment, but identical stoichiometries. The experiments performed are outlined in Table 1. Each reaction is identified by stating the group, set and run; for example, reaction 3 B 2 is the second run of set B within group 3.

Groups 1–5 were each conducted at a different temperature (398°, 333°, 267°, 453°, and 394°C, respectively) with hydrogen: oxygen ratios from 10:1–1:10, and with initial hydrogen pressures up to approximately 4 Torr and initial oxygen pressures up to approximately 5 Torr; groups 6 and 7 were conducted at approximately 332°C with initial oxygen pretreatment (that is, overnight pretreatment before the start of the group); group 8 was conducted at

331°C with no pretreatment; group 9 was conducted at 331°C with initial hydrogen pretreatment; groups 10 and 11 were stoichiometric reactions conducted at approximately 330°C with immediate oxygen pretreatment (that is, pretreatment before each reaction); groups 12 and 13 were stoichiometric reactions conducted at approximately 330°C with immediate hydrogen pretreatment; and group 14 was a single reaction at 329°C with extra doses of the stoichiometric mixture being added every few minutes.

The neodymium oxide catalysts were initially conditioned by heating for 6 days at 500°C and $<10^{-6}$ Torr. Unless otherwise stated in the results, the gases were removed from the catalyst by evacuating the system for at least 10 min. Catalyst sample No. 1 (0.118 g) was used for groups 1–9 and catalyst sample No. 2 (0.119 g) was used for groups 10–14. The structure was determined by X-ray fluorescence and powder diffraction, and by i.r. analysis.

An IBM 1130 computer was used in the analysis of the data, reaction rates being determined by cubic spline interpolation (*20*).

RESULTS

Structure of Neodymium Oxide

The stable oxide of neodymium is trivalent and can exist in three different crystal modifications: A-type (hexagonal), B-type (monoclinic), and C-type (cubic). The pure C-type readily forms $3Nd_2O_3 \cdot 2H_2O$ at room temperature in the presence of very small amounts of water. This transformation is partially reversible by heating at $<10^{-6}$ Torr to approximately 400°C. Further heating to 1000°C transforms the C-type into the A-type oxide, often with a further loss of water (*21*). X-ray analysis of the sample used in the present investigation indicated that it was the C-type $3Nd_2O_3 \cdot 2H_2O$. The i.r. analysis showed that there were no free hydroxyl groups and no molecular water, but distinct peaks were observed for hydrogen-bonded hydroxyl groups (*22*). No change in the X-ray or i.r. data was observed during the course of the experimental work.

Analysis of the Data

The data were initially analysed using the general equation

$$-\frac{dP_T}{dt} = k_1 P_{H_2}{}^x P_{O_2}{}^y, \qquad [2]$$

where P_{H_2} and P_{O_2} are the partial pressures of hydrogen and oxygen, respectively, x and y are the apparent orders with respect to hydrogen and oxygen, respectively, and k_1 is the pseudo-rate constant. For stoichiometric reactions, plots of log (rate) versus log (total pressure) gave the overall order, and for non-stoichiometric reactions, plots of log (rate) versus log (pressure minor component) gave an approximation to the order for the gas present in less than the stoichiometric amount.

Figures 1 and 2 show typical log (rate) versus log (minor component) plots giving the orders with respect to time for hydrogen and oxygen, respectively. Most of these plots showed three distinct regions: an initial section with a relatively large rate lasting for about 1 min; a second linear section; and a third section with a rapidly decreasing rate. The orders with respect to time quoted below are taken from the second, linear section.

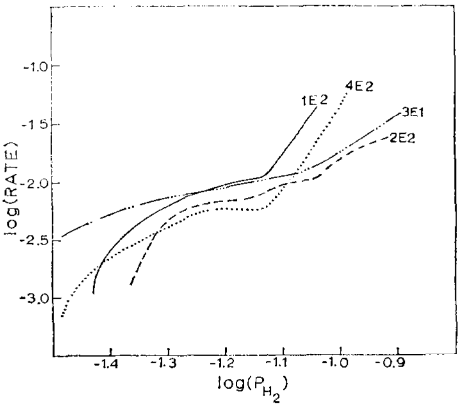

FIG. 1. Log (rate) versus log (hydrogen pressure) plot in oxygen excess. Reactions 1E2 (400°C), 2E2 (333°C), 3E1 (266°C), and 4E2 (452°C).

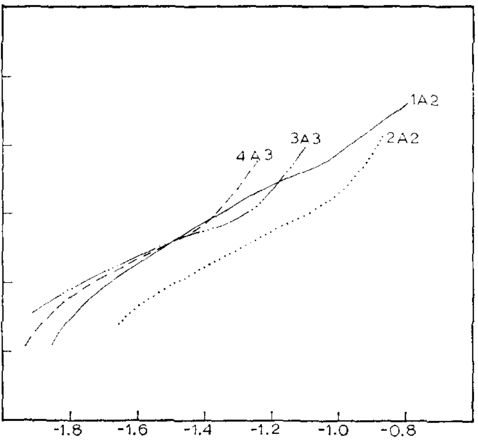

FIG. 2. Log (rate) versus log (oxygen pressure) plot in hydrogen excess. Reactions 1A2 (398°C), 2A2 (334°C), 3A3 (268°C), and 4A3 (452°C).

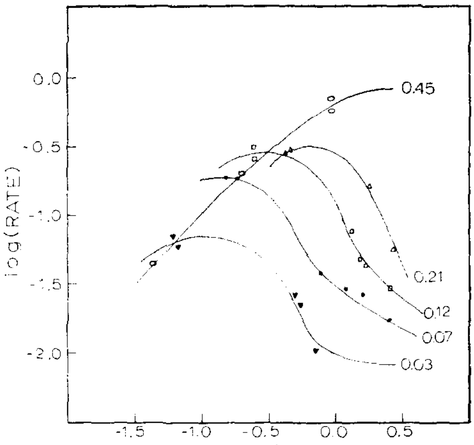

FIG. 3. Oxygen isobars drawn through some of the log (rate) versus log (hydrogen pressure) plots from group 2 at 333°C. The constant oxygen pressure in Torr is shown with each plot.

The data are presented in Tables 1 and 2. Table 1 gives the initial rate data for all reactions and Table 2 summarises the experimental conditions and the orders for the non-stoichiometric reactions. The order with respect to time for oxygen is the average for all the reactions in the group with hydrogen:oxygen ratios greater than 6:1, and the order with respect to time for hydrogen is the average using ratios less than 0.3:1. The orders with respect to concentration, calculated from initial rate data using Eq. [2], are also included in Table 2.

The data were also analysed by drawing isobaric curves through non-stoichiometric reactions at a constant temperature and with identical pretreatment conditions. Figure 3 shows a typical set of isobaric curves joining points of constant oxygen pressure on the log (rate) versus log (hydrogen pressure) plots at 333°C for group 2. The individual log (rate) versus log (hydrogen pressure) plots are not shown but the point corresponding to the pressure required is indicated. The results from the isobars are summarised in Table 3. Each isobar exhibited a maximum. The pressure of the

TABLE 2

SUMMARY OF THE RESULTS FROM THE NON-STOICHIOMETRIC HYDROGEN-OXYGEN REACTION ON NEODYMIUM OXIDE

Group	Average temp. (°C)	Range of initial hydrogen: oxygen ratio	Average order with respect to time		Average order with respect to concentration
			Oxygen	Hydrogen	
1	398	0.1–10.6	1.5 ± 0.1	1.7	0.6 ± 0.2
2	333	0.1–10.2	1.1	1.6 ± 0.2	0.8 ± 0.2
3	267	0.1–9.5	1.0	1.6	0.7 ± 0.2
4	453	0.1–10.9	1.0	2.0 ± 0.1	0.9 ± 0.2
5	394	10.1	1.1		
6	332	0.2–6.4	1.1	1.8	0.8 ± 0.3
7	332	0.1–7.5	0.9	1.4 ± 0.2	0.8 ± 0.3
8	331	0.5–1.0			1.2
9	331	0.3–5.8	1.0	1.6	0.5

TABLE 3

Summary of the Results from the Isobaric Plots at Constant Hydrogen or Oxygen Pressure

		Isobar at constant hydrogen pressure				Isobar at constant oxygen pressure			
			At maximum of isobar				At maximum of isobar		
Group (Gas used for initial pretreatment)	Average temp. (°C)	Constant hydrogen pressure (Torr)	Oxygen pressure (Torr)	Hydrogen: oxygen ratio	Rate (Torr min^{-1})	Constant oxygen pressure (Torr)	Hydrogen pressure (Torr)	Hydrogen: oxygen ratio	Rate (Torr min^{-1})
1, 5 (None)	397	0.05	0.04	1.4	0.17	0.05	0.13	2.5	0.18
		0.07	0.04	1.6	0.20	0.10	0.22	2.2	0.23
		0.10	0.07	1.5	0.22	0.12	0.24	2.2	0.30
		0.15	0.10	1.6	0.25	0.21	0.46	2.2	0.33
2 (None)	333	0.05	0.03	1.7	0.08	0.03	0.07	2.4	0.09
		0.07	0.04	1.7	0.09	0.05	0.13	2.5	0.12
		0.14	0.09	1.6	0.18	0.12	0.30	2.4	0.27
		0.50	0.29	1.7	0.27	0.20	0.51	2.5	0.34
3 (None,	267	0.06	0.04	1.6	0.09	0.05	0.13	2.5	0.11
		0.10	0.07	1.6	0.10	0.07	0.18	2.5	0.13
		0.14	0.06	1.8	0.23	0.10	0.25	2.5	0.15
		0.72	0.43	1.7	0.29	0.16	0.39	2.3	0.24

4	453	0.06	0.05	1.3	0.05	0.05	0.10	2.1	0.09
(None)		0.10	0.07	1.5	0.10	0.10	0.20	2.0	0.18
		0.40	0.25	1.6	0.29	0.16	0.33	2.0	0.22
		0.75	0.50	1.5	0.33	0.64	1.29	2.0	0.35
6, 7	332	0.04	0.02	1.7	0.09	0.04	0.08	2.1	0.08
(O_2)		0.26	0.17	1.6	0.15	0.09	0.19	2.1	0.20
		0.32	0.22	1.7	0.21	0.16	0.33	2.1	0.21
		0.47	0.29	1.6	0.25	0.21	0.43	2.1	0.23
		0.57	0.36	1.6	0.28	0.28	0.60	2.1	0.25
						0.45	0.94	2.1	0.26
						0.67	1.37	2.1	0.47
8	331	0.25	0.17	1.4	0.23	0.37	0.63	1.7	0.20
(None)		0.50	0.32	1.6	0.24	0.44	0.76	1.7	0.22
		0.75	0.24	1.6	0.24	0.60	1.07	1.8	0.24
9	331	0.08	0.05	1.5	0.12	0.04	0.08	1.9	0.09
(H_2)		0.15	0.12	1.3	0.19	0.30	0.53	1.8	0.27
		0.25	0.17	1.4	0.26	0.37	0.63	1.7	0.28
		0.30	0.20	1.6	0.29	0.44	0.76	1.7	0.27
		0.40	0.25	1.6	0.30	0.60	1.07	1.8	0.26
		0.50	0.32	1.6	0.27	0.85	1.56	1.8	0.27
		0.75	0.48	1.6	0.26	1.05	1.91	1.8	0.28
		0.90	0.55	1.6	0.26				
		1.10	0.65	1.5	0.26				

gases, the hydrogen:oxygen ratio and the rate at this maximum are shown in the table.

Summary of the Results

Effect of pretreatment. The effect of initial pretreatment can be seen from the results of groups 6 and 7 (oxygen pretreatment), group 8 (no pretreatment), and group 9 (hydrogen pretreatment). Some of the results for stoichiometric reactions are illustrated in Fig. 4. For both stoichiometric and non-stoichiometric reactions, the effects of initial pretreatment are small. It should be noted, however, that it is more difficult to determine the effect with non-stoichiometric reactions, since each reaction, if taken close to completion, will effectively pretreat the catalyst for the subsequent reaction. Oxygen pretreatment appears to lower the activity slightly but hydrogen pretreatment does not appear to have any significant effect. Comparison of groups 2 and 8 (similar groups carried out with no initial pretreatment but performed before and after the initial oxygen pretreatment experiments of groups 6 and 7) indicates a slight decrease in activity for group 8. The effect of pretreatment on the kinetic orders and the isobars will be discussed later.

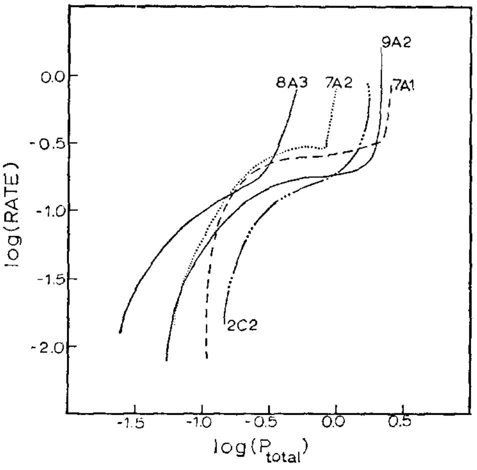

FIG. 4. Effect of initial pretreatment on the log (rate) versus log (total pressure) plots. Reactions 2C2 (no pretreatment), 7A1 and 7A2 (oxygen pretreatment), 8A3 (no pretreatment), and 9A2 (hydrogen pretreatment).

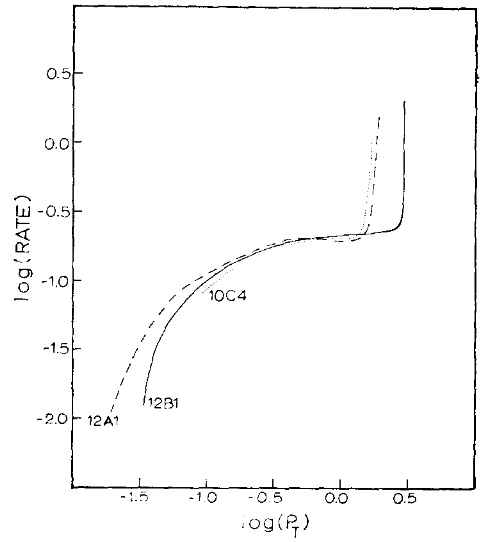

FIG. 5. Effect of immediate pretreatment on the log (rate) versus log (total pressure) plots. Reactions 10C4 (immediate oxygen pretreament), 12A1 (initial hydrogen pretreatment), and 12B1 (immediate hydrogen pretreatment).

The effect of immediate pretreatment can be seen from the results of groups 10 and 11 (oxygen pretreatment), and 12 and 13 (hydrogen pretreatment) for stoichiometric reactions. Figure 5 illustrates this effect. Immediate hydrogen pretreatment results in an increased initial catalyst activity, changing the shape of the first section of the log (rate) versus log (total pressure) plot. Immediate oxygen pretreatment decreases the degree of completion of the reaction. There is no change in these effects upon varying the pressure and time of contact of the pretreating gas.

Kinetic orders. For stoichiometric mixtures, the order with respect to time is close to zero for all reactions. Zero-order kinetics are obeyed for a large portion of the reaction, particularly at high pressures, with a rate constant that only changes slightly with temperature. Figure 6 illustrates the zero-order plots for stoichiometric mixtures at four different temperatures.

From the results for non-stoichiometric mixtures, the average order with respect to time for hydrogen is 1.7 ± 0.4 and for oxy-

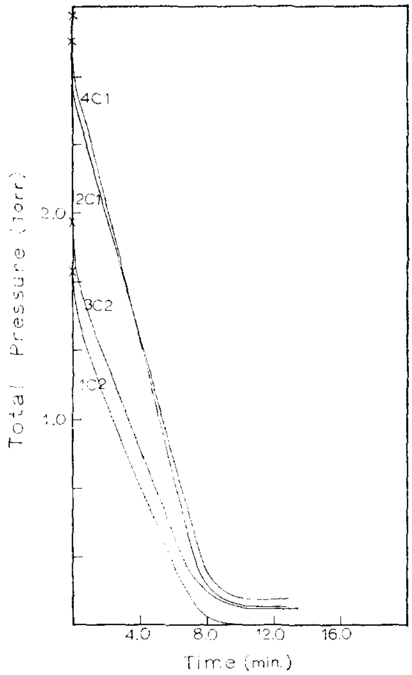

FIG. 6. Total pressure versus time plots for stoichiometric reactions at 268°C (Reaction 3C2), 333°C (Reaction 2C1), 397°C (Reaction 1C2), and 453°C (Reaction 4C1).

gen is 1.0 ± 0.1 (see Table 2), omitting the anomalously high orders for oxygen from group 1. There does not appear to be any pattern to the variation in order.

The orders with respect to concentration were impossible to determine accurately because of limited data and the inherent difficulty in measuring the initial rate. The results, summarised in Table 2, give an average order of 0.8 ± 0.3. There appears to be a tendency towards orders slightly lower than 0.5 for reactions on fresh or initially oxygen-pretreated catalysts, whereas the orders tend towards unity for reactions on catalysts that have been immediately pretreated with either hydrogen or oxygen.

All the orders are independent of the temperature, and the ratio of the reacting gases.

Isobars. The results are summarised in Tables 3 and 4. Isobars drawn through the first section of the log (rate) versus log (pressure) plots show the same general characteristics as the isobars drawn through the second section, except that the rates are slightly higher, displacing the isobars upwards. The average slopes of the isobars are given in Table 4. There is an indication of a leveling off of the oxygen isobars for groups 1–7 at high hydrogen pressures and low oxygen pressures.

Several generalisations can be made from the results shown in Tables 3 and 4 with respect to the hydrogen:oxygen ratio at the maximum of the isobars. From groups 1–5 it can be seen that there is a slight decrease in this ratio with increasing temperature. The summary of results shown in Table 4, at approximately a constant temperature, indicates that there is a decrease in this ratio for the oxygen isobar after oxygen pretreatment. Comparison of the

TABLE 4

SLOPES AND MAXIMA FOR THE ISOBARS IN THE TEMPERATURE RANGE 331–333°C

Isobar	Group	Initial pretreatment	Hydrogen:oxygen ratio at maximum of isobar	Slope of isobar: Low pressure side of maximum	Slope of isobar: High pressure side of maximum
Hydrogen	2	None	1.7	1.5	−2.0
Hydrogen	6, 7	Oxygen	1.6	1.5	−1.4
Hydrogen	8	None	1.5	1.5	−2.0
Hydrogen	9	Hydrogen	1.5 ± 0.1	2.0	−2.0
Oxygen	2	None	2.4	1.5	−2.0
Oxygen	6, 7	Oxygen	2.1	1.2	−1.0
Oxygen	8	None	1.7	1.5	−1.5
Oxygen	9	Hydrogen	1.8 ± 0.1	1.6	−1.5

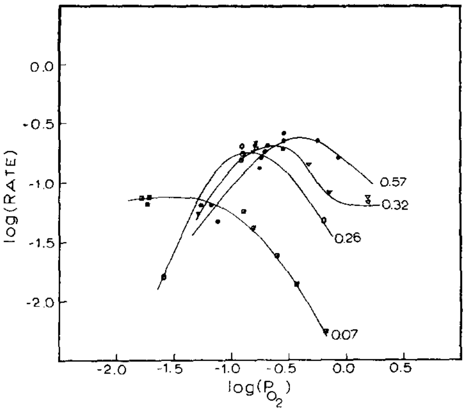

FIG. 7. Hydrogen isobars drawn through some of the log (rate) versus log (oxygen pressure) plots from groups 6 and 7 at 332°C. The constant hydrogen pressure in Torr is shown with each plot.

results from groups 2 and 8 shows that this effect is partially irreversible, although there is a slight increase again in group 9 after hydrogen pretreatment. The effect is less noticeable for the hydrogen isobars. In general, the ratio is lower for the hydrogen isobars than for the oxygen isobars.

Typical isobars are shown in Fig. 3 (oxygen isobar) and Fig. 7 (hydrogen isobar).

DISCUSSION

Kinetic Expression

In the previous paper in this series (*19*), it was shown that the stoichiometric hydrogen–oxygen reaction obeyed Eq. [1]. Assuming that the rate is dependent on the fraction of active surface covered competitively by molecular hydrogen and oxygen, and that adsorption obeys the Langmuir isotherm, Eq. [1] could be considered to be a reduced form of

$$-\frac{dP_T}{dt} = \frac{k(b_{H_2}P_{H_2})^x(b_{O_2}P_{O_2})^y}{(1 + b_{H_2}P_{H_2} + b_{O_2}P_{O_2})^{x+y}}, \quad [3]$$

where k is a proportionality constant, b_{H_2} and b_{O_2} are the adsorption coefficients for hydrogen and oxygen, respectively, and $x + y = m$ in Eq. [1].

The results will now be discussed in relation to Eq. [3] to determine the validity of this kinetic expression.

Kinetic orders. The anomalously high orders with respect to time (approximately 9) obtained from the first section of the log (rate) versus log (pressure) plots indicate that a complex process is occurring. The results from group 14 show that this effect is associated with the start of the reaction and not with the addition of extra doses of the reactants. The orders with respect to concentration also indicate that a kinetic expression of the form shown in Eq. [3] is not obeyed at the start of the reaction, and that there may be some participation of atomic species.

The orders with respect to time for the second section of the log (rate) versus log (pressure) plots can be explained in terms of Eq. [3]. Orders close to zero are obtained for stoichiometric mixtures, particularly at high pressures, and Eq. [3] predicts this when $b_{H_2}P_{H_2} + b_{O_2}P_{O_2} \gg 1$. It should be noted that zero-order kinetics could also be explained if the rate expression had been derived using the assumption that there was competitive adsorption between atomic hydrogen and oxygen, but not if one of the gases was in the atomic form and the other in the molecular form. In the previous paper (*19*), the reaction was carried out for longer times at lower temperatures than in the present study and an order between zero and one-half was observed. Adsorption is larger at the temperatures used in the present study (*10*), and thus, a greater tendency towards zero-order kinetics is expected.

In excess oxygen, the oxygen pressure is relatively constant and Eq. [3] reduces to

$$-\frac{dP_T}{dt} = k_2P_{H_2}{}^x \quad [4]$$

and in excess hydrogen Eq. [3] reduces to

$$-\frac{dP_T}{dt} = k_3P_{O_2}{}^y, \quad [5]$$

where k_2 and k_3 are effectively constant.

The experimental results show that x = 1 or 2 and y = 1. The value for x (1.7 ± 0.4) indicates that x = 2 is the more likely power.

Isobars. In order to obtain a maximum in the hydrogen and oxygen isobars, there must be competitive adsorption as reflected by Eq. [3]. Differentiation of Eq. [3] with $x = 2$, $y = 1$ shows that a maximum will occur in the hydrogen isobar when

$$\frac{P_{H_2}}{P_{O_2}} = \frac{2b_{O_2}P_{O_2} - 1}{b_{H_2}P_{O_2}}, \qquad [6]$$

and a maximum will occur in the oxygen isobar when

$$\frac{P_{H_2}}{P_{O_2}} = \frac{2b_{O_2}P_{O_2} + 2}{b_{H_2}P_{O_2}}. \qquad [7]$$

Assuming that $b_{O_2}P_{O_2} \gg 1$, Eqs. [6] and [7] reduce to

$$\frac{P_{H_2}}{P_{O_2}} = \frac{2b_{O_2}}{b_{H_2}}. \qquad [8]$$

Similarly, differentiation of Eq. [3] with $x = y = 1$ gives a maximum in the hydrogen isobar when

$$\frac{P_{H_2}}{P_{O_2}} = \frac{b_{O_2}P_{O_2} - 1}{b_{H_2}P_{O_2}}, \qquad [6a]$$

and a maximum in the oxygen isobar when

$$\frac{P_{H_2}}{P_{O_2}} = \frac{b_{O_2}P_{O_2} + 1}{b_{H_2}P_{O_2}}. \qquad [7a]$$

With $b_{O_2}P_{O_2} \gg 1$, Eqs. [6a] and [7a] reduce to

$$\frac{P_{H_2}}{P_{O_2}} = \frac{b_{O_2}}{b_{H_2}}. \qquad [8a]$$

The results in Tables 3 and 4 show that there is a maximum in all the isobars, approximately at the stoichiometric point, indicating that either $b_{O_2} \approx b_{H_2}$ (Eq. [8]) or $b_{O_2} \approx 2\ b_{H_2}$ (Eq. [8a]). Adsorption data for hydrogen and oxygen (*10*), and calculations of b_{H_2} and b_{O_2} from Eqs. [6] and [7], and [6a] and [7a], show that the general form of Eq. [3] is appropriate, but the results are inconclusive in distinguishing between the possible values for x. In the temperature range being studied slightly more oxygen is adsorbed than hydrogen; for example, at 400°C and an equilibrium pressure of 4 Torr, the relative amounts of hydrogen and oxygen adsorbed are 6.5×10^{12} and 1.0×10^{13} molecules cm^{-2}, respectively (*10*). Values for b_{H_2} and b_{O_2} cannot be calculated accurately but are of the correct order of magnitude; for example, the approximate values from group 4 are $b_{O_2} = 40$ Torr^{-1}, $b_{H_2} = 50$ Torr^{-1} (from Eqs. [6] and [7]), and $b_{O_2} = 60$ Torr^{-1}, $b_{H_2} = 30$ Torr^{-1} (from Eqs. [6a] and [7a]).

Adsorption results over the temperature range −196 to 416°C (*10*) show that hydrogen and oxygen adsorb in different forms at different temperatures, and, therefore, there is not a steady decrease in the amount of gas adsorbed as the temperature increases. In the temperature range of the present work the amount of hydrogen adsorption increases and the amount of oxygen adsorption decreases with increasing temperature. Therefore, the decrease in the hydrogen:oxygen ratio at the maximum of the isobars with increasing temperature is to be expected. The difference between the maxima for the hydrogen and oxygen isobars can be explained in terms of the difference between Eqs. [6] and [7] (or between Eqs. [6a] and [7a]).

Attempts were made to verify the kinetic expression by fitting the experimental results to the integrated forms of Eq. [3]. After the first few minutes of the reaction the best fits were obtained with $x = 2$, $y = 1$ for non-stoichiometric reactions as illus-

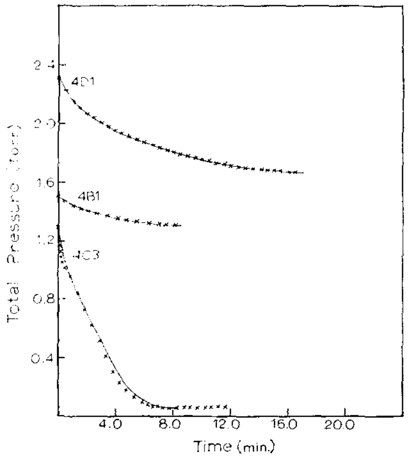

FIG. 8. Total pressure versus time plots showing the experimental data (points indicated), and the theoretical fit according to Eq. [3] with $x = 2$, $y = 1$ (solid line) for reactions 4D1 (excess hydrogen), 4B1 (excess oxygen), and 4C3 (stoichiometric mixture).

trated in Fig. 8. The analytical method predicts a poor fit for stoichiometric reactions. For the initial part of the reaction the best fits were given with $x = 1$ and $y = 0.5$.

In summary, after the first few minutes of any reaction, the kinetic results can be explained in terms of Eq. [3] with $x = 1$ or 2 and $y = 1$, with the most probable values being $x = 2$ and $y = 1$. These kinetics are not obeyed for the initial part of the reaction and there is some evidence for the participation of atomic species.

Mechanism

First section of the reactions. Previous work (*19*) has shown that the surface sites on neodymium oxide are not all equally active and that some sites are reversibly deactivated at the start of a reaction. It is possible that reversible deactivation occurs for the first few minutes and that a term $(1 - \theta_D)$, where θ_D is the fraction of the initially active surface that is deactivated, should be included in the kinetic expression.

In the temperature range 200°–300°C, oxygen adsorbs in slightly larger amounts than hydrogen, and the adsorption is dissociative and time-dependent (*10*). If oxygen adsorption is important during the initial stages of the reaction, immediate pretreatment with hydrogen would be expected to increase the initial activity, and immediate pretreatment with either gas would be expected to change the order with respect to concentration from 0.5 to 1. In addition, the adsorption coefficient for hydrogen should increase after initial oxygen pretreatment, resulting in the decrease in the hydrogen:oxygen ratio at the maximum of the isobars noticed between group 2, and groups 6 and 7. The decrease in this ratio between group 2 and group 8 indicates that the effect is partially irreversible; a fact that is in line with the anomalously high orders and ratios found in group 1. The maximum in the isobars increases again for group 9 after hydrogen pretreatment.

It is probable that during the first part of the reaction the kinetics are controlled by the adsorption of oxygen, and that some of this adsorption occurs on sites that are reversibly deactivated during the course of the reaction. There is also some evidence for irreversible adsorption, particularly as a result of pretreatment. This explains the fact that initial oxygen pretreatment lowers the activity and that immediate oxygen pretreatment decreases the percent completion of the reactions. The deactivation is probably caused by adsorption onto isolated R_2-centers.

The effect of pretreatment and the importance of the adsorption and desorption of oxygen is similar to the results obtained by other workers on neodymium oxide (*14–18*).

Second section of the reactions. It is impossible to determine the detailed mechanism, but three general schemes can be proposed. After the initial reversible adsorption of molecular hydrogen and oxygen these are:

$$\begin{aligned} &(1) && 2H_{2(ads)} + O_{2(ads)} \rightarrow 2H_2O_{(ads)} && [9]\\ & && H_2O_{(ads)} \rightleftharpoons H_2O_{(g)} && [10]\\ &(2) && H_{2(ads)} + O_{2(ads)} \rightleftharpoons 2OH_{(ads)} && [11]\\ & && 2OH_{(ads)} + H_{2(ads)} \rightarrow 2H_2O_{(ads)} && [12]\\ & && H_2O_{(ads)} \rightleftharpoons H_2O_{(g)} && [13]\\ &(3) && H_{2(ads)} + O_{2(ads)} \rightleftharpoons H_2O_{2(ads)} && [14]\\ & && H_2O_{2(ads)} + H_{2(ads)} \rightarrow 2H_2O_{(ads)} && [15]\\ & && H_2O_{(ads)} \rightleftharpoons H_2O_{(g)} && [16] \end{aligned}$$

The first two mechanisms involve termolecular rate-determining steps, whereas the last mechanism involves a bimolecular rate-determining step. However, since the two hydroxyl groups are formed on adjacent sites, there is little difference between mechanism 2 and mechanism 3. Mass-spectral analysis failed to detect any hydrogen peroxide in the gas phase. Neodymium oxide is known to contain hydroxyl groups (*11*, *22*) and, therefore, it is probable that mechanism 2 most accurately describes the process that is occurring. The uncertainty in the order with respect to hydrogen may mean that step [11] is rate-determining or that both steps [11] and [12] are slow. The importance of step [11] is shown by the order of one with respect to hydrogen obtained by Bakumenko and Chashechnikova (*17*), and the lower orders and higher activation energy obtained by Read and Conrad (*19*) at lower temperatures.

The results obtained in the present investigation show that neodymium oxide is an effective catalyst for the hydrogen-oxygen reaction. Hydrogen and oxygen are competitively adsorbed on the surface and the rate-determining step involves adsorbed hydroxyl groups. Catalyst conditioning is important and oxygen pretreatment decreases the activity of the catalyst.

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REFERENCES

1. CREMER, E., *Z. Phys. Chem.* **A144,** 231 (1929).
2. KOMAREWSKY, V. I., *Ind. Eng. Chem.* **49,** 264 (1957).
3. MCGOUGH, C. B., AND HOUGHTON, G., *J. Phys. Chem.* **65,** 1887 (1961).
4. MINACHEV, KH. M., AND KHODAKOV, YU. S., *Kinet. Katal.* **6,** 89 (1965).
5. TOLSTOPYATOVA, A. A., BALANDIN, A. A., AND CHI-CHUAN, YU., *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1,** 3 (1964).
6. MINACHEV, KH. M., MARKOV, M. A., BOGOMOLOV, V. I., AND ENGLINA, F. E., *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1,** 13 (1964).
7. SAZONOV, L. A., ARTAMONOV, E. V., AND MITROFANOVA, G. N., *Kinet. Katal.* **12,** 378 (1971).
8. WINTER, E. R. S., *J. Catal.* **15,** 144 (1969).
9. READ, J. F., *J. Catal.* **28,** 428 (1973).
10. READ, J. F., *Can. J. Chem.* **50,** 490 (1972).
11. ASHMEAD, D. R., ELEY, D. D., AND RUDHAM, R., *J. Catal.* **3,** 280 (1964).
12. MINACHEV, KH. M., AND ANTOSHIN, G. V., *Dokl. Akad. Nauk. SSSR* **161,** 122 (1965).
13. ANTOSHIN, G. V., MINACHEV, KH. M., AND DMITRIEV, R. V., *Kinet. Katal.* **9,** 816 (1968).
14. SAZONOV, L. A., PATOV, A. N., AND RATOVA, T. G., *Kinet. Katal.* **6,** 836 (1965).
15. WINTER, E. R. S., *J. Chem. Soc. A* 1832 (1969).
16. BAKUMENKO, T. T., *Kinet. Katal.* **6,** 74 (1965).
17. BAKUMENKO, T. T., AND CHASHECHNIKOVA, I. T., *Kinet. Katal.* **10,** 796 (1969).
18. ANTOSHIN, G. V., MINACHEV, KH. M., AND DMITRIEV, R. V., *Izv. Akad. Nauk. SSSR, Ser. Khim.* **8,** 1864 (1967).
19. READ, J. F., AND CONRAD, R. E., *J. Phys. Chem.* **76,** 2199 (1972).
20. DUNFIELD, L. G., AND READ, J. F., *J. Chem. Phys.* **57,** 2178 (1972).
21. GLUSHKOVA, V. B., KELER, E. K., AND SOKOLOV, YU. G., *Dokl. Akad. Nauk. SSSR* **158,** 151 (1964).
22. TOSUN, G., AND RASE, H. F., *Ind. Eng. Chem. Prod. Res. Develop.* **11,** 249 (1972).