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Catalysts for Initiating the Hydrogen–Oxygen Reaction at 78°K

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Catalysts for initiating reaction of hydrogen with oxygen in gas mixtures at temperatures down to 78°K (—195°C) were sought. A rising-temperature reactor was used for detecting onset of reaction. The platinum metals, especially iridium, platinum, and ruthenium, were the most active. With high concentrations of iridium on an alumina support, reaction initiation was observed at —195°C for a helium stream containing 3% hydrogen and 1% oxygen. Best results were obtained when the catalyst had been preheated in hydrogen and cooled in a hydrogen environment before being contacted with oxygen-containing gas. The initiation is interpreted to be the result of transient phenomena which occur when a hydrogen–oxygen mixture contacts an active catalyst. Chemisorption of oxygen and formation of some water, along with water adsorption on the support, serve to raise the temperature to a point where true catalysis can proceed.

INTRODUCTION

One challenge arising from efforts to explore space is that of learning to catalytically initiate reactions of propellants. For hydrogen–oxygen mixtures, a catalyst may provide a way of reaching a temperature at which a gas-phase combustion can be propagated. Since hydrogen and oxygen are normally transported as liquids in space vehicles, the reaction may have to be initiated in gaseous mixtures at temperatures down to that of liquid oxygen. Once reaction has started, the temperature will rise rapidly to the adiabatic value for the gas mixture, and the catalyst must withstand this temperature if it is to be used for another start. Thus, a catalyst of high activity and high stability is needed.

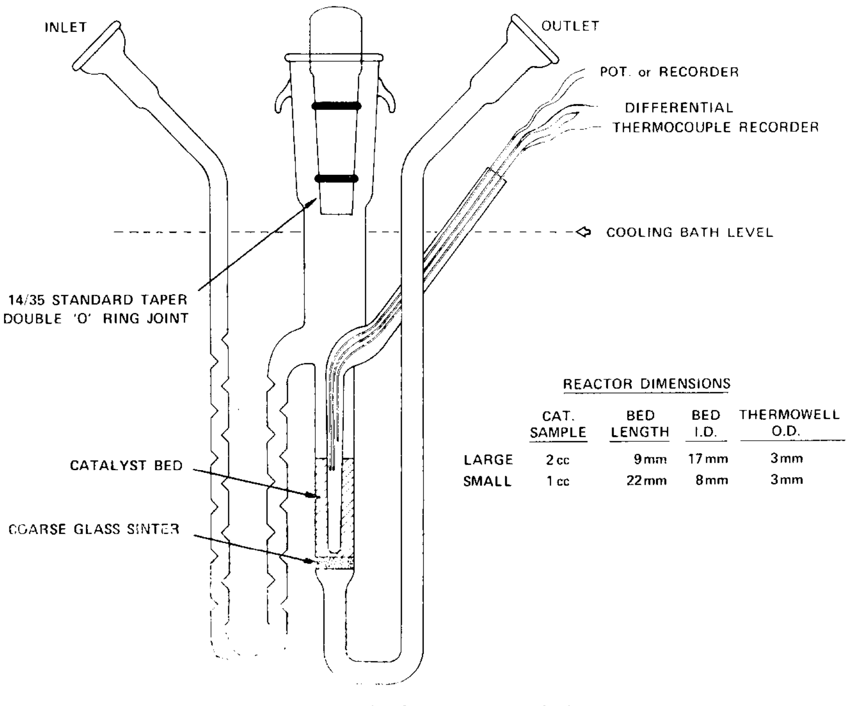
Earlier work by Ladacki *et al.* (*1*) showed that certain noble metal catalysts displayed activity for the hydrogen–oxygen reaction at —195°C. The most active catalyst was a platinum–rhodium–lead combination on alumina. Lee (*2*) studied ignition of hydrogen–oxygen by injection of powdered Raney nickel at —195°C. The purpose of the present work was to investigate a series of granular catalysts in a search for high activity. Stability of the better catalysts, as measured by activity changes on exposure to hydrogen–steam at elevated temperatures, was also investigated (*10*).

The low temperature hydrogen–oxygen reaction is of considerable scientific interest. We can ask how it is possible for a reaction with an apparent activation energy of about 10 kcal/mole at 100°C to proceed with a measurable velocity at —195°C. We also wonder about the parts played by catalyst pretreatments, supports, and reactant compositions, as well as which metals or combinations are the most active and most stable. These questions are considered later. Here we shall say a few words about practical hydrogen–oxygen ignition and the probable phenomena involved. We can visualize an effective catalyst as composed of an active metal highly dispersed on an inert and stable alumina support. If it has been well reduced and cooled in hydrogen, the surface of the metal should be covered with adsorbed hydrogen atoms. When flow of a gas containing hydrogen and oxygen is started at a low temperature, oxygen atoms are rapidly absorbed, releasing heat. If the rate of heat removal is not too great, the catalyst is warmed to the point where combination of adsorbed hydrogen atoms and adsorbed oxygen atoms starts, and this reaction rapidly heats the catalyst further. An additional contribution to the temperature increase may be made by adsorption of initial product water onto the alumina support. If the ignition is successful the temperature "runs away" toward the adiabatic limit for the gas flowing. In this situation, water has little chance to remain in the catalyst bed. For initiating propagation into the gas phase, the temperature should rise substantially above the ignition temperature of about 574°C for the homogeneous reaction of hydrogen–oxygen gas mixtures. Too high a temperature, however, would permanently damage the catalyst. A reasonable gas composition might be 92.6% H_2 and 7.4% O_2, by volume, which gives a limiting temperature of 1100°C.

The Rising Temperature Reactor

Initial attempts to develop a satisfactory isothermal test procedure for catalyst evaluation using highly dilute reactant streams or small pulses of hydrogen–oxygen mixtures in a helium stream all failed. Steady state operation at low temperatures could be obtained only with no reaction. When reaction occurred, it quickly became poisoned if the temperature was not allowed to rise above 0°C, and ice deposited in among the catalyst granules. With reactant pulses, the catalyst temperature rose several degrees with each pulse, and adsorption of oxygen onto the catalyst at low temperatures complicated the data.

The rising temperature technique finally adopted proved to be a simple, rapid, and reproducible method for comparing catalyst activity. The reactor is shown in Fig. 1. A sample of catalyst (1 cm^3 of 20–30 mesh granules or 2 cm^3 of ⅛ in. pellets) was loaded into the Pyrex glass reactor, the central opening was plugged, and the thermocouples were adjusted to be about 2 mm below the top of the catalyst bed. After a standard pretreatment in 50% H_2–50% He, by volume, at 400°C for 10 min, the reactor was cooled in this mix-



REACTOR DIMENSIONS

	CAT. SAMPLE	BED LENGTH	BED I.D.	THERMOWELL O.D.
LARGE	2 cc	9 mm	17 mm	3 mm
SMALL	1 cc	22 mm	8 mm	3 mm

FIG. 1. Standard test reactor design.

ture to liquid nitrogen temperature (—195°C). The feed of 400 ml/min 3% H_2, 1% O_2, 96% He by volume was then flowed over the catalyst while the reactor was still surrounded by the liquid nitrogen bath. Exactly 1 min later, the liquid nitrogen bath was replaced by an insulated beaker filled with —195°C air to allow the reactor temperature slowly to rise, and the temperature in the central thermowell was recorded as a function of time. When reaction commenced, it was detected as a deviation from the smooth warming curve. In this way, catalyst activity was measured by the temperature needed to give detectable reaction. The lower the temperature at which activity was detected, the more active the catalyst. All tests were made at atmospheric pressure.

To bring catalysts to a definite state, each catalyst was normally given the pretreatment described above. The reproducibility of this test procedure for catalysts which initiated reaction below —100°C was found to be about ±2°C in separate reactor loadings a few days apart, and about ±5°C for tests made several months apart on the same catalyst preparation.

Heating due to reaction was always detected first in the upper inlet layers of the catalyst bed, but exact positioning of the detecting thermocouple was not critical within a region 2–6 mm below the top of the bed. The amount of catalyst similarly had no effect on the initial reaction temperature. Reactor size did affect the temperature at which reaction could be first detected, however. In the larger reactor, a Pt–Rh on alumina catalyst first showed reaction at —116°C, whereas with the smaller reactor reaction on this catalyst was not detected until —110°C.

Catalyst Selection

Since oxide catalysts are considerably less active for the hydrogen–oxygen reaction than metals, they were not considered in this study. Ponec *et al.* (*3*), in studying electrical conductivity changes of evaporated metal films down to —195°C on adsorption of oxygen and hydrogen concluded that both gases adsorb on the noble metals Pt, Pd, and Rh to give species which can interact, and at 0°C, the reaction products desorb from the metal surface. The work of Ladacki *et al.* (*1*) showed that rapid reaction of hydrogen with oxygen is possible at low temperatures on practical catalysts containing the more active noble metals.

In general, the most active metals for this reaction are those which chemisorb both oxygen and hydrogen, but do so only weakly. A comparison of heats of adsorption data (*4*) for hydrogen and oxygen on various metals suggests that the noble metals of group VIII of the Periodic Table most closely meet these requirements followed by Fe, Co, and Ni, so most attention was directed towards optimizing catalyst preparations based on these metals. In most cases, catalysts were prepared by impregnation of high area refractory oxides using aqueous solutions of the various metal salts, followed by drying and calcining in air. Catalysts were activated *in situ* for testing.

Pretreatment Effects

Noble metal catalysts readily adsorb water vapor, oxygen, carbon dioxide, and other gases which would be very serious poisons at the low temperatures being considered, so initial tests were made to determine the effectiveness of various pretreatments for activating catalysts. All gas streams were purified to remove traces of water vapor, and of carbon dioxide. Oxygen-containing streams were passed through a molecular sieve drier, then 0.5% Pd on alumina at 100°C and through a bed of Ascarite. The hydrogen-containing and helium streams were passed through a drier, Ascarite, then beds of activated charcoal and 5% Pd on alumina at 100°C. After being separately metered, the mixed gases were flowed through beds of indicating Drierite, Ascarite, and molecular sieve before entering the reactor. Even after heating all the metal and glass lines leading to the reactor, however, traces of water vapor could still be detected in the

TABLE 1
CATALYST PRETREATMENT VARIED

Catalyst: 0.5 g (0.8 ml); 2.5% w Pt, 2.1% w Rh/Alumina. Feed: 400 ml/min; He, 3% H_2, 1% O_2 (vol).

Test no.	Catalyst pretreatment: Heating	Catalyst pretreatment: Cooling atm to −195°C	Activity detected, temp (°C)
A-3	He, H_2, O_2 feed, 5 min to approx 200°C	He, 4% H_2	−112
A-4	He, 4% H_2, 10 min to 380°C	He, 4% H_2	−111
A-5	He, 10 min to 380°C	He	−94
A-6	He, 4% O_2, 10 min to 380°C	He, 4% O_2	−54
A-7	Repeat of A-4	He, 4% H_2	−108
A-8	He, 4% H_2, 10 min to 380°C	He, 4% H_2 to 30°C; sweep He; He, 4% O_2 to −195°C	−103
B-4	He, 4% H_2, 10 min to 380°C	He, 4% H_2	−103
B-5	He, 10 min to 380°C	He to 35°C; He, 4% H_2 to −195°C	−92
B-6	He, 50% H_2, 10 min to 380°C	He, 50% H_2	−103

gases reaching the reactor in early tests, but slowly decreased in later tests.

The activity of a Pt–Rh catalyst improved continuously on pretreating at successively higher temperatures above 200°C in a 4% hydrogen in helium stream, then cooling in this gas stream to liquid nitrogen temperature for testing. The rate of improvement slowed above 400°C, however, so treatment at this temperature was made the standard pretreatment for activity comparisons.

The results in Table 1 show that exposure to oxygen at 400°C deactivated this catalyst quite badly, but it was almost completely reactivated by subsequent treatment at 400°C in hydrogen. Exposure to 4% oxygen in helium below 30°C while cooling to —195°C had surprisingly little effect on catalyst activity, however, suggesting that exposure to oxygen at high temperature oxidizes a platinum surface more deeply than exposure at lower temperatures.

In the second series of tests of Table 1, using a catalyst sample deactivated somewhat by previous treatments, heating in helium did not fully reactivate the catalyst even though it was exposed to hydrogen while cooling below room temperature. High temperature "cleaning" in hydrogen is obviously the most effective for activation.

Varying the composition and flow rate of the reactant stream from the 3% hydrogen, 1% oxygen, 96% helium mixture at 400 ml/min had only a small effect on the temperature at which activity was detected. However, as the data of Table 2 show, the time which elapsed from onset of reaction until the maximum rate was attained was sensitive to reactant concentration. The data in Table 2 were all ob-

TABLE 2
VARIATION OF FEED FLOW RATE AND COMPOSITION

Catalyst: 2.5% Pt, 2.1% Rh/alumina.

Feed gases, H_2, O_2, He: H_2 (% v)	O_2 (% v)	Total flow (ml/min)	Activity (°C): Detected	Activity (°C): Max rate attained	Δt, (sec)
3	1	400	−109	−89	38
3	1	800	−107	−85	44
2.7	1.4	400	−108	−89	42
2	2	400	−108	−93	28
3	1	400	−110	−95	27
1.5	0.5	400	−108	−91	37
17	3	875	−108	−98	2
32	5	950	−112	−110	~1
38	12.5	800	−112	−111	<1
3	1	400	−113	−87	38
3.5	0.5	400	−117	−85	60
3	1	400	−113	−93	51

tained on a single Pt–Rh catalyst loading given the standard pretreatment immediately before each test was made.

Pure Metals and Their Binary Alloys

The relative activities found for catalysts of the palladium and platinum metals and their binary alloys at concentrations atomically equivalent to 4.5% w Pt are shown in Table 3. Correlation with the old activity data of Remy and Schaefer (*5*) for bimetallic catalysts on asbestos tested at room temperature is not good, but the old results could have been strongly modified by product water inhibition effects. All of the more active catalysts of our series contained platinum. Catalysts of Ru, Rh, and Os showed no activity below room temperature.

The effect of varying metal ratio on the activity of catalysts of Pt–Rh and Pt–Ru on alumina is shown in Table 4. No definite enhancement of activity was observed from such combinations.

TABLE 3
Activity of Pt and Pd Metals and Their Binary Alloys

Catalyst		Activity detected (°C)
No.	Composition[a] on RA-1 alumina	
177	100% Pt sponge	−90
8A	2.4% Ru	>+20
8D	2.4% Rh	>+20
10A	2.4% Pd	−84
47A	4.5% Os	>+20
8B	4.5% Ir	−70
8C	4.5% Pt	−112
9C	1.2% Ru, 1.2% Rh	>+20
10B	1.2% Ru, 1.2% Pd	−69
9A	1.2% Ru, 2.2% Ir	+4
9B	1.2% Ru, 2.2% Pt	−107
10E	1.2% Rh, 1.2% Pd	−71
9E	1.2% Rh, 2.2% Ir	+13
9F	1.2% Rh, 2.2% Pt	−107
10C	1.2% Pd, 2.2% Ir	−78
10D	1.2% Pd, 2.2% Pt	−106
9D	2.2% Ir, 2.2% Pt	−113

[a] Weight percent of metal. Corresponds to 1:1 atomic ratio in alloys. All catalysts of same total metal atom content on RA-1 (700) alumina support except Pt sponge.

TABLE 4
Platinum Alloys of Varying Metal Ratios

Catalyst		Activity detected (°C)
No.	Composition (% w)	
8D	2.4% Rh	>+20
16A	0.72% Pt, 1.89% Rh	−26
16B	1.44% Pt, 1.52% Rh	−87
9F	2.2% Pt, 1.2% Rh	−107
16C	2.86% Pt, 0.75% Rh	−112
16D	3.57% Pt, 0.38% Rh	−112
8C	4.5% Pt	−112
53B	2.3% Pt, 2.2% Re	−86
106B	0.8% Pt, 2.0% Ru	−89
9B	2.2% Pt, 1.2% Ru	−107
106A	3.8% Pt, 0.4% Ru	−102

Effect of the Support

Activity temperatures for 2.2% Pt–1.2% Rh catalysts similarly prepared from the aqueous chlorides on various supports are shown in Table 5. At this metal loading, it is apparent that high surface area supports are not necessary for good metal dispersion. In fact, calcination of the Reynold's RA-1 alumina at 1000°C in air for 1 hr, rather than the 2 hr at 700°C which all other supports were given prior to catalyst preparation, decreased the alumina surface area considerably, but gave a more active catalyst. Catalysts prepared on aluminas, alumina–silicas, zirconia–silicas, and zirconias having surface areas greater than about 5 m^2/g all gave very similar activities.

Catalysts of Varying Metal Content

The activity increase obtained with increasing metal loading of the catalyst is clearly shown by the data in Table 6. In the Pt–Rh, Pt–Ru, and Pt-on-alumina series, activity was high at the lower metal loadings and increased further with increasing metal content. Above about 15% metal, however, these catalysts showed little further improvement with increasing metal content. The Pt/alumina series, in fact, passed through a maximum activity

TABLE 5

ACTIVITY OF Pt–Rh ON VARIOUS SUPPORT MATERIALS

Catalyst: 2.2% w Pt, 1.2% w Rh on each support material.

Catalyst support material		Surface area	Activity detected
Source	Composition (% w)	(m^2/g)	(°C)
Reynolds RA-1	Al_2O_3	135	−107
Reynolds RA-1 (1000°C)	Al_2O_3	32	−114
Harshaw Al-0104	Al_2O_3	100	−120
Girdler T-708	Al_2O_3	7–8	−119
Norton LA-617	19 SiO_2, 79 Al_2O_3	56	−121
Norton LA-622	19 SiO_2, 79 Al_2O_3	36	−122
Norton BA-121	19 SiO_2, 79 Al_2O_3	9–15	−122
Norton LA-848A	19 SiO_2, 79 Al_2O_3	1.5	−110
FMC Seasorb 5	MgO	117	−79
Laboratory prep	ZrO_2	ca. 75	−117
	30 SiO_2, 70 ZrO_2	—	−122
	Y_2O_3	62	−64
	BN	17	−58

at about 20% metal. Iridium catalyst preparations, on the other hand, showed somewhat inferior activity at low metal loadings but continued to improve even at very high metal loadings until 29% Ir gave activity at −195°C, the limit of our tests. Hydrogen chemisorption values, determined using the method described by Benesi *et al.* (*6*) are listed in Table 6 and give a measure of the effectiveness of metal dispersion on the alumina support.

TABLE 6

CATALYSTS OF VARYING METAL CONTENT

Support Reynolds RA-1 alumina, calcined 700°C.

Catalyst		
Composition (% w)	Hydrogen sorption (μmoles of H_2/g)	Activity detected (°C)
1.1% Pt, 0.6% Rh	41	−89
2.2% Pt, 1.2% Rh	67	−107
4.5% Pt, 2.4% Rh	107	−123
8.5% Pt, 4.2% Rh[a]	69	−125
4.5% Pt	—	−112
8.85% Pt	—	−116
17.0% Pt	—	−120
29% Pt	—	−115
2.3% Pt, 1.2% Ru	—	−107
8.5% Pt, 4.2% Ru[a]	—	−137
3.4% Ir	143	−89
14% Ir[b]	278	−181
26% Ir[b]	373	−192
29% Ir[b]	—	−195
32% Ir (Shell 405)[b]	418	−195

[a] Support calcined at: 1100°C; [b] 400°C.

The 32% iridium catalyst listed in Table 6 is commercially available as the Shell 405 catalyst. It was developed in this laboratory several years ago for the spontaneous decomposition of hydrazine monopropellant, and is now so used in space applications for thrust and power generation. The effectiveness of the iridium metal dispersion on this catalyst at various metal loadings is shown in Fig. 2. Although the available metal surface per gram of metal falls as the iridium content increases, the active metal area per gram of catalyst continues to increase even at very high metal loadings. The surface characterization of a commercial Shell 405 catalyst preparation has recently been reported by Brooks using similar gas adsorption techniques (*7*).

A typical test curve for a 32% Ir/Al_2O_3 catalyst is shown in Fig. 3, along with the curve for a 17% Pt/Al_2O_3 catalyst. In several tests, 32% Ir/Al_2O_3 catalysts

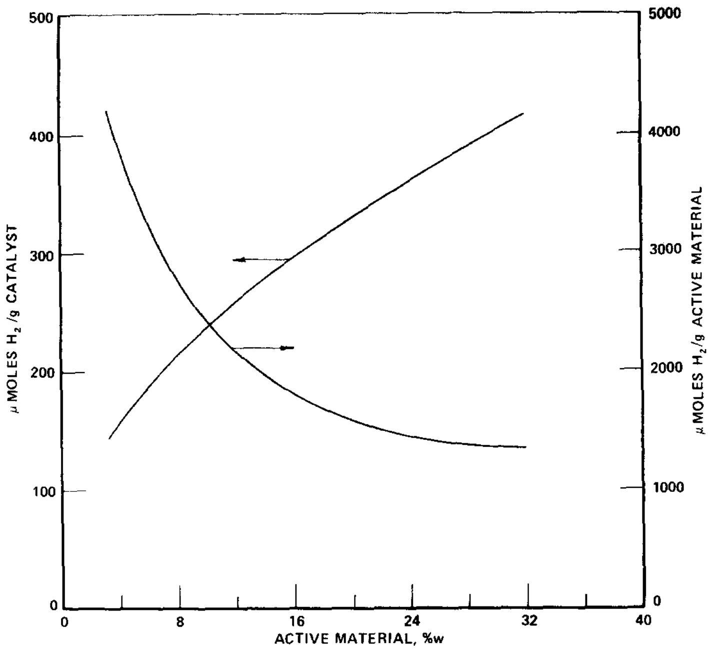


FIG. 2. Hydrogen chemisorption on Shell 405 type catalysts.

showed activity at —195°C as soon as the 1% oxygen, 3% hydrogen in helium stream was flowed to the reactor even though it was still being efficiently cooled by the liquid nitrogen bath.

In general, activity of the catalysts of Tables 6 and 7 correlated roughly with the available metal area as measured by hydrogen chemisorption. These catalysts were prepared on various aluminas, some of which had been heated to 700 or 1100°C prior to catalyst preparation. Support sur-

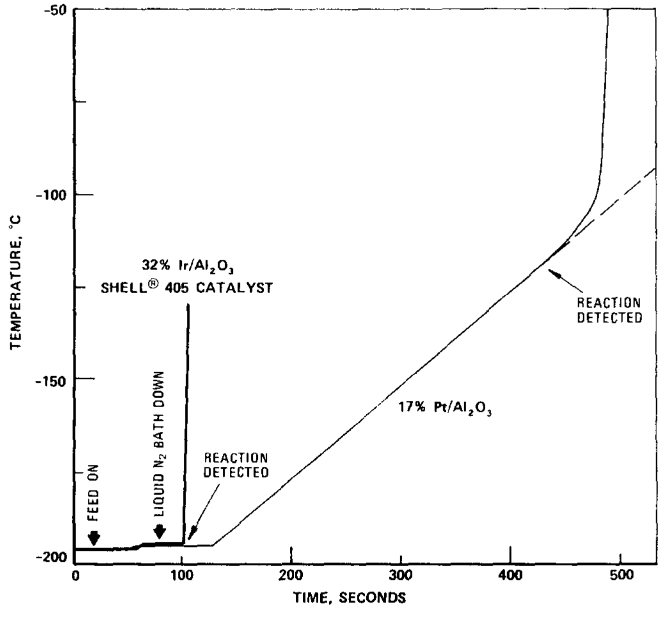


FIG. 3. Typical experimental activity test warming curves.

TABLE 7
VARIATION OF ACTIVITY WITH SURFACE AREA AND HYDROGEN CHEMISORPTION

Composition (% w)	Surface area (m^2/g)	Chemisorption (μmoles of H_2/g)	Activity detected (°C)
Pt, Rh, Pb[a]	231	25	−115
8.6% Pt, 4.4% Ru	19	32	−137
8.5% Pt, 8.5% Ir	21	80	−150
0.76% Pt, 2.0% Ru	70	26	−89
1.1% Pt, 0.6% Rh	118	41	−89
2.2% Pt, 1.2% Rh	118	67	−107
4.5% Pt, 2.4% Rh	118	107	−123
2.3% Pt, 1.2% Rh	29	37	−114

[a] Catalyst A-4 of Ref. (*1*).

face area, if above about 5 m^2/g, appears to play little part. However, many deviations from exact correlation of activity with hydrogen chemisorption were evident.

DISCUSSION

Catalytic initiation of the hydrogen–oxygen reaction at low temperatures, as carried out in the rising temperature reactor, is a complex process involving transient phenomena. When the hydrogen–oxygen mixture is flowed to the reactor, oxygen reaching a bare or hydrogen-covered surface is chemisorbed with large heat evolution. Some reaction to form water probably occurs simultaneously. Water formed is adsorbed on the alumina support. If these three processes occur rapidly, they release sufficient heat to warm the catalyst to a temperature at which the true catalytic reaction can continue. If these initial processes occur too slowly, the reaction quenches. The catalyst for this process must have a high metal surface area per unit volume, and the metal must be a very active one, preferably either iridium or platinum. The Shell 405 Catalyst satisfies these requirements.

Evidence for the above transient phenomena was obtained by experiments and calculations. When a stream of 4% oxygen in helium was flowed to a 30% iridium catalyst that had been heated in hydrogen at 400°C, cooled in hydrogen to −195°C, and then flushed with helium at −195°C, a temperature rise of 54°C was observed within 2 sec after placing the cold-air bath around the reactor. The observed temperature rise, while the liquid nitrogen bath was still in place, was only 3°C in this experiment, but in a similar experiment in which the catalyst was flushed with helium at 400°C to remove adsorbed hydrogen before cooling, an 18°C temperature rise was observed on admitting the 4% oxygen stream, even though the liquid nitrogen bath was still in place. In another test with this catalyst, the hydrogen–oxygen feed was flowed over the catalyst for 5 min while it was cooled by liquid nitrogen, instead of for the 1 min used in the standard test. On replacing the liquid nitrogen bath with the cold-air bath, activity was not detected until the reactor warmed to −150°C; whereas in the standard test activity was detected immediately on replacing the liquid bath before any warming from −195°C occurred.

Reliable values for the heat of adsorption of oxygen onto hydrogen-covered iridium or platinum are not available. However, an estimate can be made as follows. The adsorption of oxygen onto clean platinum releases about 65 kcal/mole. The adsorption of hydrogen onto clean platinum releases about 30 kcal/mole. In both cases, one H or O atom will combine with one surface Pt. Thus, it can be expected that adsorption of oxygen onto a hydrogen-covered platinum surface will release 35 kcal/mole if no water is formed, and even more if water forms simultaneously. The corresponding differential for iridium is expected to be somewhat larger. Using 35 kcal/mole, an adsorption capacity of 400 μmoles of hydrogen or oxygen, and the specific heat capacity of a 25% platinum–alumina catalyst at low temperature, the adsorption of oxygen onto a hydrogen-covered platinum catalyst can raise the temperature from −196 to −36°C. Temperature changes as large as this were not observed. It is clear, however, that momentary catalyst surface temperatures in such a system can be well above those registered by a thermocouple inside a thermowell.

A transient temperature rise caused by oxygen chemisorption, augmented perhaps by some initial water formation and by adsorption of water onto the alumina support surface, appears to account for the initiation at the lowest temperatures. Even so, it is doubtful whether the activation energy can be as high as the values of 11–17 kcal/mole reported for platinum catalysts at 100–225°C (*8, 9*). Many of the less active catalysts showed reaction initiation at −120 or −130°C, and for them any rapidly liberated heat from initial oxygen chemisorption must have been dissipated, since almost 7 min elapsed between the time of admission of oxygen-containing gas and reaching a temperature of −130°C. Thus we assume that the true surface temperature for such a catalyst was close to −130°C. A maximum possible rate for −130°C can be calculated from the rate of collision of gas molecules with the catalyst metal surface and the Boltzmann energy distribution law. From such calculations, combined with an estimate of the amount of reaction actually taking place when activity was detected, it is indicated that the activation energy cannot be higher than 5 kcal/mole for the hydrogen–oxygen reaction on platinum or iridium.

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