JOURNAL OF CATALYSIS 24, 502-509 (1972)

Stability of Noble Metal Catalysts for the Hydrogen–Oxygen Reaction

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Received June 29, 1971

Stability of various supported noble metal catalysts for initiation of the hydrogen–oxygen reaction was tested by means of steam–hydrogen treatment at 1000–1200°C followed by a simple activity test. Many catalysts were stable to 1100°C, but all lost some activity at 1200°C. The most active with very good stability was an iridium/alumina catalyst of high iridium content.

INTRODUCTION

This paper presents data on high temperature stability of catalysts developed for initiating the reaction of hydrogen with oxygen at temperatures as low as −195°C. As noted in the previous paper (*1*), such catalysts operate best in a hydrogen-rich atmosphere. For many space applications, repetitive low temperature ignitions would be required. To meet this requirement, the catalyst must be able to withstand exposure to 1000–1200°C in a steam–hydrogen atmosphere and still retain sufficient activity for a new low temperature initiation. Such stability calls for a refractory support carrying an active component that has low surface and vapor mobility and low reactivity with the support or the hot gases.

The presence of oxygen and/or steam in the atmosphere adds additional constraints. It is well known that an unstable volatile platinum oxide accelerates crystallite growth of platinum in high temperature exposure to atmospheres containing oxygen (*2*). Steam renders both silica and carbon unsuitable as catalyst supports.

Hydrogen–oxygen flame temperatures can exceed 3000°C, but can be controlled to lower values by suitably metering the feed gases. The stability of the catalyst will normally limit the maximum temperature which can be used. Since a hydrogen-rich mixture is preferred, a hydrogen–steam mixture simulates the environment the catalyst must withstand. The general procedure used in this work was to first test the activity of a catalyst by means of the rising temperature technique, then expose the catalyst to hydrogen–steam at 1000–1200°C for a definite time and remeasure the activity. In some cases, surface area and hydrogen chemisorption changes were also obtained.

RISING TEMPERATURE ACTIVITY TEST

As has been noted (*1*), it is quite difficult to measure the activity of low temperature hydrogen–oxygen catalysts under steady state conditions. A rising temperature technique, however, gives good comparative values. Details of this technique were given previously. Briefly, the method consisted of giving a 20–30 mesh catalyst a standard reduction in hydrogen at 400°C for 10 min, then cooling in a liquid nitrogen bath to −195°C while still in hydrogen, starting the flow of a reactant stream composed of 1% oxygen, 3% hydrogen, and 96% helium, and 1 min after the start of the flow removing the liquid nitrogen bath and replacing it with an insulated empty beaker precooled to −195°C. The catalyst warmed slowly, and when reaction started it was detected by a deviation of the temperature from that of the smooth warming curve. Activity was thus characterized by the temperature at which reaction was first detected by this method.

CATALYST STABILITY TESTING

The method used to test stability consisted of exposing the catalyst to a constant high temperature in an atmosphere of 85% hydrogen and 15% steam. This mixture is like that which would be formed from a hydrogen-rich mixture giving a flame temperature of about 1000°C. After exposure, the catalyst was removed and tested in the rising temperature reactor.

Figure 1 shows the apparatus for steaming. The tube was of fused quartz. It was mounted vertically in a 12 in. furnace. At the top was a tapered joint which fitted loosely into a section of Pyrex tubing carrying a side arm through which nitrogen could be flowed. In steaming, hydrogen was passed upward through a thermostatted water saturator, past the sample bucket, and out the loosely fitting joint. The temperature of the sample was measured with a Pt/90 Pt–10 Rh thermocouple.

The procedure consisted of loading a 1–2 cm^3 sample of catalyst into a fine mesh gauze platinum bucket, approximately 1 cm i.d. and 2 cm deep, and suspending it from the thermocouple in the upper chamber. After sweeping out air with nitrogen, and then with hydrogen–steam, the sample was lowered into the center of the heated section of the tube and held there for a definite period of time. At the end of this period, the sample was quickly raised into the upper chamber, the hydrogen flow was stopped, and the sample was flushed with dry nitrogen and cooled in nitrogen. After removal, samples could be stored in screw-capped bottles for several days without effect on their activity.

The temperature in the region in which the sample was held varied ±5°C from the nominal value. The thermocouple reached the furnace temperature in less than 2 min when it was lowered into position. Standard exposures were as follows: 1000 or 1100°C for 30 min; 1200°C for 15 min.

SUPPORT MATERIALS

The desired temperature of operation, from 1000 to 1200°C, is at the upper limit of stability for the best known catalyst supports of high or even moderate surface area. The presence of steam increases the difficulty. However, exposure times for aerospace catalysts are expected to be relatively short. From catalyst studies (*1*), it was judged that a support should retain at least 10 m^2/g surface area after exposure to 1100°C for 30 min. Refractory oxides and their combinations were considered to be the most promising supports. Although alumina has a lower melting point (2030°C) than many other oxides (thoria, 3000°C; zirconia, 2700°C; magnesia, 2500°C), it retains surface area as well or better. Alumina was the best support tested. Two aluminas were used for many catalysts. Reynolds RA-1, a gamma alumina, had 280 m^2/g initial area, which decreased to 35 m^2/g on calcining in air at 1000°C for 1 hr. Harshaw Al-1404, a partly amorphous eta alumina, retained 2–3 times as much area after similar calcination.

Table 1 shows the activity and stability of a number of platinum–rhodium catalysts prepared on different supports. The catalysts were prepared using aqueous metal chlorides. These catalysts had rather a low metal content, and were not active below −122°C. Surface area of the support did not appear to be very important for activity in this series, as long as the value was above about 7 m^2/g. In a few cases, small increases in activity were seen after high temperature steam–hydrogen treatment. Possible causes of such increases are discussed later.

Silica–aluminas from the Norton Company produced similar activities in the series of Table 1 when initial support areas were about 12, 36, and 56 m^2/g. A silica–alumina of 1.5 m^2/g area, however, had lower activity, both before and after steaming.

A few catalysts of higher metal content are collected in Table 2. Some of these show greater initial activity than the previous series, and also higher activity after

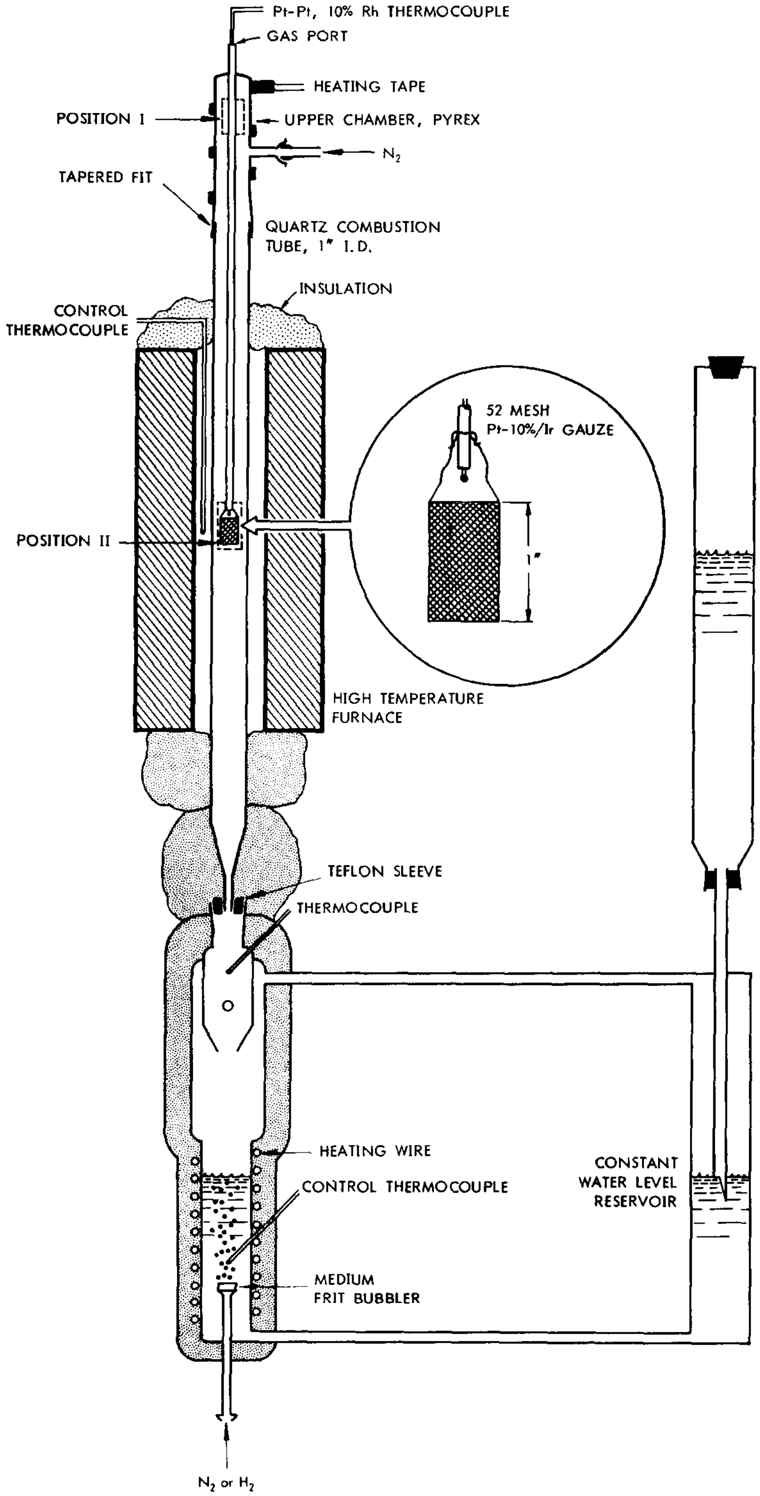

FIG. 1. Apparatus for stability tests.

TABLE 1

ACTIVITY AND STABILITY OF Pt–Rh ON VARIOUS SUPPORT MATERIALS

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

Catalyst support material			Catalyst			
			Activity detected (°C)			
		Surface area		Steamed (°C)		
Composition (% w)	Source	(m²/g)	As prepared	1000	1100	1200
Al_2O_3	Reynolds RA-1	135	−107	−114	−113	−124
Al_2O_3	Reynolds RA-1 (calc 1000°)	32	−114	−116	−112	—
Al_2O_3	Harshaw Al-0104	100	−120	—	—	−113
Al_2O_3	Girdler T-708	7–8	−119	—	−110	−116
19 SiO_2, 79 Al_2O_3	Norton LA-617	56	−121	—	−106	—
19 SiO_2, 79 Al_2O_3	Norton LA-622	36	−122	—	−112	—
19 SiO_2, 79 Al_2O_3	Norton BA-121	9–15	−122	—	−119	−127
19 SiO_2, 79 Al_2O_3	Norton LA-848A	1.5	−110	—	−100[a]	—
MgO	FMC Seasorb 5	117	−79	—	+20	—
ZrO_2	Laboratory prep.	ca 75	−117	—	−122	0
40 SiO_2, 60 ZrO_2	Laboratory prep.	ca 75	−119	—	—	—
30 SiO_2, 70 ZrO_2	Laboratory prep.	—	−122	−135	−118[a]	—
Y_2O_3	Laboratory prep.	62	−64	—	—	—
BN	Laboratory prep.	17	−58	—	—	—

[a] Activity transient; temperature rise irregular.

steaming. A high purity alpha alumina from Aluminum Industrie A. G. (Switzerland) displayed activity at —171° after steaming at 1200°C, in spite of an estimated initial surface area of only about 5 m²/g. A catalyst based on zirconia had good initial activity, but lost almost all on steaming at 1200°C. However, incorporation of 5% calcium oxide into zirconia by coprecipitation stabilized it so that activity was seen at —137°C after steaming at 1200°C.

VARIOUS METALS AND COMBINATIONS

A complete series of catalysts containing Ru, Rh, Pd, Ir, and Pt and their binary

TABLE 2

PLATINUM-RUTHENIUM CATALYSTS ON VARIOUS SUPPORTS

Support material			Catalyst				
					Activity detected (°C)		
		Surface area				Steamed (°C)	
Composition and source	Calcination	(m²/g)	Pt (%)	Ru (%)	Fresh	1100	1200
Al_2O_3, RA-1	700°C	135	8.5	4.2	−123	−127	−134
Al_2O_3, RA-1	1100°C	20	8.4	4.3	−137	−132	−129
Al_2O_3, AIAG	None	ca. 5	9.2	4.8	−140	—	−171
ZrO_2	None	49	10.1	5.3	−178	—	>0
95 ZrO_2, 5 CaO	700	—	4.5	2.3	−125	−137	−137

TABLE 3
BINARY CATALYSTS ON REYNOLDS RA-1 ALUMINA
Support precalcined at 700°C.

Catalyst composition (% w)	Activity detected (°C)			
		Steamed (°C)		
	As prepared	1000	1100	1200
4.5% Pt	−112	−109	−102	—
1.2% Ru, 1.2% Pd	−69	—	−17	—
1.2% Ru, 2.2% Pt	−107	−113	−124	−127
1.2% Rh, 2.2% Pt	−107	−114	−113	−124
1.2% Pd, 2.2% Ir	−78	—	−66	—
1.2% Pd, 2.2% Pt	−106	−107	−107	—
2.2% Ir, 2.2% Pt	−113	−106	−120	−114

alloys was prepared on Reynolds RA-1 alumina. All were prepared to contain the same number of gram-atoms of metal. Only the more active of the series were tested after steam–hydrogen treatment. Results are given in Table 3. In this series, which again was of rather low metal content, only platinum and its alloys led to catalysts of good stability. The Pt–Ru, Pt–Rh, and Pt–Ir pairs retained higher activity after steaming than did platinum alone.

Further noble metal catalysts, progressing to quite high metal contents, are listed in Table 4. The platinum catalysts here,

TABLE 4
CATALYSTS OF VARYING METAL CONTENT
Support Reynolds RA-1 alumina, calcined 700°C.

Catalyst		Activity detected (°C)			
			Steamed (°C)		
Composition (% w)	H_2 Chemisorption (μ moles/g)	As prepared	1000	1100	1200
4.5% Pt	—	−112	−109	−102	—
8.8% Pt	—	−116	—	−60	—
17% Pt	—	−120	—	−105	—
29% Pt	—	−115	—	−108	—
1.1% Pt, 0.6% Rh	41	−89	−100	−106	—
2.2% Pt, 1.2% Rh	67	−107	−114	−113	−124
4.5% Pt, 2.4% Rh	107	−123	−120	−118	—
8.5% Pt, 4.2% Rh[a]	69	−125	—	−118	—
2.3% Pt, 1.2% Ru	—	−107	−113	−124	−127
8.5% Pt, 4.2% Ru[a]	—	−137	—	−132	−129
8.5% Pt, 8.5% Ir[a]	80	−150	—	−132	−123
4.5% Ir	—	−70	—	—	—
14% Ir[b]	278	−181	—	—	—
26% Ir[b]	373	−192	—	−195	—
29% Ir[b]	—	−195	—	—	—
32% Ir[b]	418	−195	—	−195	−123, 137[c]

[a] Support calcined at about 1100°C.
[b] Support calcined at 400°C.
[c] Similar catalyst containing 31% Ir.

TABLE 5
Effects of Steaming on Catalyst Properties

Catalyst	Steam-H_2 Treat. (°C)	Surface area (m^2/g)	H_2 Chemisorption (μ moles/g)	Activity detected (°C)
Pt, Rh, Pb/Al_2O_3 [Catalyst A-4 of Ladacki *et al.* (*5*)]	None	231	25	−115
	1100	38	7	−125
	1200	11	5	−116
8.5% Pt, 4.2% Ru/RA-1 Al_2O_3[b]	None	19	32	−137
	1100	17	20	−132
	1200	12	13	−129
8.5% Pt, 8.5% Ir/RA-1 Al_2O_3[b]	None	21	80	−150
	1100	19	53	−132
	1200	14	40	−123
32% Ir/RA-1 Al_2O_3[c]	None	119	418	−195
	1100	35	130	−195[a]
	1200	22	100	−123, −137[d]

[a] Temperature rise slower than for untreated catalyst.
[b] Support calcined at 1100°C.
[c] Support calcined at 400°C.
[d] Similar catalyst containing 31% Ir.

except for Pt–Ru and Pt–Ir, do not show high initial activities, but often increase moderately in activity after high temperature steaming. Most outstanding, however, were catalysts of high iridium content (Shell 405) which even after steaming for 30 min at 1100°C were capable of initiating the hydrogen–oxygen reaction at −195°C. A temperature of 1200°C, however, is too severe even for this catalyst, as activity then is only seen at −123 to −137°C. Most of the better catalysts were leveled to a similar activity corresponding to initiation at about −130°C, by the 15-min treatment at 1200°C.

Attempts to correlate changes in activity following the steam–hydrogen treatments with changes in surface area or active metal area were only partly successful. Some data are collected in Table 5 for treatments at 1100 and 1200°C. Surface areas were determined using physical adsorption of nitrogen, while metal areas were determined by hydrogen chemisorption at 7.6 mm hydrogen partial pressure and 0°C (*3*). In all cases, total surface area and hydrogen chemisorption decreased steadily with increase in the steaming temperature; but, in several cases, apparent activity increased at the same time. In general, nevertheless, a high chemisorption value was associated with high activity.

Increases in activity following high temperature steaming are hard to understand, especially if accompanied by a decrease in surface area or hydrogen chemisorption. There are several conceivable explanations:

a. Migration of components, as in alloys, may alter the chemical nature of the active surface.

b. Changes of porosity may change rates of diffusion and thus affect initiation phenomena.

c. Impurities that hinder reaction may be removed from the active metal or from the support.

We are inclined to favor the last explanation. For one thing, the 10-min treatment in hydrogen that preceded normal testing was carried out at 400°C, and probably left some impurities that were removed from the metal in the 500°C pretreatment preceding measurement of hydrogen chemisorption. Further evidence for removal of impurities came from two series of tests listed in Table 6. In one series, a 32% iridium catalyst was pretreated for 30 min in pure hydrogen in a reactor

TABLE 6
HIGH TEMPERATURE TREATMENT OF SHELL 405 CATALYST

Pretreatment temp (°C)	Time before activity detected at −195°C (sec)	
	30 min in H_2	30 min in H_2/60 min vacuum
400	69	86
600	66	65
300	38	45
1000	38	42

constructed of Vycor at several temperatures between successive activity tests. In the other series, a fresh sample of the same catalyst was likewise treated in pure hydrogen, then evacuated for 1 hr at the same temperature. In the first series, the catalyst was cooled in hydrogen, and in the second, it was cooled in vacuum to —130°C, then in helium-hydrogen to —195°C. In both series, the catalysts initiated reaction at —195°C, but the time between introduction of the reactant gases and the rapid rise of temperature varied, and this delay gave an indication of relative activity. In both series, the activity was improved following the high temperature hydrogen treatments. It is well known that hydrogen at high temperatures removes impurities such as sulfur, oxygen, and halogens from the surface of noble metals.

Another effect to be considered with respect to high temperature activation is dehydration of the support. We have speculated that the support participates in initiation by adsorbing water first formed to release heat. In agreement with this hypothesis, we have found that the heat of wetting of an alumina support increases following heating in vacuum. Heating in a steam atmosphere, moreover, should also be effective in diminishing the concentration of surface hydroxyl groups according to the model for alumina surfaces described by Peri (*4*).

Some data obtained for the Reynolds RA-1 gamma alumina are shown in Figure 2. Samples of the alumina were heated for 1 hr in vacuum at the indicated temperature. Following heating, the sample was sealed in a small bulb, which was then broken under water in a simple calorimeter. The

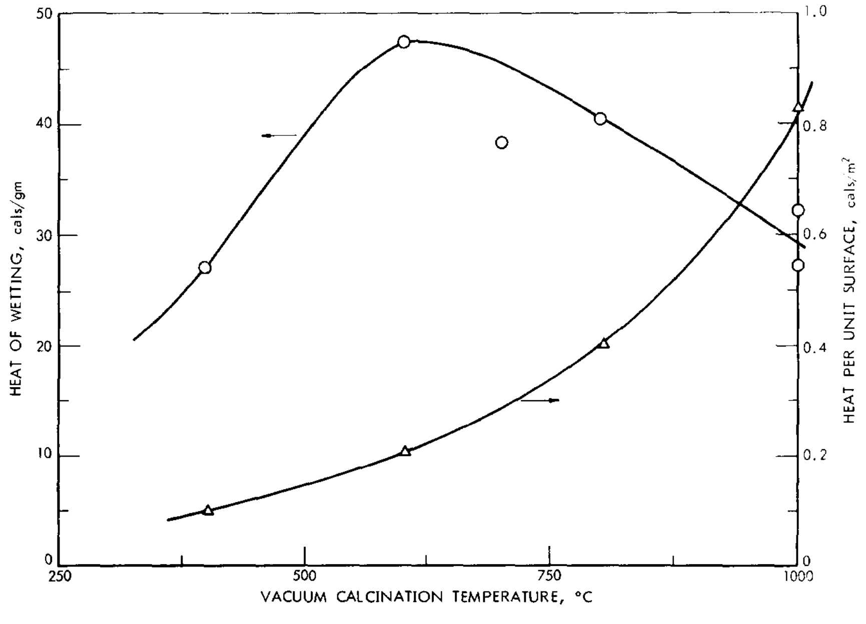

FIG. 2. Affinity of γ-alumina for water after vacuum calcination.

latter had been calibrated by means of electrical heat. The results show that the heat of immersion per gram increases steeply and passes through a maximum after evacuation at about 700°C. The heat of immersion per unit surface area, which probably more closely parallels heat of adsorption of incremental initial amounts of water, continues to rise up to a pretreatment temperature of 1000°C. In the study of Morimoto *et al.* (*6*), the heat of immersion per unit area of a gamma alumina increased with evacuation temperature up to 700°C, and then declined. Our evidence indicates, however, that the heat can be quite dependent on the cleanliness of the vacuum system. From our data, high temperature treatment in vacuum to at least 1000°C strongly increases the specific affinity of the alumina surface for water, and thereby increases its ability to aid the hydrogen–oxygen reaction by removing water from the active metal surface.

ACKNOWLEDGMENTS

T. R. Connolly, L. W. Doxsee, Jr., and Y. Sakauye participated in experimental phases. This work was part of a project sponsored by the National Aeronautics and Space Administration, Office of Advanced Research and Technology (Contract No. NAS 7-387). Technical liaison and advice were furnished by Paul N. Herr of the Lewis Research Center of NASA, Cleveland, Ohio.

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