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# Development of Hydrogen-Oxygen Catalysts

for

National Aeronautics and Space Administration

Contract No. NAS 7-387

Final Report

August, 1965 - July, 1966

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## ABSTRACT

This report presents results of a program designed to develop catalysts of improved activity and thermal stability for catalytic ignition of an oxygen-hydrogen mixture at low temperatures. A rising temperature testing technique was developed to determine the activity of many catalysts at temperatures down to that of liquid nitrogen (-195°C, - 320°F). Several formulations showed improved activity over catalysts previously available. Of these, the Shell 405 type catalyst developed under a classified government contract for the decomposition of hydrazine was the most active. It caused reaction of the dilute hydrogen-oxygen test mixture to occur at -195°C when tested in both the "as prepared" state and after exposure to a hydrogen-steam atmosphere at 1100°C (2012°F) for 30 minutes. After more severe exposure, namely 1200°C (2192°F) for 15 minutes, the Shell 405 catalyst was somewhat deactivated, and, like several other catalysts, gave reaction at about -140°C (-220°F). Of the others, Pt-Ru on "super-pure" alumina and Pt-Ru on zirconia-thoria were the more active.

## SUMMARY

The objective of this program was to develop catalysts of improved activity and thermal stability for the ignition of oxygen-hydrogen mixtures at extremely low temperatures. The feasibility of such ignition at temperatures approaching that of liquid hydrogen had been proven by previous NASA contract studies, but more dependable performance was required.

In initial tests it was quickly discovered that the oxygen-hydrogen reaction could not readily be studied at a constant catalyst temperature below room temperature. The reaction is so highly exothermic that even with 1% oxygen, 3% hydrogen in helium, either the reactor temperature rose uncontrollably until oxygen conversion was complete, or water and ice formation poisoned the catalyst causing the reaction to slow and stop. The technique which was developed to measure catalyst activity employed a rising-temperature reactor to detect onset of reaction. A one gram catalyst sample was heated to 400°C (752°F) in hydrogen for ten minutes, then cooled in hydrogen to -196°C (-320°F). While still cooling with liquid nitrogen a feed of 400 cc/min 3% hydrogen, 1% oxygen, 96% helium was flowed over the catalyst, then one minute later the liquid nitrogen was replaced by a pre-cooled (-196°C) air bath and the whole allowed slowly to warm. The temperature at which reaction began was a measure of catalyst activity. The lower the temperature at which reaction could be detected the more active the catalyst. Thermal stability of the catalyst was tested by subjecting a sample to a hydrogen-steam atmosphere at 1000°C to 1200°C (1832°F to 2192°F) for 15-30 minutes then testing by the standard procedure described above.

Many catalysts were prepared and tested in this way, most attention being given to catalysts of the palladium and platinum group metals since these promised to be most active according to previous literature. Considerable improvement in activity over commercial catalysts previously available was obtained by using high metal contents on various supports. A Shell 405 catalyst (classified) was the most active composition found and gave reaction at the limit of the testing technique, -196°C (-320°F) as prepared and after hydrogen-steam treatment at 1100°C (2012°F) for 30 minutes. Hydrogen-steaming for 15 minutes at 1200°C (2192°F) lowered its activity, however, and reaction was not detected until warmed to -137°C (-215°F). Several high metal content platinum-iridium and platinum-ruthenium catalysts on alumina supports gave reaction at about -140°C (-220°F) as prepared and retained this activity after hydrogen-steam treatment at 1200°C for 15 minutes. By comparison the best commercial catalyst tested, the Engelhard MFSA-4X, gave reaction only on warming above -115°C (-175°F) as received, improved to -125°C after treating at 1100°C, but again gave reaction only above -115°C after hydrogen-steaming 15 minutes at 1200°C.

The results presented in this report demonstrate that catalysts can cause reaction of hydrogen-oxygen gas mixtures at temperatures at least down to that of liquid nitrogen (-196°C). The next step in applying the catalytic ignition concept should involve tests with undiluted gases under practical operating conditions. A range of starting temperatures and pressures should be surveyed, and catalyst stability should be judged from repeated ignitions.

# DEVELOPMENT OF HYDROGEN-OXYGEN CATALYSTS

## Introduction

The reaction of hydrogen with oxygen as a rocket propellant combination offers the advantages of high specific impulse, low combustion temperature, fast burning rate, and good regenerative cooling capability, coupled with ready availability of the non-toxic and non-corrosive reactants. The combination, however, suffers the disadvantage that it is not hypergolic and requires an ignition system. Further, since the hydrogen-oxygen system is used for upper-stage engines, it is required that the ignition system be capable of giving multiple re-starts with high reliability.

Several potential ignition systems were listed in a study contract carried out earlier to consider the feasibility of such systems.[1] Of these, 1) spark igniters, 2) hypergolic additives, and 3) catalytic igniters offered the most promise for obtaining a system capable of giving reliable repeated ignitions. Spark igniters in use at present are not completely satisfactory for repeated ignitions, and are complicated by requiring additional equipment for electrical power generation. The use of hypergolic additives mixed in with the fuel or oxidizer, or both, in reservoir storage would involve only simple equipment and presents an interesting possibility, but has yet to be developed. A catalytic igniter unit would also involve only simple equipment, yet would avoid the dangers inherent with hypergolic mixtures.

The feasibility of catalytic ignition of hydrogen-oxygen mixtures at very low temperatures (near-liquid hydrogen temperatures) has already been shown in other studies[2][3] made earlier under the sponsorship of the National Aeronautics and Space Administration. In that work, commercial catalysts were used and ignition of hydrogen-oxygen mixtures was obtained immediately after liquid hydrogen had flowed through the catalyst bed for several minutes. However, the catalysts available for that study[3] were somewhat unreliable in giving ignition at such low temperatures, and it was considered desirable that improved catalysts be developed specifically for use in hydrogen-oxygen ignition systems. Especially desired were more stable catalysts which would retain restart capability after exposure to "flame" temperatures of 1100-1300°C (2012-2372°F).

This report covers the results obtained in attempts to develop catalysts capable of repeatedly igniting hydrogen-oxygen mixtures at the low temperatures possibly encountered by feeding this combination as liquids. Such conditions could lead to temperatures in the region of -180°C (-290°F) or lower just prior to ignition, yet shortly after ignition the catalyst would be subject to temperatures at least as high as 1000°C (1832°F), and if tolerable even to 1200°C (2192°F) or higher. With this objective, a test method was developed to compare catalyst activities, catalysts were prepared, and activities were determined both before and after exposure to a steam-hydrogen atmosphere at 1000°C-1200°C.

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1) See Bibliography.

## The Probable Phenomena Involved in Catalytic Ignition

In the majority of studies of exothermic catalytic reactions, steady state conditions have been a prime requirement. As a result, very little is known of the phenomena which occur during the period of rapidly rising temperature characteristic of the "runaway reactor" conditions desired in this study.[33] For runaway conditions to exist, the heat evolved on the catalyst due to the reaction must exceed that removed from the catalyst by the incoming cold gases (or liquids) and by cool walls. In general, the processes involved in a successful ignition can be separated into four stages:

i) Adsorption of reactants

ii) Commencement of catalytic reaction

iii) Rapid temperature rise

iv) Homogeneous flame reaction

### i) Adsorption of Reactants

Previous studies on platinum-metal catalysts have suggested greater activity for catalysts cooled and stored in hydrogen rather than in oxygen. If such a procedure is used in the catalytic igniters being considered, then the catalyst surface will be mostly covered with pre-adsorbed hydrogen at the moment the hydrogen-oxygen mixture is admitted to it. Oxygen is adsorbed considerably more strongly on bare platinum metals than is hydrogen, as the data of Table 1 show, but unfortunately there is little information on the heat of adsorption of oxygen onto a hydrogen covered surface. If we assume a heat of adsorption as low as 30 kcal/mole oxygen, this heat liberated on a highly dispersed 25%w platinum catalyst should by itself raise the temperature of the whole catalyst from 90°K (-297°F) to about 250°K (-10°F), according to calculations detailed in the Appendix. Since both the amount of heat liberated and the activity for the reaction are proportional to the amount of active metal available to reactants in a given catalyst volume, catalysts having a well-dispersed, high metal content are desirable.

### ii) Commencement of Reaction

The initial heat of adsorption, even if not as large as calculated, should raise the temperature of the catalyst to a temperature at which the adsorbed hydrogen and oxygen interact at least slowly. Such reaction will generate more heat at the active metal, and if the rate of this heat generation exceeds the rate of loss of heat, then its temperature will rise and the reaction rate will accelerate rapidly. Adsorption of formed water on the support surface can contribute heat also, as discussed later. If the rate of removal of heat exceeds that of generation by adsorption and reaction, then the temperature will fall following the heat of adsorption spike, and no ignition will occur.

Since heat is removed from the catalyst granules by the flowing gases, the active metal crystallites on the outer surfaces and close to the mouths of pores will lose heat more rapidly than those situated deep inside

the pores of the support granules. As a result, it is anticipated that the reaction will be occurring mostly deep in the pores of the catalyst granules during this initial acceleration period.[35] Any feature of the system which increases the rate of cooling of the catalyst granules will, of course, slow the acceleration of the reaction, and may cause it to die out. Feeding the reactants as liquids during this stage will impose severe conditions on the catalyst, for in addition to the low temperature of the incoming feeds, all of the liquid must be evaporated, requiring extra heat for vaporization before the catalyst temperature can start to rise.

iii) Rapid Temperature Rise

As the initial acceleration of the reaction gains momentum, the rate on the more active catalysts quickly becomes so great in the pores that all of the minor reactant is converted before it reaches the center of a catalyst granule, and the reaction becomes diffusion limited. Similarly, as the temperature in the catalyst bed climbs, a condition is quickly reached when all of the minor reactant is converted before reaching the end of the catalyst bed. Once this conditions is reached, the rate of rise of temperature becomes almost constant, depending mostly on the rate at which heat, in the form of the reactants, is fed to the catalyst, and the reaction zone narrows to a very small volume at the inlet of the bed.

At the low temperatures being considered the rate of reaction is extremely sensitive to any small change in temperature. If an activation energy for the hydrogen-oxygen reaction of 10 kcal/mole should pertain, at 90°K (-183°C, -297°F) the rate of reaction would double for a 1.1°C temperature rise, and would increase 10 times for a 3.9°C rise. Even if the activation energy is only 2 kcal/mole, at 90°K the rate would double for a 6°C, and increase about 10 times for a 24°C rise, according to calculations detailed in the Appendix. Similarly, of course, the rate of reaction would halve, and decrease 10 times for the corresponding temperature decreases. Such calculations, though based on very approximate assumptions, do tend to indicate the probable sensitivity of the reaction to temperature in this region, and the great advantages to be gained by feeding the hydrogen and oxygen as gases at as high a temperature as practical to the catalyst during the first few moments of startup.

To aid in achieving such conditions at startup, a small pre-warming bed of low surface area material, inert but having a high heat capacity, would probably be of value if placed just ahead of the catalyst bed. Such a pre-warming bed would serve to retain sufficient heat from previous reactor firings to volatilize the initial liquid feeds, and at the same time aid in mixing the reactants to avoid high temperature zones through the catalyst bed.

iv) Homogeneous Flame Reaction

As the rate of reaction rapidly increases with the rising temperature, the reactants diffuse less into the pores of the granules before reacting. This causes the reaction zone to become confined more and more to the outer layers of each catalyst granule, until finally, at temperatures above about 600°C, the reaction proceeds to completion on only a very thin outer "skin" of the catalyst and in the vapor phase between the granules.

Following this, the reaction temperature is limited only by the composition of the reactant mixture at any practical feed flow rate.

A serious complication to the simple mechanism of ignition outlined by these four stages, however, is poisoning of the catalyst by water vapor, the product of the reaction. If the catalyst is not thoroughly dried, rapid chemisorption of reactants at low temperatures is diminished, with a corresponding loss in the usable heat of adsorption and of the active metal available for reaction. In addition to these direct effects on the catalytic metal, water vapor may also have other indirect effects on the startup. It is known that the heat of adsorption of water vapor on support materials such as alumina is very high,[28] and that the optimum drying temperature to obtain the greatest capacity for subsequent re-adsorption of water is in the range 400-700°C (750-1292°F). Even with catalysts of about 30%w platinum, the surface of a support granule is probably only about 25% covered by metal, and so this bare alumina surface may aid in removing the initially produced water from the active metal. Such an effect may play an important role in the initial stage of the reaction, and could help explain the improvement found in activity on regenerating catalysts at above 300°C before testing.[3]

Table 1. HEATS OF ADSORPTION ON METALS

Ref: G. C. Bond, "Catalysis by Metals", Academic Press, N.Y., pp. 75-84, 1962.
D. O. Hayward and B.M.W. Trapnell, "Chemisorption", Butterworths, pp. 203-214, 1964.

| Metal | Initial Heat of Adsorption, kcal/mole | |
|---|---|---|
| | Hydrogen | Oxygen |
| Ti | - | 236 |
| Cr | 45 | 174 |
| Mn | 17 | 150 |
| Fe | 32 | 136 |
| Co | 24 | 100 |
| Ni | 29-43 | 107-150 |
| Nb | - | 208 |
| Mo | 40 | 172 |
| Rh | 26-28 | 100-120 |
| Pd | 26 | 67 |
| Ta | 38-45 | 212 |
| W | 45,52 | 194 |
| Pt | 28 | 70 |
| Si | - | 210 |
| Ru | 26 | - |
| Ir | 26 | - |

## Literature Review

### The Hydrogen-Oxygen Reaction

In the absence of an active catalyst hydrogen reacts with oxygen mainly at the walls of porcelain or silica vessels at temperatures below 500°C (~930°F). Above this temperature, however, a homogeneous gas phase reaction becomes prominent, and under certain conditions its rate is proportional almost to the cube of the hydrogen partial pressure, and to a power greater than unity of the oxygen partial pressure.[4] The reaction of hydrogen and oxygen to produce water is one of the most highly exothermic reactions known, having a heat of reaction ($-\Delta H$) of 5.78 kcal/mole of hydrogen at -183°C (-297°F). This high heat of reaction, coupled with the fact that the homogeneous gas phase reaction is a chain process having a high temperature coefficient, produces a rapid acceleration of the reaction and temperature rise in the gases. This in turn, depending on the conditions, can lead quickly to propagation of a flame and temperatures in excess of 3000°C (~5500°F) can be obtained. The rate of this reaction acceleration to ignition, and the reliability of ignition under varying mixture ratios, flow rates, etc., increases greatly with temperature. Hence, to obtain rapid and reliable ignition in a rocket engine, part of the hydrogen-oxygen mixture must be heated to a temperature in excess of about 800°C (~1500°F). This fact fixes the lower operating temperature needed of any igniter. The efficiency and reliability of the igniter improves continuously with increasing operating temperature, but the upper temperature for a catalytic igniter is set by the stability of the catalyst. The catalyst temperature is controlled by the mixture ratio - normally fuel rich. A higher upper limit gives more leeway for fluctuations in ratio.

As is well known, the presence of a catalyst in contact with reactants facilitates reaction but does not affect the thermodynamics of the reaction. Although the homogeneous vapor phase reaction of hydrogen with oxygen becomes extremely slow below about 500°C, catalysts have recently been reported which initiate reaction at temperatures below -183°C (-297°F), and reaction is extremely rapid on these catalysts at 0°C.[5] In spite of this great increase in rate over a catalyst, however, the heat liberated by reaction on the catalyst is the same as that of the homogeneous reaction.

Bond[12] observes that the noble metals of group VIII and IB of the Periodic Table are very efficient catalysts for the hydrogen-oxygen reaction at temperatures below 0°C, but in spite of the apparent simplicity of the reaction, the kinetics of the reaction are not well established for these more active metals. Recently, Acres[13] has reported that the rate of the hydrogen-oxygen reaction on thermostated platinum wires at 100°C (212°F) obeyed the relationship

$$\text{Rate} = kP_{O_2} \cdot P_{H_2}^{-1}$$

when hydrogen was in excess and was retarded by water vapor, while previous workers have reported rate dependences over platinum of

$$\text{Rate} = kP_{O_2}^{x}, P_{H_2}^{y} ,$$

where x varies between 0 $\longrightarrow$ 1 and y from -1 to +1.

The kinetics of the reaction change for temperatures much above room temperature. On silver powder, for example, the rate of reaction of hydrogen with oxygen was proportional to $P_{H_2}^{0.63}$ at 100°C, and $P_{H_2}^{0.52}$ at 110°C, and was independent of the oxygen concentration but retarded by the product water vapor.[14] In this temperature range oxygen is strongly adsorbed on silver while hydrogen is only weakly adsorbed. Above about 650°C (1200°F), however, the reaction order becomes zero in hydrogen and first order in oxygen suggesting that the hydrogen chemisorption has become strong compared to that of the oxygen.[15]

The activation energy for this reaction is also not well established. Reliable values of the activation energy for the hydrogen-oxygen reaction on platinum (determined from the temperature variation of the rate of reaction) are very difficult to determine, for the extremely high heat of reaction makes isothermal conditions difficult to maintain, and inhibition by traces of product water causes further uncertainty. For reaction on platinum, an activation energy of 17 kcal/mole below 225°C (450°F) has been reported,[17] but surface temperatures were ill-defined. In other work an activation energy on bulk platinum of 11 kcal/mole was obtained at temperatures between 100 and 200°C,[18] while values varying between 9 kcal/mole and 19.5 kcal/mole have been reported on Pd-Ag alloys.[24] These values would appear large in view of the high rates of reaction observed on high surface area catalysts of these metals at low temperatures. The rates of reaction observed in this study suggest that at temperatures below about -50°C (-58°F) the activation energy for reaction on a platinum-rhodium catalyst cannot be above 5 kcal/mole and is probably about 2 kcal/mole (see Appendix). A similarly low activation energy value of 1.8 kcal/mole has been reported for the hydrogen-oxygen reaction on bulk palladium in the temperature range 230-380°C.[19]

Little data exists in the literature on the reaction of hydrogen and oxygen at temperatures much below 0°C, except that obtained under previous NASA contracts.[5] In this temperature region, steady-state operation is impossible since product water is not removed from the catalyst, and the catalyst is quickly poisoned. Ponec[20] has studied the changes in electrical conductivity of evaporated films of several metals at temperatures down to -196°C (-320°F) during the separate adsorption of oxygen and of hydrogen, and also of one of these gases onto a surface on which the other was already adsorbed. From these results he concluded that both hydrogen and oxygen adsorb on the noble metals Pt, Pd, and Rh at -196°C to give species which can interact, and at 0°C the products of reaction desorb from the metal surface. On other transition metals, oxygen did not react at -196°C with hydrogen subsequently adsorbed, and did not react on Fe, Mo, or Mn even at 0°C. However, in spite of this lack of reaction on low area metal films at low temperatures, the work at Rocketdyne[5] has shown that rapid reaction at low temperatures is possible on practical catalysts of the more active metals.

The order of decreasing activity for the hydrogen-oxygen reaction at low temperature found by Ponec was Pt, Pd, Rh > Ni > Mo, Fe, Mn, Cu, and is generally in good agreement with the activity of these metals for the $H_2$-$D_2$ exchange at similar temperatures, and for the hydrogen-oxygen and various other reactions involving hydrogen or oxygen at higher temperatures.[7][21] In general, the most active metals are those which chemisorb

both oxygen and hydrogen, but do so only weakly. Comparing the heats of adsorption shown by Figure 1 and Table 1, it is obvious that the metals which most closely meet both of these requirements are the noble metals of group VIII of the Periodic Table, with the other three metals of group VIII, Fe, Co, and Ni, following.

The relative activities of the noble metals and their 1:1 by weight ratio binary alloys on an asbestos fiber support were studied previously by a simple technique at room temperature.[22] The results, in bar form, are in part reproduced in Figure 2. The catalysts were evacuated at about 500-600°C (~1000-1100°F) and cooled in vacuo before pre-adsorbing the gas listed, then a stoichiometric hydrogen-oxygen mixture diluted with nitrogen, hydrogen, or oxygen was passed over the catalyst. With oxygen pre-adsorption, iridium was the most active pure metal and Pd-Rh or Pt-Os the more active metal alloys. With hydrogen pre-adsorbed, osmium was the most active metal, and Pt-Rh and Ru-Rh the more active alloys. Later a similar study of Fe, Co, and Ni metals and their binary alloys with the Pt and Pd series metals was made, but none of these proved to be more active than a pure platinum catalyst.[23] Similarly, addition of varying amounts of silver to palladium gave alloys all of which were less active than pure palladium as catalysts for the hydrogen-oxygen reaction.[24]

In general, oxide catalysts are considerably less active for the hydrogen-oxygen reaction, as the high temperature necessary for any appreciable reaction rate indicates (see Table 2).

Table 2. ACTIVITY OF OXIDE CATALYSTS FOR THE HYDROGEN-OXYGEN REACTION

From G. K. Boreskov, "Catalysis and Chemical Kinetics", Academic Press, Inc., New York, 1964

| Catalyst | 150°C Reaction Rate, Moles $H_2$/hr $cm^2$ | Apparent Activation Energy, kcal/mole | Pre-exponential Constant |
|---|---|---|---|
| $TiO_2$ | $6.3 \times 10^{-16}$ | 21 | 15 |
| $V_2O_5$ | $1.8 \times 10^{-13}$ | 18 | 110 |
| $Cr_2O_3$ | $4.8 \times 10^{-13}$ | 18 | 6,000 |
| $MnO_2$ | $7.4 \times 10^{-10}$ | 14 | 80,000 |
| $Fe_2O_3$ | $1.4 \times 10^{-11}$ | 15 | 13 |
| $Co_3O_4$ | $6.5 \times 10^{-9}$ | 11 | 30,000 |
| NiO | $2.6 \times 10^{-10}$ | 8 | 30 |
| CuO | $1.6 \times 10^{-9}$ | 13 | 21,000 |
| ZnO | $1.3 \times 10^{-13}$ | 24 | 21,000 |

## High Temperature Stability of Catalysts

As mentioned earlier, the operating temperature of the catalyst required to ignite large rocket engines using hydrogen-oxygen mixtures as propellant is at least 800°C (1500°F), and higher temperatures in the region of 1100°C (2012°F), or even 1370°C (~2500°F) would be preferred. Further, multiple ignition capability is also desired, so the catalyst must retain sufficient activity after this severe high temperature treatment to re-ignite the hydrogen-oxygen mixture at a low temperature.

 Figures 1 and 2 follow

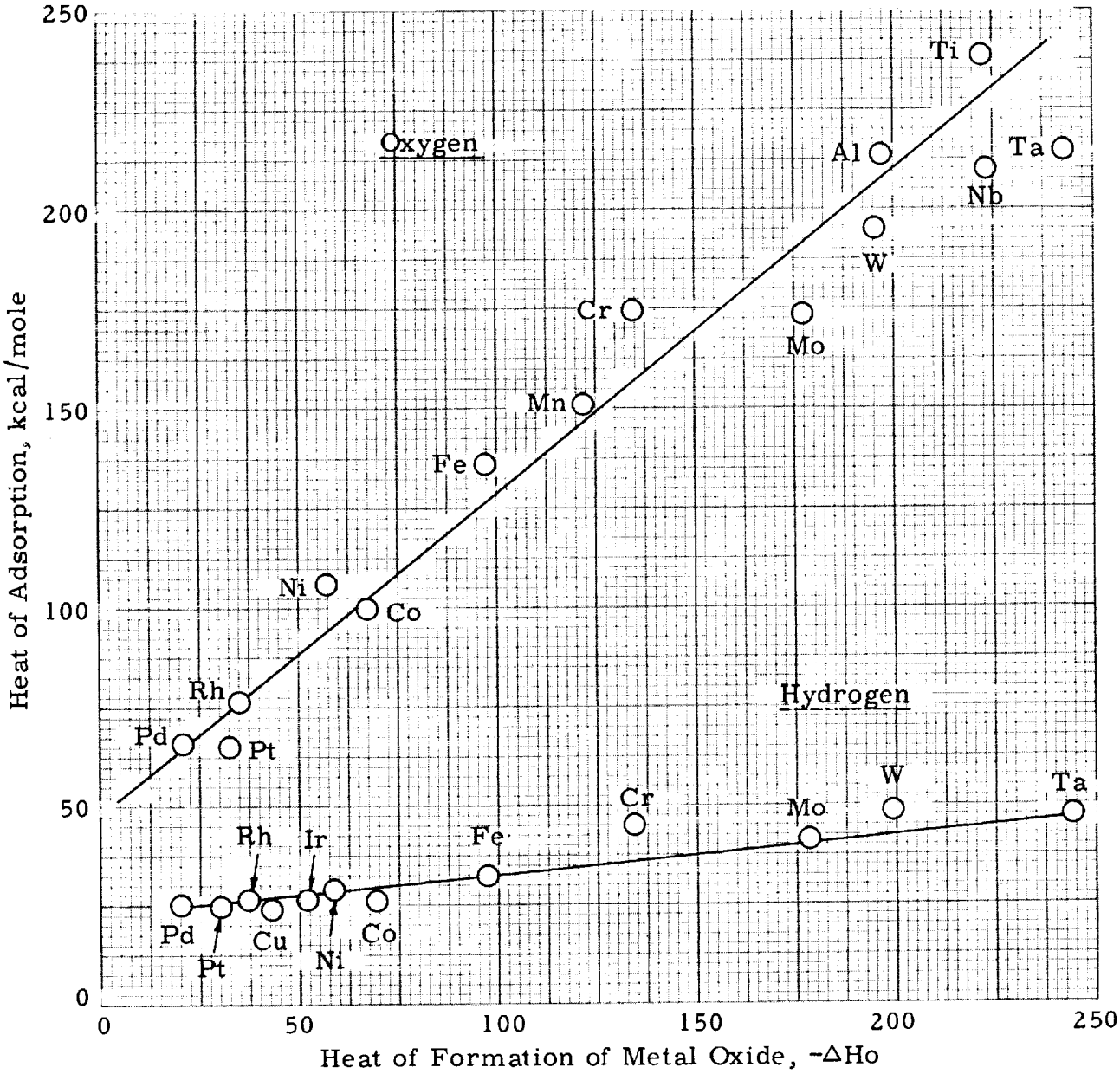


Figure 1. HEATS OF ADSORPTION OF VARIOUS GASES ON METALS

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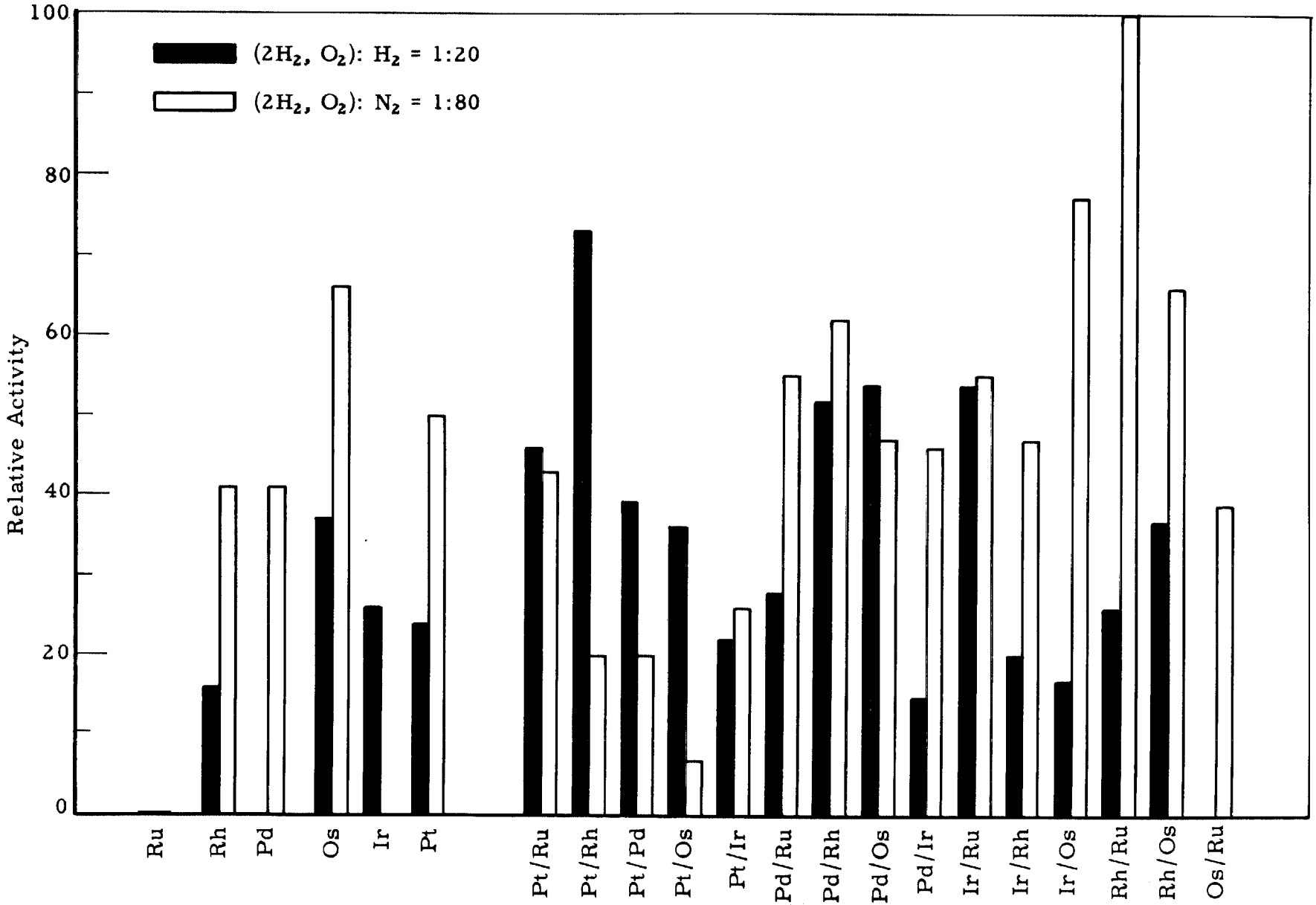


Figure 2. RELATIVE ACTIVITIES OF CATALYSTS OF Pt AND Pd METALS AND THEIR BINARY ALLOYS AFTER HYDROGEN PRETREATMENT[22)]

Such high temperature operation obviously requires the active metal to have a high melting point. Values are listed for the possible catalytic metals in Table 3. However, bulk melting is not the sole criterion for stability of catalysts to high temperature treatment. For a catalytic metal to be highly active for a reaction, almost every atom of the metal must be exposed to the reacting gases. This can be achieved in a practical manner only by depositing the active metal on a porous support material of high surface area per unit volume. On such a support the active metal is deposited as small isolated crystallites, and the smaller these crystallites are the higher the percentage of exposed metal atoms, assuming that the deposited metal does not interact chemically with the support material. When such a catalyst is subjected to high temperature treatment, the active metal becomes more mobile and transfer can occur, probably through the vapor phase, from one crystallite to another. In such a process the larger crystallites tend to grow even larger at the expense of the smaller ones, which tend to disappear. The net effect of this process is to decrease the surface area of the active metal available to catalyze the reaction, and the catalyst loses activity. Hence, the thermal stability of a catalyst depends not only on the melting point of the active metal, but also upon its volatility, and that of any of the compounds it is likely to form by reaction with the support or gas atmosphere. As a result of this, the gas atmosphere in contact with the catalyst at high temperatures is critical. For example, an unstable platinum oxide is the main species through which platinum transport and crystallite growth occurs on platinum catalysts subjected to high temperatures in atmospheres containing oxygen or water vapor,[26] and sintering in these gases occurs much more rapidly than in hydrogen or vacuum.

Although vapor transport and crystallite growth of the active metal is a critical consideration for catalyst stability, the high temperatures involved also test the limits of stability of all known high surface area support materials. High surface area supports are usually pellets or granules which are made up of extremely small particles joined together at their points of contact. The pores of the support then, are the channels between these minute particles. Here again, surface area is a function of particle size, and loss of surface area consists mostly of particle growth at the expense of the smaller particles. Also, surface stability depends not only on the materials melting point but on its volatility and that of the compounds it forms with the gas atmosphere. Silica, for example, is extremely susceptible to water vapor,[25] while carbon, one of the highest melting materials (see Table 4), is rapidly oxidized to carbon monoxide by steam at the operating temperatures here considered. A further disadvantage of carbon as a catalyst support is that carbon monoxide is known to strongly poison the activity of noble metals for most reactions.

Oxides are by far the more commonly used catalyst support materials, and of these alumina is probably the most common. Alumina exists in several different crystalline modifications.[27] The high temperature stable form, $\alpha$-alumina, melts about 2030°C (3686°F), but is not suitable as a support for high activity catalysts of the type desired in this work due to its low surface area. The high surface area alumina modifications, $\eta$- and $\alpha$-aluminas, tend to recrystallize to the $\alpha$-form at temperatures above about 700°C (1292°F), and this process becomes fairly rapid above 1000°C (1832°F). Other possibly suitable oxide supports, the high surface area forms of zirconia and thoria, also undergo phase changes with accompanying loss in surface area at

Table 3. MELTING POINTS OF METALS

| Metal | Melting Point, °C | Metal | Melting Point, °C |
|---|---|---|---|
| Ti | 1812 | Fe | 1535 |
| V | 1730 | Co | 1493 |
| Cr | 1550 | Ni | 1455 |
| Mn | 1535 | Cu | 1083 |
| Zr | 1852 | Ag | 861 |
| Nb | 2487 | Au | 1063 |
| Mo | 2610 | Pd | 1555 |
| Th | 1845 | Pt | 1770 |
| Hf | 2330 | Rh | 1960 |
| Ta | 2977 | Ir | 2443 |
| W | 3380 | Ru | 2506 |
| Re | 3147 | Os | 2700 |

Table 4. MELTING POINTS OF SUPPORT MATERIALS

| Material | Melting Point, °C | Absolute Density, g/cc | Notes |
|---|---|---|---|
| $ThO_2$ | 3000 | 9.69 | High density. |
| $UO_2$ | 2820 | 10.96 | High density. |
| $ZrO_2$ | 2700 | 5.56 | Phase change at 1000°C. |
| CaO | 2600 | 3.23 | Hygroscopic. |
| BeO | 2530 | 3.03 | Surface area loss ~1000°C. |
| MgO | 2500 | 3.65 | Surface area loss ~1200°C. |
| SrO | 2450 | 4.70 | Hygroscopic. |
| $Y_2O_3$ | 2420 | 4.84 | |
| $La_2O_3$ | 2320 | 6.51 | |
| $HfO_2$ | 2800 | 9.68 | High density. |
| $Al_2O_3$ | 2030 | 3.97 | Low surface area above ~1200°C. |
| BaO | 1923 | 5.72 | Hygroscopic. |
| $MgO-Al_2O_3$ | 2135 | 3.6 | |
| $3Al_2O_3,2SiO_2$ (Mullite) | 1800 | | |
| Carbon | >3500 | 1.8-2.1 | Unstable at high temp in $H_2O$ or $O_2$. |
| SiC | >2700 | 3.17 | Unstable at high temp in $H_2O$ or $O_2$. |
| $W_2C$ | 2880 | 16.1 | Very high density. |
| WC | 2780 | 15.7 | Very high density. |
| TiC | 3180 | 4.25 | |

temperatures about 1000°C. Some improvement in high temperature stability of the high surface area forms has been obtained by purification to remove sodium and other ions, and also by addition of small amounts of stabilizing oxides, such as calcium oxide to zirconia. At present, however, no suitable support material is known which retains a high surface area for any extended period at temperatures above 1100°C (2013°F).

## Adsorption of Hydrogen and Oxygen on Solids

For reaction between oxygen and hydrogen to occur at any appreciable rate, at least one of them must be activated. Activation can occur in several ways by supplying energy in some form, or by the action of a catalyst. In all cases, however, the bonds between the atoms in the parent molecules are weakened, or completely broken, so that new bonds between the oxygen and hydrogen can more readily be formed. A catalyst facilitates reaction by allowing it to proceed via several easier reaction steps, each involving smaller energy exchanges, rather than via the few difficult reaction steps involving large energy transfers that are required for direct reaction. For activation to occur on a catalyst surface, at least one, and probably both, of the reactant species must be adsorbed (chemisorbed) strongly enough so that the bond between the atoms of the original molecule is weakened or broken. The fundamental principles involved in such activation have been the subject of many discussions,[6] and it is generally agreed that for the surface to function as a catalyst, the interaction of the reactant molecules with the surface needs to be strong enough to weaken the original bonds, but not so strong that the activated species cannot form new bonds to the other reactant species.

The heat liberated when a gas adsorbs on a surface is a good indication of the extent of the interaction which is occurring, and many studies of this type have been made. Accepted values[11] for the initial heats of adsorption of hydrogen and oxygen on various metals are shown in Figure 1, which shows that more heat is liberated per mole on adsorption of oxygen on metals than on adsorption of hydrogen.

Various attempts to correlate the activity of a metal for chemisorption of these gases with its physical properties have been made, but none has been entirely successful.[7] In general, hydrogen chemisorption appears to depend strongly on the d-bond character of the metal, whereas the adsorption of oxygen is universal on all metals except gold, tending to form largely ionic bonds with the s and p bonds of non-transition metals, and more covalent bonds with the d-bonds of the transition metals.[10] Sachtler[11] used the correlation as in Figure 1 to show that the heats of adsorption varied almost linearly with the heat of formation of the metal oxide, and decreased in the order $O_2 > C_2H_4 > N_2 > NH_3 > H_2$ on many metals.

Beeck,[8] on studying the heats of adsorption on evaporated metal films, concluded that the activation energy for chemisorption of hydrogen on metals such as nickel, iron, and tungsten was extremely small, since the rate of hydrogen chemisorption was so very fast at about 0°C. Further, since this activation energy is so small, the heat of adsorption should vary only slightly with temperature, and chemisorption of hydrogen should readily occur on certain metals even at liquid hydrogen temperature (-253°C; -423°F). However, differences in the rate of adsorption of hydrogen on different metals can be expected to appear at these very low temperatures. At 0°C the heat of adsorption

decreases with the amount of hydrogen adsorbed, usually falling quite rapidly as fractional coverage of the surface, $\theta$, approaches 1. Beeck[8] considered this to indicate that the adsorbed atoms of hydrogen are mobile on the metal surface and are able to migrate to the sites of highest energy, or at least able to move away from one another to decrease the repulsive interaction between atoms adsorbed on neighboring sites. On an evaporated iron film at 23°C an initial heat of adsorption of hydrogen of 32 kcal/mole was observed, which slowly decreased to about 10 kcal/mole at $\theta \approx 1.0$.[8] At -183°C, however, the heat of adsorption was about 28 kcal/mole and did not decrease with increasing coverage until $\theta \approx 1$ was reached, above which the heat of adsorption decreased rapidly. Similar results were obtained by Aston[9] for adsorption of hydrogen on platinum powder, and Beeck's interpretation of this data would suggest that hydrogen adsorbed on these metals at -183°C (-297°F) is no longer mobile across the surface.

Oxygen adsorbs considerably more strongly than does hydrogen on transition metals, as the values obtained by Trapnell[16] and Bond[12] listed in Table 1 indicate. At room temperature, the heat of adsorption of oxygen on the noble metals rhodium, palladium and platinum gradually decreased with increasing oxygen coverage of the surface, which would suggest that the adsorbed oxygen was mobile over the surface. The heats of adsorption on other transition metals were higher than on the noble metals and remained almost constant with increasing oxygen adsorption to fractional coverages greater than unity. This suggests that oxide formation was occurring and that adsorbed oxygen is not mobile on these metals.

Both oxygen and hydrogen chemisorb rapidly at -195°C onto a clean platinum surface formed by baking for a few hours in high vacuum ($10^{-8}$ torr).[20] Chemisorption of hydrogen and oxygen at this low temperature onto a platinum surface previously exposed to the other gas was also detected. Evidence from the present study however, suggests that oxygen chemisorbs only slowly onto a hydrogen covered platinum surface at -195°C, and takes longer than one minute to reach completion in 0.04 atm oxygen.

## Experimental Techniques

### Isothermal Reaction Studies

Initially an attempt to develop a satisfactory technique for measuring the activity of catalysts for the hydrogen-oxygen reaction at extremely low temperatures was made using a constant temperature, steady flow system. A dilute feed gas containing 3% hydrogen, 1% oxygen, 1% argon, and 95% helium by volume was flowed at 400 cc/min over 1 cc of the catalyst cooled in a constant temperature bath, and the effluent gases were analyzed directly by bleeding a small stream to a mass spectrometer. At reactor temperatures down to -131°C (-203°F) the oxygen to argon ratio in the effluent gases could readily be compared with that of the feed gases to determine the oxygen conversion. At -196°C (-320°F), however, physical adsorption of both argon and oxygen occurred on the high surface area catalysts to such an extent that adsorption was still continuing after 10 minutes on samples previously out-gassed in helium or hydrogen at 300°C (572°F) for 30 minutes. Much of this argon and oxygen adsorbed at -196°C was readily desorbed at this same temperature in pure helium. Approximately 18 cc of oxygen adsorbed onto 1 cc of a 2.5%w Pt, 2.5%w Rh on alumina catalyst (9418-5) at -196°C.

As the data of Table 5 indicate, no reaction was detected on the catalysts at -196°C. Two catalysts showed some activity at -131°C (203°F), but when reaction occurred, the catalyst temperature rose rapidly and isothermal reaction conditions were not maintained. Steady state operation of the reactor could be attained only under those conditions which gave complete oxygen conversion or no reaction. When incomplete oxygen conversion was obtained, or when the temperature did not rise above about 0°C, the temperature and oxygen conversion passed through a maximum, then gradually declined. In all such cases ice was deposited on the walls of the reactor and in between the catalyst granules.

In a further attempt to obtain isothermal activity data, the mixed reactants were fed in the form of a small pulse carried over the catalyst by a steady helium stream. This technique greatly limited the heat liberated at the catalyst on reaction of the hydrogen-oxygen fed, but the temperature of the catalyst still rose several degrees above that of the constant temperature bath. Moreover, physical- and chemisorption of the oxygen onto the catalyst complicated the determination of conversion at the low temperatures necessary to obtain less than complete oxygen conversion. A pulse technique could probably be developed to compare the activity of catalysts, but it would be necessary to use the hydrogen conversion or heat release to measure the extent of reaction.

## The Rising Temperature Reactor

The rising temperature technique finally adopted provided a simple and rapid means of comparing catalytic activity for the hydrogen-oxygen reaction. Details of the apparatus and technique used are given in the Appendix. Briefly, the catalyst sample (1 cc of 20-30 mesh granules or 2 cc of 1/8 inch pellets) was loaded into a Pyrex glass reactor (Figure 3) and the thermocouples in a central thermowell 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 minutes, the reactor was cooled in this mixture to liquid nitrogen temperature (-196°C, -320°F). The feed of 400 cc/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 one minute later the liquid nitrogen bath was replaced by a cold air bath 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, and although a time lag must exist between the start of reaction and its detection at the central thermocouple, temperature differences between the bulk catalyst and the thermocouple were probably small at that instant. 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.

In order to bring catalysts to a definite state, each catalyst was given the standardized pretreatment described above with the object of drying and reducing it without sintering. The reproducibility of this test procedure is shown by the data of Table 6, which lists repeated tests of catalysts of varying activity and including a "reference preparation" catalyst over a period of several months from December through June. Storage in a screw-capped bottle, repeatedly opened to the air without any special precautions over this period, had negligible effect on the catalytic activity. The cause

 Figure 3 follows

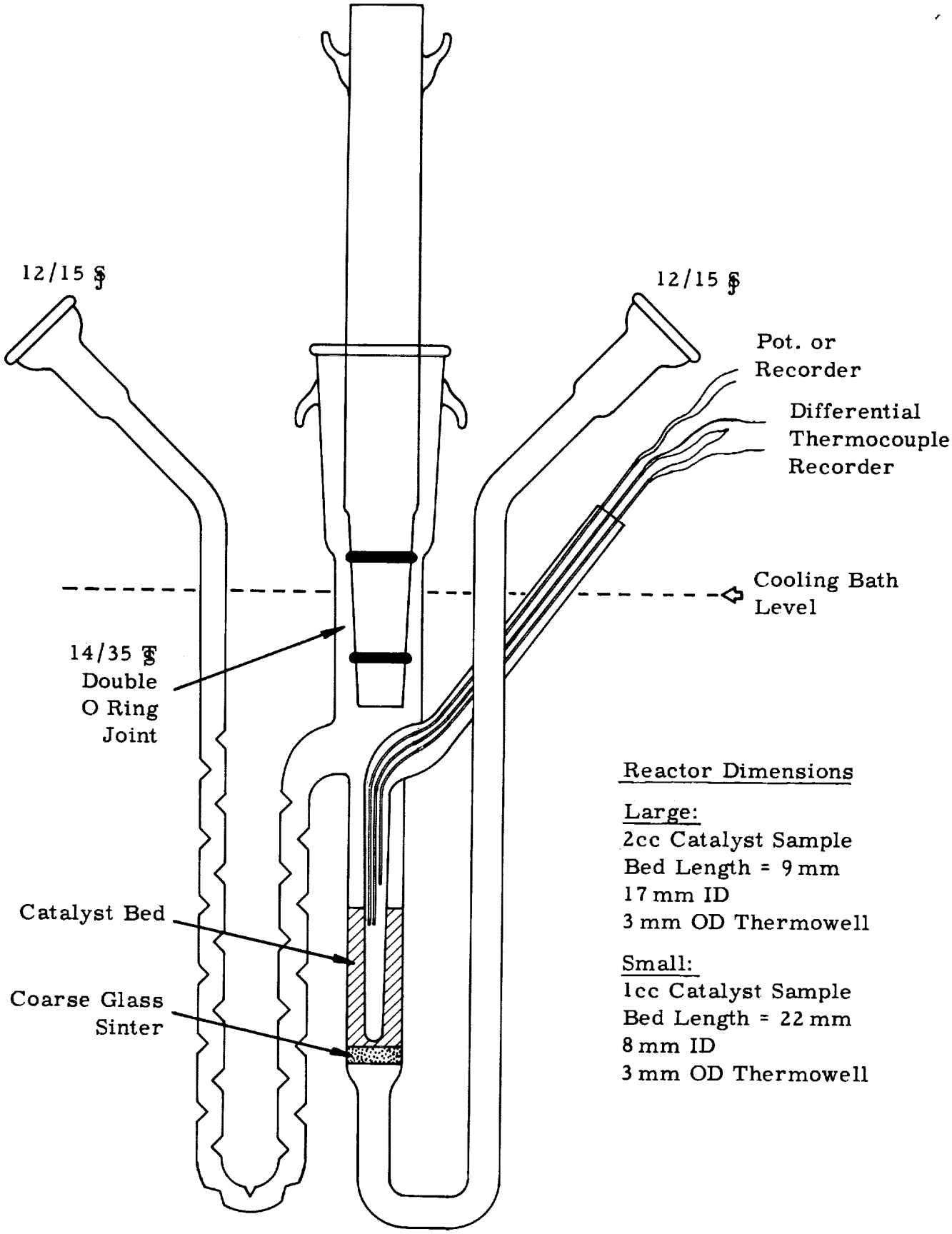


Figure 3. STANDARD TEST REACTOR DESIGN

Table 5. ATTEMPTED ISOTHERMAL CATALYST EVALUATION

Feed Gases: 3% $H_2$; 1% $O_2$; 1% Ar by volume in helium, 400 cc/min
Catalyst: 1 cc, 20-30 mesh (except MFSA, which passed 10 mesh after crushing)

| Catalyst[c] (Fresh for Each Entry) | Wt, g | Pretreatment | | | | $O_2$ Conversion at, % | | |
|---|---|---|---|---|---|---|---|---|
| | | Gas | Min | °C | Cooled in | -78°C[b] | -131°C | -196°C |
| 9418- 5 | 0.74 | $HeH_2$[a] | 10 | 25 | | 77 | - | 0 |
| 9418- 5 | 0.72 | $H_2$ | 20 | 300 | $HeH_2$ | 98 | - | - |
| | | $HeH_2$ | 20 | 300 | $HeH_2$ | - | 2 | 0 |
| | | He | 20 | 300 | He | 92 | 2 | - |
| 9414- 65C | 0.49 | $H_2$ | 20 | 300 | $HeH_2$ | 0 | - | - |
| | | He | 20 | 300 | He | 16 | - | - |
| | | $HeO_2H_2$[a] | 10 | ~100 | He | 6 | - | - |
| 9223-118E | 1.02 | $H_2$ | 20 | 300 | $HeH_2$ | 100 | - | - |
| | | He | 20 | 300 | He | - | 21 | - |
| | | $HeH_2$ | 20 | 300 | $HeH_2$ | - | 70 | 0 |
| | | $HeO_2$[a] | 20 | 300 | $HeO_2$ | - | 0 | - |

a) $HeH_2$: 4% hydrogen in helium (volume);
$HeO_2$: 4% $O_2$, 4% Ar in helium;
$HeO_2H_2$: feed gas as above.
b) Temperatures are bath temperatures. Where reaction occurred, the temperature rose to about 30°C above bath at 70% conversion.
c) See Tables 6 and 10 for catalyst compositions.

Table 6. REPRODUCIBILITY OF RISING TEMPERATURE DATA

1 cc catalyst sample in small reactors except as noted.
Feed: 400 cc/min of 3% $H_2$, 1% $O_2$ in He.

| Catalyst | | Test | | Activity Detected, °C[a] |
|---|---|---|---|---|
| No. 9418- | Composition, %w | No. 9414- | Date | |
| 11A | 2.2% Pt, 1.2% Rh/$ZrO_2$, $SiO_2$ | 85-06 | 12- 9 | (-122) |
| " | " " " " " | 88-02 | 12-10 | (-123) |
| 9E | 2.2% Ir, 1.2% Rh/Alumina | 83-07 | 12- 8 | (+13) |
| " | " " " " " | 88-01 | 12-10 | (+7) |
| 9F | 2.2% Pt, 1.2% Rh/Alumina | 81-02 | 12- 7 | (-107) |
| " | " " " " " | 111-05 | 12-31 | (-106) |
| 5 | 2.5% Pt, 2.1% Rh/Alumina | 79-01 | 12- 7 | (-110) |
| " | " " " " " | 88-03 | 12-10 | (-109) |
| " | " " " " " | 104-01 | 12-28 | (-105) |
| " | " " " " " | 108-05 | 12-30 | (-110) |
| " | " " " " " | 123-01 | 1-27 | -125 (-106)[c] |
| " | " " " " " | 134-01 | 2-14 | -109 |
| " | " " " " " | 150-01 | 3-29 | -107 |
| " | " " " " " | 153-01 | 3-31 | -111 |
| " | " " " " " | 164-01 | 4-12 | -100 |
| " | " " " " " | 182-01 | 5- 2 | -109 |
| " | " " " " " | 200-01 | 6- 6 | -107 |
| 5[b] | " " " " " | 90-01 | 12-13 | (-116) |
| " | " " " " " | 184-01 | 5- 3 | -120 |

a) The temperature at which activity first detected. The bracketed data is that obtained using less sensitive single thermocouple, the remainder using differential thermocouples (see apparatus description in Appendix).
b) 2 cc Sample in large reactor. See Figure 3.
c) See text.

of the anomalously high activity (low temperature activity) observed on one occasion for the 9418-5 catalyst is not known. Activity in this case was detected only by the more sensitive (10X) differential couple and reaction acceleration was slow until the more usual "activity temperature" was reached.

The data of Table 6 suggest that activity could be detetected at temperatures approximately 10°C lower in the larger reactor with 9418-5 catalyst than in the smaller reactor. Data that were obtained in the larger reactor have not been corrected, and this possible difference between reactors should be given consideration when comparing data.

In order to determine if sample size was critical, several tests were made of the same catalyst with different sample sizes in the small reactor. These results are shown in Table 7. In preliminary testing it was observed that reaction always seemed to start near the top of the catalyst bed, and so in all routine tests the detecting thermocouple was located in the central thermowell at a level about 2 mm below the top of the 20-30 mesh bed. In Table 7, however, a result is shown in which the thermocouple was placed at a level about 6 mm below the top of the bed. These data clearly show that neither catalyst bed size nor exact positioning of the thermocouple in a given reactor are critical. The difference between the large and small reactors is probably due to their different heat exchanging characteristics.

## High Temperature Stability Testing

As mentioned earlier, the higher the operating temperature attained in the catalytic igniter, the more efficient and reliable it would be for igniting the main engine. Since the hydrogen-oxygen flame temperature can exceed 3000°C (~5500°F), it is the stability of the catalyst which determines the upper limit on the operating temperature, and the hydrogen-oxygen ratio of the feed to the igniter has to be accurately controlled so that this limit is not exceeded and the catalyst destroyed.

In order to determine the stability of the various catalyst preparations, each catalyst was subjected for a given time at temperatures above 1000°C (1832°F) to hydrogen-steam atmosphere similar to that resulting from reaction of a hydrogen-rich $H_2$-$O_2$ mixture. The temperatures at which these treatments were made are listed in the catalyst activity data in the tables which follow. Further details on the steam-hydrogen treatment and apparatus are given in the Appendix.

In actual practice the maximum temperature as determined by the hydrogen-oxygen ratio of the feed to the igniter will be experienced only by the catalyst in the burning zone of the reactor. The catalyst downstream of this zone will experience somewhat lower temperatures. At these high temperatures platinum or platinum alloy wires are very efficient catalysts for the hydrogen-oxygen reaction, and are far more stable than the high activity catalysts necessary for the low temperature reaction. Thus it may be advantageous for catalyst stability to have a platinum wire screen some distance ahead of the catalyst bed, with some provision for heat conduction forward from the bed to the screen. As high temperatures are approached in the catalyst bed, such an arrangement might serve to move the burning zone forward to the wire screen and give some protection to the catalyst.

Table 7. CATALYST BED LENGTH VARIATION

Catalyst: 9418-5; 2.5%w Pt, 2.1%w Rh/RA-1 $Al_2O_3$ (20-30 mesh)
Reactor: Pyrex glass; 8 mm ID with ~3 mm ID thermowell

| Catalyst Bed | | Activity Detected, °C |
|---|---|---|
| Length, mm[a)] | Volume, cc | |
| 45 | 2.0 | -97 |
| 22 | 1.0 | -105 |
| 12 | 0.5 | -104 |
| 5 | 0.2 | -103 |
| 22 | 1.0 | -103 |
| 22[b)] | 1.0 | -102 |

a) Thermocouple ~2 mm below top of catalyst bed except as in footnote (b).
b) Thermocouple ~6 mm below top of catalyst bed.

## Effect of Feed Composition and Flow Rate on Catalyst Activity

As previously mentioned, platinum metal catalysts readily adsorb from the atmosphere water vapor, oxygen and other gases which tend to decrease their activity. Most of these gases are desorbed on heating in vacuum or hydrogen, so initial tests were made of the effect of varying pretreatments of this type on activity. Catalyst activity improved continuously on heating to successively higher temperatures for 10 minutes in 4% hydrogen in helium, and cooling in this gas to liquid nitrogen temperature (-196°C) for testing, but the rate of improvement slowed at about 400°C (750°F), and this pretreatment temperature was made "standard". Higher temperatures were not used for fear of sintering the catalyst.

The effects of contacting the catalyst with various gas atmospheres during this heating and the following cooling periods are shown in Table 8. Pretreatments in an atmosphere containing excess hydrogen at or above 200°C (390°F), and cooling in hydrogen led to the greatest activity of the Pt-Rh/$Al_2O_3$ catalyst (9418-5). Heating and cooling in helium gave a less active catalyst, while heating in 4% oxygen in helium at about 400°C gave still lower activity. However, cooling in 4% oxygen in helium from 30°C to -196°C, following heating and cooling to 30°C in hydrogen, had no deactivating effect on the catalyst. It would appear that high temperature reduction in hydrogen is needed with these catalysts to obtain high activity, and such pretreatment was given to each catalyst sample before testing to eliminate any reversible activity variations that might have occurred on storage.

Increasing the reactant concentration to as high as 38% $H_2$, 12.5% oxygen by volume in helium gave some improvement (lowering) in the temperature (Table 9). The higher reactant concentrations also caused the acceleration of the temperature rise to be much greater than with the lower reactant concentrations as could be expected from the higher rate of input of fuel to the reactor.

Similarly, doubling the feed flowrate to the reactor caused the rate of rise of temperature when reaction started to be more rapid, but had little, if any, effect on the reaction detection temperature.

Varying the $H_2$:$O_2$ ratio in the feed had little effect on the temperature at which reaction could be detected, as the data of Table 9 indicate. The apparent improved activity at low oxygen ratio needs to be confirmed.

Table 8. CATALYST PRETREATMENT VARIED

Catalyst: 0.5 g (0.8 cc); 9418-5; 2.5%w Pt, 2.1%w Rh/Alumina
Feed: 400 cc/min; He, 3% $H_2$, 1% $O_2$ (volume)

| Test No. 9414- | Catalyst Pretreatment | | Activity Detected, Temp, °C |
|---|---|---|---|
| | Heating | Cooling Atmos to -195°C | |
| 76-03 | He, $H_2$, $O_2$ feed, 5 min to approximately 200°C | He, 4% $H_2$ | -112 |
| -04 | He, 4% $H_2$, 10 min to 380°C | He, 4% $H_2$ | -111 |
| -05 | He, 10 min to 380°C | He | -94 |
| -06 | He, 4% $O_2$, 10 min to 380°C | He, 4% $O_2$ | -54 |
| -07 | Repeat of 76-04 | He, 4% $H_2$ | -108 |
| -08 | 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 |
| 77-04 | He 4% $H_2$, 10 min to 380°C | He, 4% $H_2$ | -103 |
| -05 | He, 10 min to 380°C | He to 35°C; He, 4% $H_2$ to -195°C | -92 |
| -06 | He, 50% $H_2$, 10 min to 380°C | He, 50% $H_2$ | -103 |

Table 9. VARIATION OF FEED FLOW RATE AND COMPOSITION

Standard Catalyst Pretreatment:
10 min in He, 50%v $H_2$ at 400 cc/min to ~400°C (752°F), then cooled in He, 50% $H_2$ to -196°C (-320°F)

| Catalyst No. 9418- | Feed Gases, $H_2$, $O_2$, He | | | Activity, °C | | $\Delta t$, d) sec |
|---|---|---|---|---|---|---|
| | $H_2$, %v | $O_2$, %v | Total Flow, cc/min | Detected | Maximum Attained | |
| 5 a) | 3 | 1 | 400 | -109 | -89 | 38 |
| 5 b) | 3 | 1 | 800 | -107 | -85 | 44 |
| 5 b) | 2.7 | 1.4 | 400 | -108 | -89 | 42 |
| 5 c) | 2 | 2 | 400 | -108 | -93 | 28 |
| 5 c) | 3 | 1 | 400 | -110 | -95 | 27 |
| 5 c) | 1.5 | 0.5 | 400 | -108 | -91 | 37 |
| 5 c) | 17 | 3 | 875 | -108 | -98 | 2 |
| 5 c) | 32 | 5 | 950 | -112 | -110 | ~1 |
| 5 c) | 38 | 12.5 | 800 | -112 | -111 | < 1 |
| 5 b) | 3 | 1 | 400 | -113 | -87 | 38 |
| 5 b) | 3.5 | 0.5 | 400 | -117 | -95 | 60 |
| 5 b) | 3 | 1 | 400 | -113 | -93 | 51 |

a) Fresh catalyst load, 1 cc.
b) Same catalyst load as used in previous test (data of line above) and given standard pretreatment between each test.
c) As in footnote (b), but with 1 cc of 10-20 mesh glass chips above catalyst as flame arrestor bed.
d) Time from detection to first attaining maximum rate of temperature rise.

## Activity and Stability of Catalysts

### More Active Catalysts

Data on the more active catalysts tested in this program are listed in Table 10 and shown diagrammatically in Figure 4. Of these, the Shell 405 type hydrazine-decomposition catalyst (a classified composition)[31] was the most active, and it retained its high activity after heating in a hydrogen-15% steam atmosphere for 30 minutes at 1100°C (2012°F). However, after similar hydrogen-steaming at 1200°C (2192°F) for 15 minutes the activities of these 405 type catalysts and certain other more active catalysts tended to have similar medium activity, and gave reaction between -130°C (-202°F) and -140°C (-220°F) on routine testing. But when similar tests were made with 11% hydrogen, 4% oxygen in helium over the 15-minute 1200°C hydrogen-steamed sample of 9223-118A, a Shell 405 type catalyst, activity was obtained at -195°C immediately on removing the liquid nitrogen bath. With the more dilute reactants, 3% hydrogen, 1% oxygen in helium, used in routine testing, activity was detected with this catalyst only after warming to -116°C. This result shows the importance of high concentrations and rapid runaway for ignition.

One 1200°C catalyst in Table 10 gave reaction at -171°C on routine testing, but in this test the initial reaction acceleration was unusually slow and rapid acceleration occurred only above -140°C. It is possible, however, that with more concentrated hydrogen-oxygen feeds, rapid acceleration would have been obtained at -170°C or below. Further, it must also be remembered in interpreting the data of Table 10, that the procedure used in testing these catalysts eliminates most of the initial temperature rise that could be expected from the heat of adsorption of oxygen. Such an effect could be considerable (see Appendix). In separate tests with a 3.4% Pt-Rh catalyst, reaction was detected at -122°C on testing in the usual manner which eliminates the heat of adsorption of oxygen. When the He, 3% $H_2$, 1% $O_2$ feed was admitted at -140°C to this catalyst while warming, however, rapid reaction acceleration was obtained.

Catalyst samples similar to the Engelhard MFSA and MFSA-4X catalysts were examined by other investigators under a NASA contract and were indicated to be slightly superior to a Shell 405 type catalyst similar to 9223-104I that was briefly tested. As can be seen from the data of Table 10, in this study the Shell 405 type catalysts were considerably more active than the Engelhard catalysts. The reason for disagreement is not known, but in both this study and that made at Rocketdyne it has been found that catalyst pretreatment is extremely critical, and greater attention should be given to catalyst conditioning in future testing.

The exact compositions of the MFSA and MFSA-4X catalysts are not available, but they are reported to be Pt-Rh on alumina. Further, in both these catalysts the active material is concentrated in a narrow region close to the surface of the 1/8-inch diameter support spheres. They differ in this respect from the catalysts prepared during this study, most of which consisted of 20-30 mesh granules and 1/8-inch diameter by 1/8-inch long cylindrical pellets with active material throughout each granule in both cases. The relative merits of these two types of dispersion of the active material on the support was not determined.

Table 10. MORE ACTIVE CATALYSTS

| Catalyst | | Activity Detected, °C | | |
|---|---|---|---|---|
| Number | Composition, %w | As Prepared | Steamed 1100°C[a)] | Steamed 1200°C[b)] |
| 9223-104H | Shell 405 type, 30% (classified)/RA-1, $Al_2O_3$ | -195 | -195[e)] | -137 |
| 9418-190C | 9.2% Pt, 4.8% Ru/RA-P "Superpure $Al_2O_3$" | -140 | - | -171[c)] |
| 9418-190A | 9.5% Pt, 4.9% Ru/80% $ZrO_2$-20% $ThO_2$ | - | - | -140 |
| 9418-190G | 17.5% Pt, 9.1% Ru/RA-P "Superpure $Al_2O_3$" | -147 | - | -137 |
| 9418-152E | 8.5% Pt, 4.4% Ru/Alcoa F-110 $Al_2O_3$ | -141 | -142 | -137 |
| 9418-107C | 4.5% Pt, 2.3% Ru/$ZrO_2$, 5% CaO stabilized | -125 | -137[e)] | -137 |
| 9418-190E | 18% Pt, 9.3% Ru/80% $ZrO_2$-20% $ThO_2$ | - | - | -137 |
| 7327-135A | Similar to Shell 405 type, 30% (classified) | -135 | - | -135 |
| 9418- 97C | 8.4% Pt, 4.3% Ru/RA-1 $Al_2O_3$ [$Al(NO_3)_3$ washed] | -123 | -127 | -134 |
| 9418-101D | 8.5% Pt, 4.4% Ru/RA-1 $Al_2O_3$ [$Ca(NO_3)_2$ washed] | -131 | -122 | -131 |
| 9418- 90C | 8.5% Pt, 4.2% Ru/RA-1 $Al_2O_3$[d)] | -137 | -132 | -129 |
| 9223-104I | Shell 405 type, 32% (classified)/RA-1 $Al_2O_3$ | -195 | -195[e)] | -123 |
| 9223-102E | Shell 405 type, 1/8", 30% (classified)/Al-1404 | -194 | -195[e)] | - |
| 9223-102C | Shell 405 type, 1/8", 20% (classified)/Al-1404 | -181 | -195[e)] | - |
| 9223-118A | Shell 405 type, 26% (classified)/RA-1 $Al_2O_3$ | -192 | -194[e)] | -116 |
| 9418- 90D | 8.3% Pt, 8.2% Ir/RA-1 $Al_2O_3$[d)] | -150 | -132 | -123 |
| 9414- 65C | Engelhard MFSA-4X Pt, Rh/$Al_2O_3$ | -115 | -125 | -116 |
| 9414- 65A | Engelhard MFSA Pt, Rh/$Al_2O_3$ | -101 | -101 | -107 |

a) Activity after 30 minutes at 1100°C in hydrogen - 15% steam atmosphere.
b) Activity after 15 minutes at 1200°C in hydrogen - 15% steam atmosphere.
c) Unusually slow acceleration of reaction rate.
d) Alumina support probably calcined at 1000°C basis surface area measurements.
e) Transient activity.



**Figure 4 Follows**

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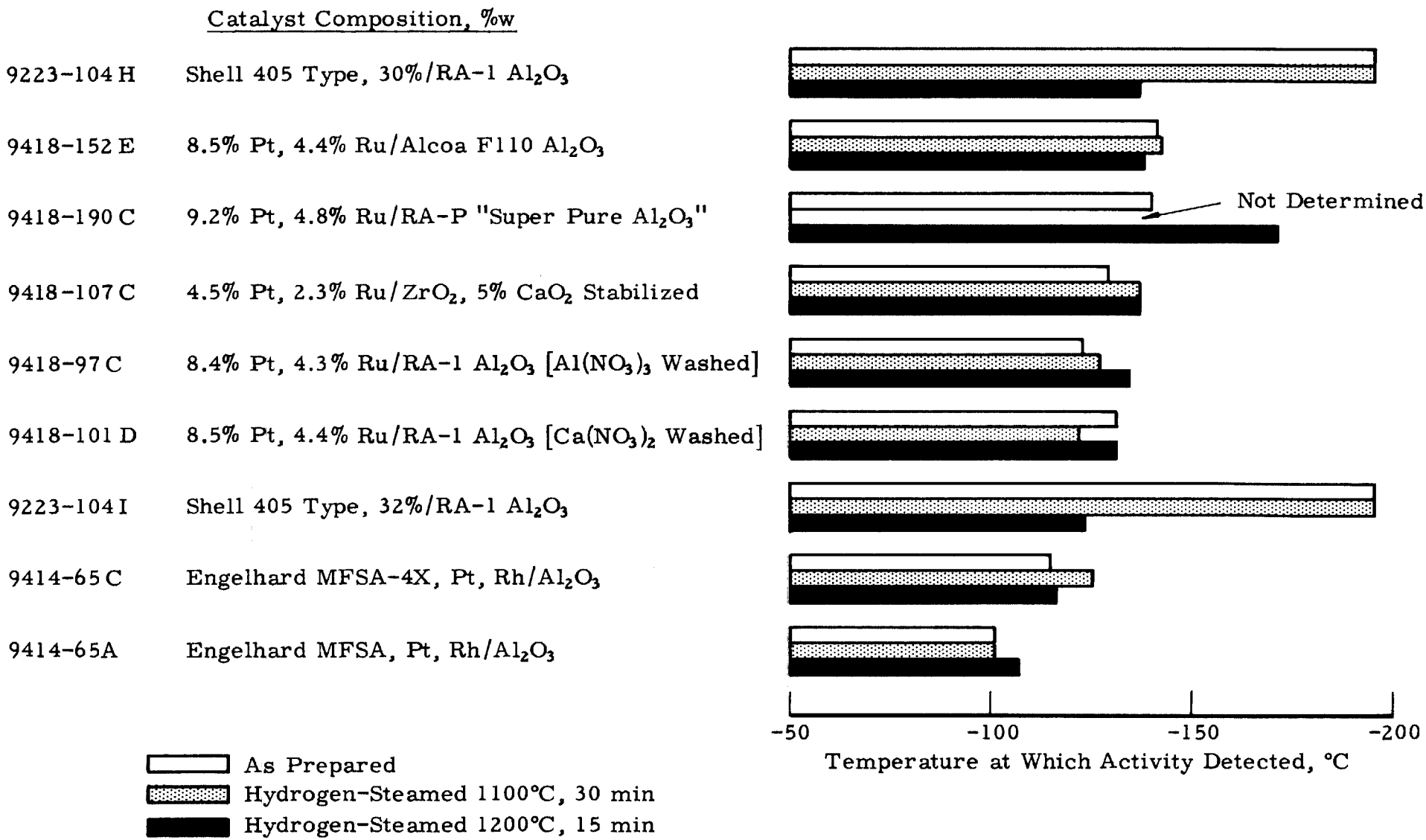


Figure 4. ACTIVITY AND STABILITY OF MORE ACTIVE CATALYSTS

## Catalyst Preparation

In view of past experience reported in the literature and discussed earlier in this report, the study of catalytic promotors for the hydrogen-oxygen reaction was concentrated within the platinum group metals. Osmium, however, was more or less bypassed because of scarcity and the ease of forming its highly toxic volatile oxide, $OsO_4$.

Platinum group metals have long been known to be more active for this reaction than other elements. In fact, Döbereiner showed in 1823 that platinum sponge would ignite a stream of hydrogen mixed with air. This discovery developed into the "Döbereiner Lamp", preceding the phosphorus match for lighting domestic lamps and candles.[29]

While a sample of platinum sponge, prepared by decomposing ammonium chlorplatinate, showed activity at -90°C the high temperatures reached during a practical application of the hydrogen-oxygen reaction can quickly sinter the unsupported finely divided platinum metal and destroy its surface. This can happen easily because the platinum atoms are clustered in close proximity and contact one another. Even relatively large platinum clusters (150 μ diameter spheres) have been shown to sinter at 850 to 1020°C.[30] In order to circumvent sintering of the active metal groups a high surface area carrier (also called support or substrate) of high thermal stability such as the oxide of aluminum or zirconium is employed to disperse the platinum metal which is adsorbed from a solution of its salt.

## Catalyst Support Materials

Catalyst support materials must meet the following severe criteria to be suitable for the hydrogen-oxygen reaction reaching 1200°C or even higher.

1) High melting point, above 2000°C.

2) Inert or relatively stable to hydrogen, oxygen or steam at temperatures up to 1200°C.

3) Thermally stable with respect to surface area and porosity to 1200°C.

4) Surface area above 5 $m^2/g$, preferably higher.

5) Pore volume >0.1 cc/g; pore diameter >12 A.

6) Mechanically stable to thermal shock.

7) Physically strong.

In view of the above requirements, the most likely supports are the more refractory oxides or combination of oxides which are stable to hydrogen reduction. Table 4 lists some of the highest melting oxides. These have highly positive free energies in the reaction

$$MO + H_2 = M + H_2O$$

so that even traces of steam in the hydrogen rich gases suffice to prevent reduction. Although, of the above group, alumina ($Al_2O_3$) is about the lowest melting candidate, the availability of alumina in high surface area form (>100 $m^2/g$) with reasonable stability directed its selection for the bulk of our catalyst studies. Some earlier studies on the stability and character of high temperature supports for similar requirements are given in a confidential report on hydrazine decomposition.[31] The support materials used for our studies are listed in later tables with physical data. Most catalysts were prepared on RA-1 alumina, a high area granular support. The tests discussed later showed alumina to have superior stability relative to the other supports studied, except for zirconia which appeared promising to 1100°C. Further work with stabilized zirconia appears justified.

Metal Promoters

The metal promoters were put onto the supports by impregnation so as to obtain high dispersion. Metal salts used for catalyst preparation were normally aqueous solutions made by dissolving the acid chlorides. The salts are reported to form the common complex anions shown below,[32] but were found to have the following acid titers to neutrality.

| Metal | Anion | Titer H+/Metal |
|---|---|---|
| Ru | $(RuCl_4)^{-1}$ | 3 |
| Rh | $(RhCl_6)^{-3}$ | 0.5 |
| Pd | $(PdCl_4)^{-2}$ | 5 (dissolved in excess HCl) |
| Ir | $(IrCl_6)^{-2}$ | 2 |
| Pt | $(PtCl_6)^{-2}$ | 2 |

Only platinum and iridium appear stoichiometric for the chloro-acid. Ruthenium and palladium have excess acid while rhodium does not appear to be complexed and may be mostly cationic $Rh^{+++}$ as $RhCl_3$ hydrate. Qualitative examination of the different salt solutions by adsorption down a capillary column of 100-200 mesh RA-1 alumina showed uniform adsorption from the platinum and rhodium solutions, two color phase adsorptions from ruthenium and three or four colors from the palladium and iridium solutions. Iridium formed an approximately 10% longer colored column than found for the other metal chlorides showing a weaker adsorption by the alumina than for the rest. As the metals were definitely adsorbed by the alumina, with clear or very pale solution left at the exit of the column, one can expect that the metals, at least at first, were dispersed fairly evenly on the support and would remain dispersed instead of forming crystals within the catalyst pores upon drying. One can also expect different degrees of adsorption from a single solution as well as from the various solutions because of increasing hydrolysis products during adsorption and from depletion of the solutions. Different final surface coverages can occur during the heating or decomposition step, for the volatility and stability will differ for each salt.

In spite of the preceding possible complication, most catalysts were prepared by a similar technique so that the effects of different metals, their concentration and binary ratios could be closely compared. The procedure was generally as follows: Standard aqueous solutions of 0.19 molar

ruthenium trichloride, rhodium trichloride, palladium trichloride, iridium tetrachloride and chloroplatinic acid were added separately or mixed as binary compositions in amounts just sufficient to wet the porous support. Supports were usually graded 20 to 30 mesh (U.S. series sieve) and preheated from 700°C up to as high as 1100°C. After wetting the support with the platinum metal solution (total impregnation) the material was dried and heated to about 400°C for 30 minutes in air to decompose the salt and further distribute the metal. In those instances where more metal was required, this procedure was repeated from two to eight times, as necessary. In a few cases a more concentrated solution was used. Following the final decomposition step the material was reduced in a stream of hydrogen at 200°C and then heated in hydrogen to 500°C and cooled to room temperature in nitrogen.

No. 9418-90 is a specific example of a catalyst made in a typical preparation. Reynolds alumina No. RA-1 was calcined 2 hours at 700°C as 20-30 mesh granules. A 9.5-gram portion was placed in a 400-cc beaker and wet with a mixture of 3.0 grams of 3.66% Pt solution and 3.0 grams 1.90% Ru solution (both chlorides). The material was then dried by a 14-amp hot air "gun" and decomposed on a hot plate at about 400°C for 30 minutes. The material was cooled and the above wetting, drying and decomposing repeated eight times. Finally, the granules were transferred to a vertical tube and brought to 200°C under nitrogen, the hydrogen started at a rate of 400 cc per minute. The temperature was raised to 500°C over a period of 30 minutes. The catalyst was cooled in nitrogen, and weighed 10.23 grams; there was a gain of 0.73 grams, but 1.34 grams of metal was added. The difference is attributed to losses. The final catalyst was estimated to contain 8.5% Pt and 4.2% Ru.

Pure Metals and Their Binary Alloys

The relative activities of a series of catalysts of the platinum and palladium metals and their binary alloys are shown in Table 11, and the same data diagrammatically in Figure 5. The correlation with the data Remy and Schaefer (Figure 2) obtained at room temperature is not good. In our study, catalysts of Ru, Rh and Os were not active below room temperature.

The catalysts of Pt-Ir and platinum alone showed slightly better activity than those of Pt-Ru, Pt-Pd and Pt-Rh in the as-prepared state. On hydrogen-steaming at 1000°C and above, however, the catalysts of Pt-Ru, Pt-Ir, and Pt-Rh retained better activity than that of pure platinum. Since ruthenium, iridium, and rhodium all have higher melting points than platinum, alloys of these metals would be expected also to have higher melting points than pure platinum. The reason for improvement in activity on hydrogen-steaming at temperatures above 1000°C is not known, but possible causes are mentioned later in discussing the correlation of catalysts' activities and physical properties.

The catalysts of Table 11 all contained the same total atomic fraction of metal, and each binary composition contained the metals in a 1:1 ratio. All of the more active catalysts contained platinum. In Table 12, the effect of varying the metal ratio of various binary compositions with platinum was investigated and all catalysts had approximately the same number of metal atoms per gram. In the Pt-Rh series, catalysts of atomic ratio of above 1Pt:1Rh showed activity similar to that of pure platinum, as-prepared,

Table 11. ACTIVITY OF Pt and Pd METALS AND THEIR BINARY ALLOYS

| Catalyst | | Activity Detected, °C | | | |
|---|---|---|---|---|---|
| No. 9418- | Composition[a] on RA-1 Alumina | As Prepared | Steamed 1000°C | Steamed 1100°C | Steamed 1200°C[b] |
| 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 | -109 | -102 | - |
| 9C | 1.2% Ru, 1.2% Rh | >+20 | - | - | - |
| 10B | 1.2% Ru, 1.2% Pd | -69 | - | -17 | - |
| 9A | 1.2% Ru, 2.2% Ir | +4 | - | - | - |
| 9B | 1.2% Ru, 2.2% Pt | -107 | -113 | -124 | -127 |
| 10E | 1.2% Rh, 1.2% Pd | -71 | - | - | - |
| 9E | 1.2% Rh, 2.2% Ir | +13 | - | - | - |
| 9F | 1.2% Rh, 2.2% Pt | -107 | -114 | -113 | -124 |
| 10C | 1.2% Pd, 2.2% Ir | -78 | - | -66 | - |
| 10D | 1.2% Pd, 2.2% Pt | -106 | -107 | -107 | - |
| 9D | 2.2% Ir, 2.2% Pt | -113 | -106 | -120 | -114 |

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.

b) 15 min at 1200°C, 30 min at 1000°C and 1100°C.



Figure 5 follows

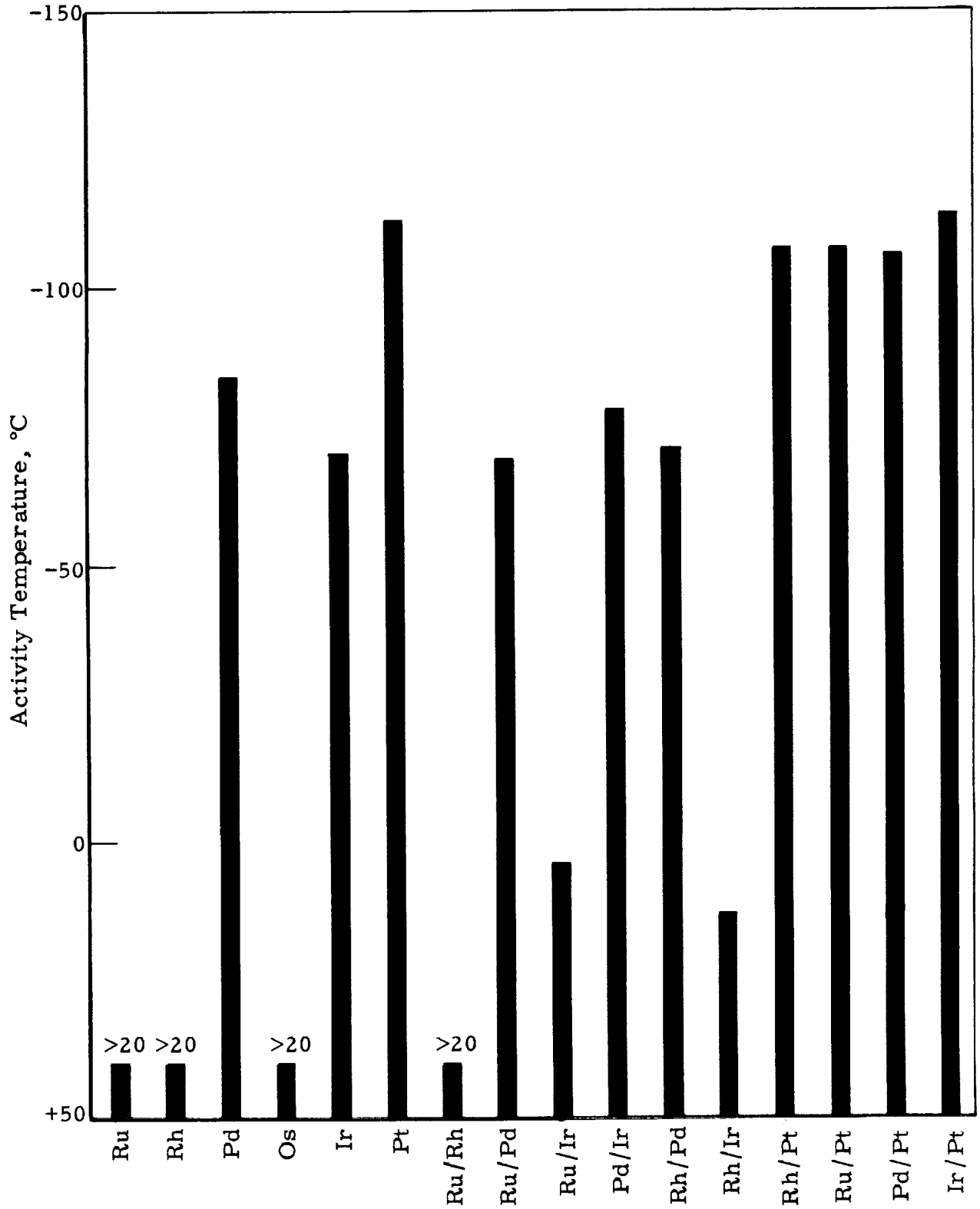


Figure 5. CATALYSTS OF Pt AND Pd METALS AND 1:1 ATOMIC RATIO ALLOYS

Data of Table 11

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Table 12. PLATINUM ALLOYS OF VARYING METAL RATIOS

| Catalyst | | Activity Detected, °C | | |
|---|---|---|---|---|
| No. 9418- | Composition, %w | As Prepared | Steamed 1000°C | Steamed 1100°C |
| 8D | 2.4% Rh/RA-1 (700) $Al_2O_3$ | >+20 | - | - |
| 16A | 0.72% Pt, 1.89% Rh/RA-1 (700) $Al_2O_3$ | -26 | - | - |
| 16B | 1.44% Pt, 1.52% Rh/ " " " | -87 | - | - |
| 9F | 2.2% Pt, 1.2% Rh/RA-1 (700) $Al_2O_3$ | -107 | -114 | -113 |
| 16C | 2.86% Pt, 0.75% Rh/RA-1 (700) $Al_2O_3$ | -112 | - | -102 |
| 16D | 3.57% Pt, 0.38% Rh/ " " " | -112 | - | - |
| 8C | 4.5% Pt/RA-1 (700) $Al_2O_3$ | -112 | -109 | -102 |
| 39B | 3.02% Pt, 1.42% W/RA-1 (700) $Al_2O_3$ | -102 | -100 | -112 |
| 39A | 2.25% Pt, 2.16% W/ " " " | -94 | -99 | - |
| 39C | 1.5% Pt, 2.84% W/ " " " | -81 | -84 | - |
| 39D | 4.3% W/RA-1 (700) $Al_2O_3$ | >+20 | >+20 | - |
| 53A | 4.4% Re/RA-1 (700) $Al_2O_3$ | >+20 | - | - |
| 53B | 2.3% Pt, 2.2% Re/RA-1 (700) $Al_2O_3$ | -86 | - | -113[b] |
| 106B | 0.8% Pt, 2.0% Ru/RA-1, Al, (700)[a] | -89 | - | -120 to -138 |
| 9B | 2.2% Pt, 1.2% Ru/RA-1 (700) | -107 | -113 | -124 |
| 106A | 3.8% Pt, 0.4% Ru/RA-1, Al, (700)[a] | -102 | - | - |

a) RA-1 $Al_2O_3$ washed to remove sodium by $Al(NO_3)_3$ solution, then calcined at 700°C.
b) Transient temperature.

but the 1:1 atom ratio catalyst retained better activity on hydrogen-steaming than did those of higher platinum content.

Addition of tungsten and rhenium, two high melting metals, to platinum on RA-1 alumina led to no outstanding improvement in retention of activity on hydrogen-steaming, and gave less active as-prepared catalysts. Variation of the Pt:Ru ratio about 1:1 in three catalysts suggested that the 1:1 composition was probably the most active and stable.

Activity of Platinum Metals on Various Supports

Tables 13 and 14 show activities and stabilities of Pt-Rh and Pt-Ru on different supports. Table 13, for similarly prepared catalysts of 2.2% Pt and 1.2% Rh by weight shows that activity was detected at about -120°C for catalysts prepared on alumina, alumina-silica, zirconia, or zirconia-silica supports of about 10 $m^2/g$ or greater surface area. Very low surface area zirconia (0.1 $m^2/g$) gave a poor catalyst, and a catalyst from alumina silica of 1.5 $m^2/g$ was less active than from supports of greater surface. One of the higher surface area aluminas, "pseudoboehmite" gave unusually low activity, and is believed due to degradation of this support by the acidic Pt and Rh reagents. Magnesia, yttria, boron nitride and low-surface silica gave inferior catalysts. Magnesia supports containing silica or alumina were too low in surface area for good activity, and also showed poor stability and little promise as candidates in comparison with aluminas of comparable surface areas. Catalysts on alumina and zirconia appeared to improve on 1100°C steaming in some instances but those on alumina-silica declined somewhat in activity. After 1200°C steaming, catalysts on alumina and alumina-silica were stable, while a catalyst on zirconia (unstabilized) was deactivated. Alumina RA-1 support appeared to be improved by calcining at 1000°C, though the surface area decreased from 278 to 32 $m^2/g$ (Table 15).

Table 14, for catalysts of Pt-Ru, a better promoter than Pt-Rh, shows that on various supports increasing activity is attained with increasing metal content. Precalcination or purification of the RA-1 alumina enhanced slightly the stability of catalysts to steaming. A catalyst from a "super-pure" alumina, No. RA-P, gave better activity and stability than catalysts from the other alumina. A catalyst from Harshaw Al-1404 1/8 inch pellets, although of very good activity as prepared, was not stable to steam-$H_2$ at 1200°C. This was unexpected for the support showed better thermal stability than found for RA-1 alumina as shown in Figure 6. Again zirconia gave a fairly active catalyst but was unstable to steaming. In contrast, zirconia stabilized with 5% CaO or 20% $ThO_2$ was still active after steaming at 1200°C. Alumina did not appear to stabilize the zirconia and gave a low activity catalyst after steaming at 1100°C. Pore volume did not appear to be critical. The value for RA-1 alumina is 0.22-0.25 cc/g, but supports 7508-26 and 7508-41, with values of 0.07 and 0.05 cc/g led to active catalysts.

The data shown in Figure 7 suggest that Pt-Rh on a silica-zirconia support (9418-11A) would have good stability over long periods at 1000°C, and that Pt-Rh on RA-1 alumina (9418-9F) also retained similar activity to that of the as-prepared catalyst after 2 hr in a steam-hydrogen atmosphere at 1000°C. However, catalyst 9418-11A showed only transient activity after steaming at 1100°C for 30 min (Table 13) while catalyst 9418-9F retained its activity after 1100°C treatment.

 Figure 6 follows

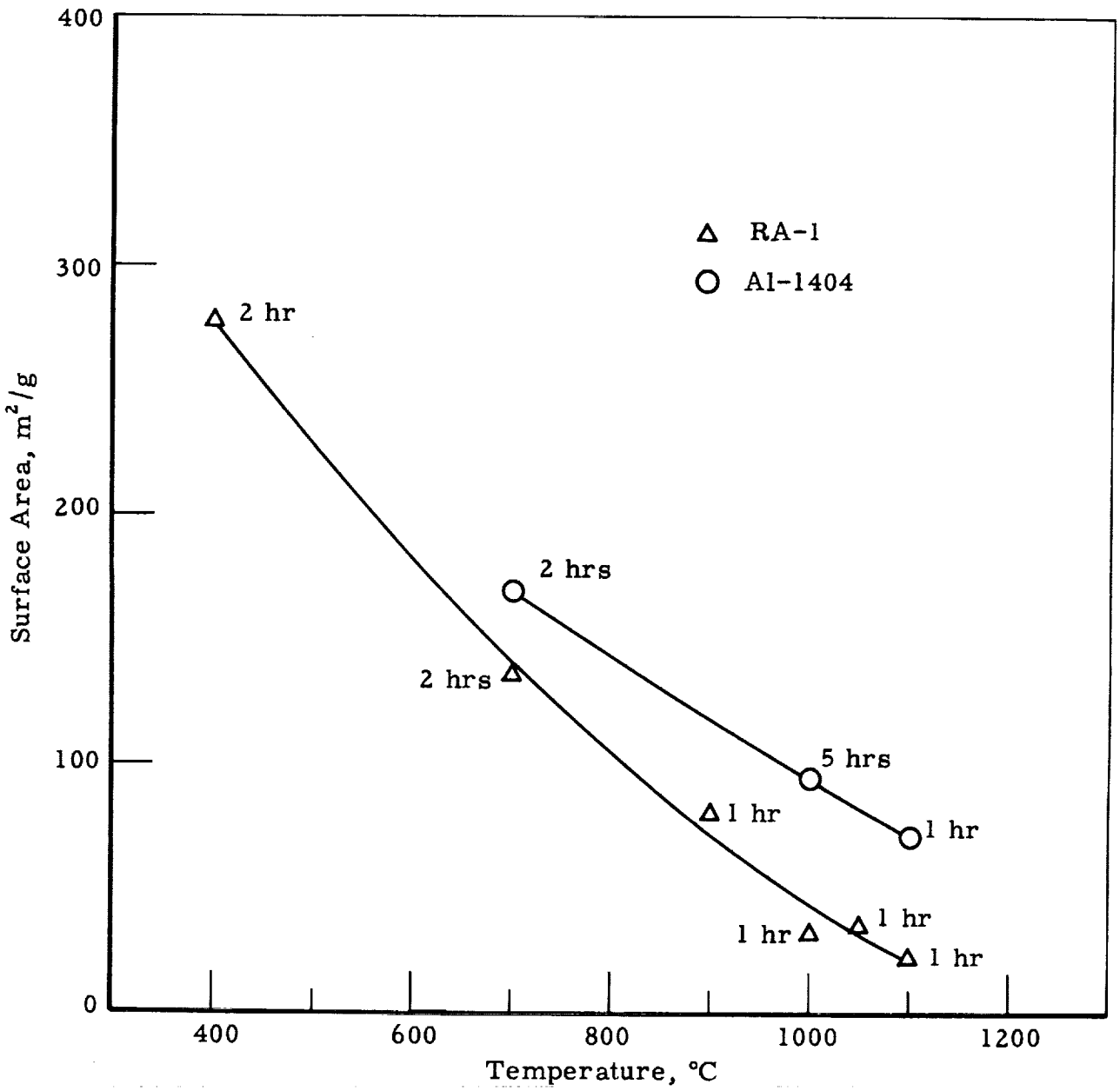


Figure 6. THERMAL STABILITY OF RA-1 AND Al-1404 ALUMINA SUPPORTS

Table 13. 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[b] | | | | Catalyst | | | | |
|---|---|---|---|---|---|---|---|---|
| Number | Source | Composition, %w | Surface Area, $m^2/g$ | No. 9418- | Activity Detected, °C | | | |
| | | | | | As Prepared | Steamed 1000°C | Steamed 1100°C | Steamed 1200°C |
| RA-1 | Reynolds | $Al_2O_3$, 0.5% Na | 135 | 9F | -107 | -114 | -113 | -124 |
| RA-1, (1000) | Lab treat,1000° | $Al_2O_3$, 0.5% Na | 32 | 17A | -114 | -116 | -112 | - |
| Al-0104 | Harshaw | $Al_2O_3$ | 80-100 | 45M | -120 | - | - | -113 |
| T-708 | Girdler | $Al_2O_3$ | 7-8 | 45E | -119 | - | -110 | -116 |
| Lot 334-93 | Harshaw | $Al_2O_3$, | ~200 | 66 | -95 | - | - | - |
| LA-617 | Norton | 19 $SiO_2$, 79 $Al_2O_3$ | 56 | 45L | -121 | - | -106 | - |
| LA-622 | Norton | 19 $SiO_2$, 79 $Al_2O_3$ | 36 | 45I | -122 | - | -112 | - |
| BA-121 | Norton | 19 $SiO_2$, 79 $Al_2O_3$ | 9-15 | 45G | -122 | - | -119 | -127 |
| LA-848A | Norton | 19 $SiO_2$, 79 $Al_2O_3$ | 1.5 | 45C | -110 | - | -100[a] | - |
| 622 | Davison | Molecular sieve | >100 | 48A | -116 | - | +4 | - |
| Celite 410 | Johns-Mansville | $SiO_2$ (Diatomite) | 3 | 45B | -42 | - | - | - |
| LM-705 | Norton | 97 MgO, 2.7 $SiO_2$ | <1 | 45D | -67[a] | - | - | - |
| LMA-703 | Norton | 29 MgO, 79 $Al_2O_3$ | 3 | 45F | -70 | - | -107[a] | - |
| Seasorb + 5 | FMC Corp. | MgO | 117 | 45J | -79 | - | >+20 | - |
| LZ-700 | Norton | $ZrO_2$ | 0.1 | 45A | -20 | - | +9 | - |
| 9418-14A | Laboratory prep | $ZrO_2$ | 50-100 | 15A | -117 | - | -122 | >0 |
| 9418-14B | Laboratory prep | 40 $SiO_2$, 60 $ZrO_2$ | 50-100 | 15B | -119 | - | - | - |
| 8799-53 | Laboratory prep | 30 $SiO_2$, 70 $ZrO_2$ | | 11A | -122 | -135 | -118[a] | - |
| 7508-18 | Laboratory prep | $Y_2O_3$ | 62 | 45H | -64 | - | - | - |
| 7508-83A | Laboratory prep | BN | 17 | 45K | -58 | - | - | - |

a) Activity transient. Temperature rise irregular.
b) All supports calcined 2 hr at 700°C, except where indicated.

Table 14. ACTIVITY AND STABILITY OF Pt-Ru ON VARIOUS SUPPORT MATERIALS

| Catalyst Support Material | | | | | Catalyst | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Activity Detected, °C | | |
| Number | Source | Composition, %w | Laboratory Treatment | Surface Area, $m^2/g$ | No. 9418- | Pt, %w | Ru, %w | As Prepared | Steamed 1100°C | Steamed 1200°C[a] |
| RA-1, (700) | Reynolds | $Al_2O_3$, 0.5% Na | Calc 700°C, 2 hr | 135 | 9B | 2.3 | 1.2 | -107 | -124 | -127 |
| RA-1, (700)[d] | Reynolds | $Al_2O_3$, 0.5% Na | Calc 700°C, 2 hr | ~20 | 90C | 8.5 | 4.2 | -137 | -132 | -129 |
| RA-1, (1100) | Reynolds | $Al_2O_3$, 0.5% Na | Calc 1100°C, 30 min | ~22 | 92C | 8.6 | 4.4 | -140 | -130 | - |
| RA-1, Al, (700) | Reynolds | $Al_2O_3$ | Aq $Al(NO_3)_3$ calc 700°C | - | 97A | 4.5 | 2.3 | -120 | -124 | - |
| RA-1, Al, (700) | Reynolds | $Al_2O_3$ | Aq $Al(NO_3)_3$ calc 700°C | - | 97C | 8.4 | 4.3 | -123 | -127 | -134 |
| RA-1, Ca, (700) | Reynolds | $Al_2O_3$ | Aq $Ca(NO_3)_2$ calc 700°C | - | 97B | 4.5 | 2.3 | -111 | -116 | - |
| RA-1, Ca, (700) | Reynolds | $Al_2O_3$ | Aq $Ca(NO_3)_2$ calc 700°C | - | 97D | 8.4 | 4.3 | -116 | -115 | -123 |
| RA-1, Al, (1000) | Reynolds | $Al_2O_3$ | Aq $Al(NO_3)_3$, 1000°C, 30 min | - | 101A | 4.4 | 2.3 | -122 | -125 | - |
| RA-1, Al, (1000) | Reynolds | $Al_2O_3$ | Aq $Al(NO_3)_3$, 1000°C, 30 min | - | 101C | 8.3 | 4.3 | -127 | -124 | -129 |
| RA-1, Ca, (1000) | Reynolds | $Al_2O_3$ | Aq $Ca(NO_3)_2$, 1000°C, 30 min | - | 101B | 4.4 | 2.3 | -112 | -114 | - |
| RA-1, Ca, (1000) | Reynolds | $Al_2O_3$ | Aq $Ca(NO_3)_2$, 1000°C, 30 min | - | 101D | 8.3 | 4.3 | -131 | -122 | -131 |
| Al-1404, (700) | Harshaw | $Al_2O_3$ | Calc 700°C, 24 hr | - | 152A | 8.1 | 4.2 | -134 | - | - |
| Al-1404, (700) | Harshaw | $Al_2O_3$ | Calc 700°C, 24 hr | - | 152C | 14.4 | 7.5 | -156 | - | -34[c] |
| F-110 | Alcoa | $Al_2O_3$ | - | 180-280 | 152E | 8.5 | 4.4 | -141 | - | -137 |
| Zr 0304 | Harshaw | $ZrO_2$ | - | 49 | 152B | 8.5 | 4.4 | -145 | - | - |
| Zr 0304 | Harshaw | $ZrO_2$ | - | 49 | 152D | 10.1 | 5.3 | -178 | - | >0 |
| RA-P | AIAG[b] | Pure $Al_2O_3$ | - | 170 | 190C | 9.2 | 4.8 | -140 | - | -171 |
| RA-P | AIAG | Pure $Al_2O_3$ | - | 170 | 190G | 17.5 | 9.1 | -147 | - | -137 |
| 8799-19 | Lab. | 95 $ZrO_2$, 5 CaO | Calc 700°C, 90 min | - | 107A | 1.1 | 0.6 | -82 | -129[c] | - |
| 8799-19 | Lab. | 95 $ZrO_2$, 5 CaO | Calc 700°C, 90 min | - | 107D | 4.5 | 2.3 | -125 | -137[a] | -137 |
| 8799-41 | Lab. | 90 $ZrO_2$, 10 $Al_2O_3$ | Calc 700°C, 2 hr | - | 107C | 1.2 | 0.6 | -103 | -27 | - |
| 8799-41 | Lab. | 90 $ZrO_2$, 10 $Al_2O_3$ | Calc 700°C, 2 hr | - | 107F | 4.4 | 2.2 | -122 | >0 | - |
| 8799-32 | Lab. | 33 $ZrO_2$, 67 $Al_2O_3$ | Calc 700°C, 3 hr | - | 107B | 1.2 | 0.6 | -102 | - | - |
| 8799-32 | Lab. | 33 $ZrO_2$, 67 $Al_2O_3$ | Calc 700°C, 3 hr | - | 107E | 4.2 | 2.2 | -126 | - | - |
| 7508-26 | Lab. | 80 $ZrO_2$, 20 $ThO_2$ | - | 150 | 190A | 9.5 | 4.9 | - | - | -140 |
| 7508-26 | Lab. | 80 $ZrO_2$, 20 $ThO_2$ | - | 150 | 190E | 18 | 9.3 | - | - | -137 |
| 7327-133C | Lab. | $Al_2O_3$, 1% HF | Calc 650°C | ~80 | 190B | 10.7 | 5.5 | - | - | -122 |
| 7327-133C | Lab. | $Al_2O_3$, 1% HF | Calc 650°C | ~80 | 190F | 19.3 | 10.0 | - | - | -137 |
| 7508-41 | Lab. | 75 $UO_3$, 25 $ZrO_2$ | Calc 430°C | 35 | 190D | 4.6 | 2.4 | - | - | -122[c] |

a) Hydrogen-steamed 30 min at 1100°C, 15 min at 1200°C.
b) Aluminum-Industrie-Aktien-Gesellschaft (Switzerland).
c) Activity transient. Temperature rise irregular.
d) Support calcination temperature in doubt. Surface area data of Tables 15 and 19 suggest temperature was 1100°C rather than 700°C.

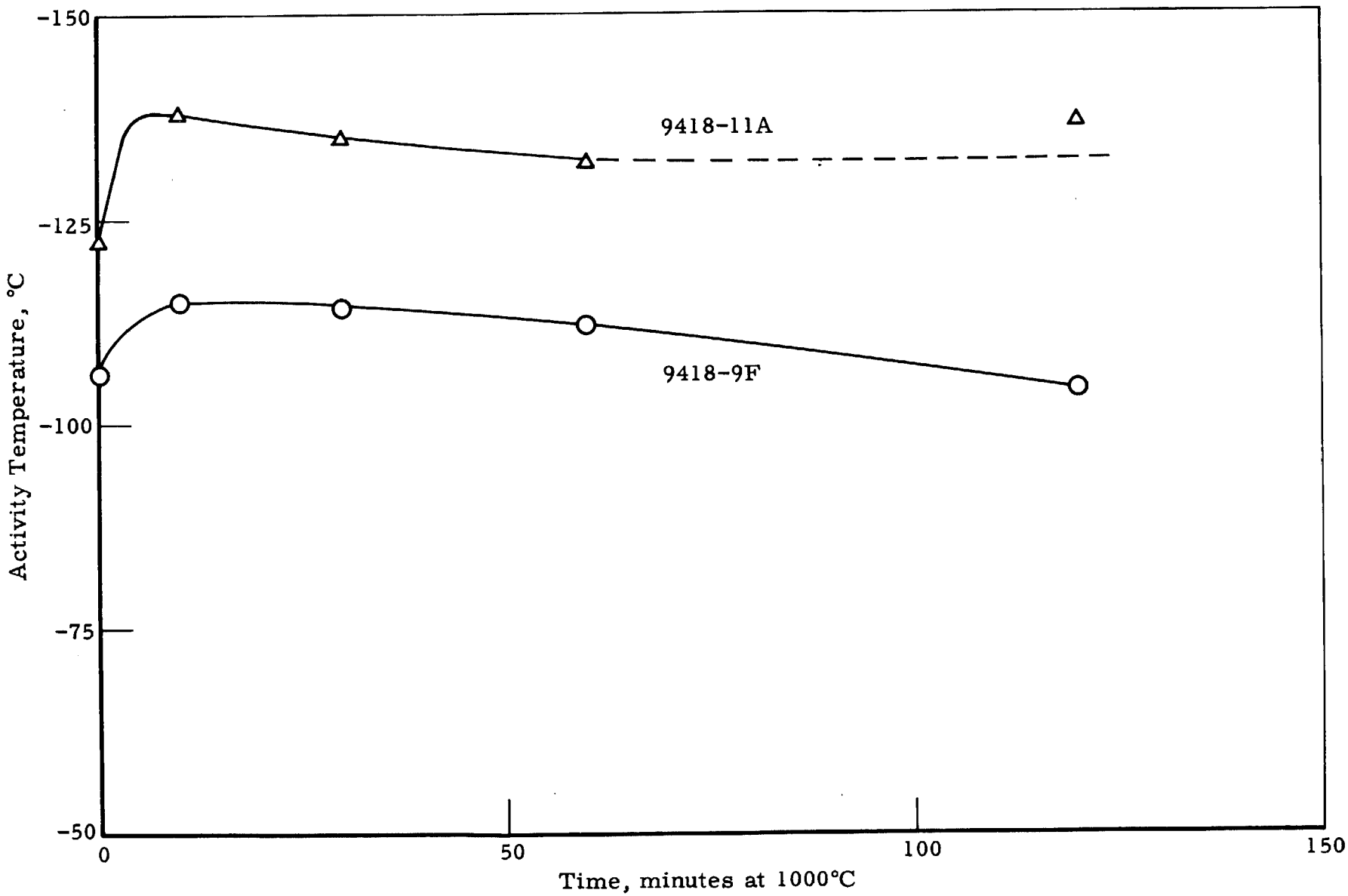


Figure 7. STABILITY OF CATALYSTS TO HYDROGEN-STEAMING AT 1000°C

Table 15. EFFECT OF HEATING IN AIR ON SURFACE AREA OF RA-1 ALUMINA

| Heat Treatment Temperature, °C | Time, Hours | Surface Area, $m^2/g$ |
|---|---|---|
| 400 | 2 | 278 |
| 700 | 2 | 135 |
| 900 | 1 | 79 |
| 1000 | 1 | 32 |
| 1050 | 1 | 34 |
| 1100 | 1 | 22 |

Effect of Increasing Metal Content on Catalyst Activity

The effects of varying metal content of constant compositions are shown by the data of Tables 16 and 17. In Table 16, several series of increasing Pt and Pt-Rh on various support materials are shown. At the lower metal contents, catalyst activity increased greatly with increasing metal, but at higher total metal contents little further improvement was obtained in these series. This effect is shown more clearly by this same data plotted in Figure 8. As can be seen from this figure, the activity of of the Shell 405 type catalysts (data of Table 17) continues to improve with increasing active material content to much higher contents than any of the preparations of Table 16.

The rate of reaction, assuming first-order kinetics can be written as

$$\text{Rate} = A \exp(-E/RT)$$

where E is the activation energy of the rate determining step of the reaction and T is the absolute temperature in °K. A and R are constants. If further assumptions are made that a) the rate of reaction needed for detection is the same for each member of a given series, and b) that when reaction is detected the recording thermocouple is at the same temperature as the catalyst, and c) the active metal area increases linearly with total metal content, then an apparent activation energy E can be calculated as detailed in the Appendix.

Such a calculation made using the data for the Pt-Rh/RA-1 $Al_2O_3$ catalysts of Table 16, up to 6.9% total metal content, gave an apparent activation energy of 2.2 kcal/mole. Using this value for E, the expected activity detection temperatures were extrapolated for this catalyst to higher total metal content values, and are shown by the broken line in Figure 8. As can be seen, the observed activities begin to fall well below the theoretical activities for the preparation containing about 13% Pt-Rh. The activities of the Pt catalysts of high metal content fall even further below these calculated values, and the 29%w Pt preparation shows lower activity than the 17%w Pt one. Such deviations can be explained by poorer metal dispersion in the higher metal content catalysts, and have been

## Table 16. CATALYSTS OF VARYING METAL CONTENT

| Catalyst | | | Activity Detected, °C | | | |
|---|---|---|---|---|---|---|
| No. 9418- | Composition, %w | Hydrogen Sorption, μmoles $H_2$/g | As Prepared | Steamed 1000°C | Steamed 1100°C | Steamed 1200°C[a)] |
| 12A | 1.1% Pt, 0.6% Rh/RA-1 (700) $Al_2O_3$ | 41 | -89 | -100 | -106 | - |
| 9F | 2.2% Pt, 1.2% Rh/RA-1 (700) $Al_2O_3$ | 67 | -107 | -114 | -113 | -124 |
| 12B | 4.5% Pt, 2.4% Rh/RA-1 (700) $Al_2O_3$ | 107 | -123 | -120 | -118 | - |
| 90B[b)] | 8.5% Pt, 4.2% Rh/RA-1 (700) $Al_2O_3$ | 69 | -125 | - | -118 | - |
| 8C | 4.5% Pt/RA-1 (700) $Al_2O_3$ | - | -112 | -109 | -102 | - |
| 59 | 8.85% Pt/RA-1 (700) $Al_2O_3$ | - | -116 | - | -60 | - |
| 59A | 17.0% Pt/RA-1 (700) $Al_2O_3$ | - | -120 | - | -105 | - |
| 59B | 29% Pt/RA-1 (700) $Al_2O_3$ | - | -115 | - | -108 | - |
| 9B | 2.3% Pt, 1.2% Ru/RA-1 (700) $Al_2O_3$ | - | -107 | -113 | -124 | -127 |
| 90C[b)] | 8.5% Pt, 4.2% Ru/RA-1 (700) $Al_2O_3$ | - | -137 | - | -132 | -129 |
| 97A | 4.5% Pt, 2.7% Ru/RA-1, Al (700) $Al_2O_3$ | - | -120 | - | -124 | - |
| 97C | 8.4% Pt, 4.3% Ru/RA-1, Al (700) $Al_2O_3$ | - | -123 | - | -127 | -134 |
| 64A | 8.8% Pt/T-708 (700) $Al_2O_3$ (7 $m^2/g$) | - | -91 | - | - | - |
| 64C | 18% Pt/T-708 (700) $Al_2O_3$ (7 $m^2/g$) | - | -99 | - | - | - |
| 64E | 32% Pt/T-708 (700) $Al_2O_3$ (7 $m^2/g$) | - | -101 | - | -106 | - |
| 64B | 9.0% Pt/BA-121 (700) 19% $SiO_2$, 81% $Al_2O_3$ | - | -97 | - | - | - |
| 64D | 17% Pt/BA-121 (700) 19% $SiO_2$, 81% $Al_2O_3$ | - | -104 | - | - | - |
| 64F | 32% Pt/BA-121 (700) 19% $SiO_2$, 81% $Al_2O_3$ | - | -99 | - | -95 | - |

a) Hydrogen steamed 15 min at 1200°C, 30 min at 1000 and 1100°C.
b) Calcination temperature of support in doubt. See Table 15.

Table 17. EFFECT OF INCREASING METAL CONTENT FOR SHELL 405 CATALYST ON ACTIVITY AND STABILITY

| Catalyst | | | Physical Properties | | Activity Detected, °C |
|---|---|---|---|---|---|
| No. 9223- | Composition, %w (on RA-1 $Al_2O_3$) | Steaming, °C | Surface Area, $m^2/g$ | $H_2$ Chemisorption, μmoles/g | |
| 104A | Shell 405 type, 3.4 | None | - | 143 | -89 |
| 104B | Shell 405 type, 14 | None | - | 278 | -181 |
| | | 1100 | - | - | -71 |
| 104F | Shell 405 type, 26 | None | - | 373 | -192 |
| | | 1100 | - | - | -195[a)] |
| 104G | Shell 405 type, 29 | None | - | - | -195 |
| 104H | Shell 405 type, 31 | None | - | - | -195 |
| | | 1100 | - | - | -195[a)] |
| | | 1200 | - | - | -137 |
| 104I | Shell 405 type, 32 | None | 119 | 418 | -195 |
| | | 1100 | 35 | 130 | -195[a)] |
| | | 1200 | 22 | 100 | -123 |

a) Extremely transient. Irregular temperature rise.

observed frequently in other studies. Variation of the method of catalyst preparation, however, failed to give significantly more active platinum catalysts (Table 20).

Similar data for the activity of several Shell 405 type catalysts of varying active material content are given in Table 17, and also plotted in Figure 8. The activity of these catalysts increased rapidly with increasing active material and reached the limit capable of being tested by the procedure of cooling to -196°C used in this study. Again, making the same assumptions as were made for the Pt-Rh catalysts of Table 16, an apparent activation energy can be calculated from data for catalysts of low active material content, and then this value used to calculate the activity expected at higher contents. The results of such calculations are shown in Table 18, and the calculated activity curve plotted as a broken line in Figure 8. The observed activity temperatures of the Shell 405 type preparations closely follow the calculated values based both on the active material content of the catalysts and on the experimentally determined hydrogen chemisorption values. Since hydrogen chemisorption is considered to be a direct measure of the active material surface area, the data calculated on this basis should be the better values. The surface area of the active material, as measured by hydrogen chemisorption, does not increase linearly with increasing active material content as is shown by Figure 9.

Table 18. CALCULATED ACTIVATION ENERGIES AND EXTRAPOLATED CATALYST ACTIVITY TEMPERATURES FOR INCREASING ACTIVE MATERIAL OF SHELL 405 TYPE CATALYSTS

| Active Material, %w | Hydrogen Chemisorption, μmoles/g | Activity Detected, °C | Calculated Activity Temperatures | |
|---|---|---|---|---|
| | | | Basis Active Material Content | Basis $H_2$ Chemisorption |
| 3.4 | 143 | -89 | E = 495 cal/mole | E = 232 cal/mole |
| 14 | 278 | -181 | | |
| 26 | 373 | -192 | -196 | -198 |
| 32 | 418 | -195 | -203 | -203 |

The greater activities of the Shell 405 type catalysts than of the Pt and Pt-Rh catalysts can be explained by the much lower apparent activation energy, 230 cal/mole, of the Shell 405 catalyst compared to an apparent activation energy of about 1480 cal/mole calculated for the Pt-Rh catalysts based on hydrogen chemisorption values. This would suggest that hydrogen reacts with oxygen more readily on unit surface of the active material of the Shell 405 catalysts than on a Pt-Rh surface, and this may be so. However, it must be recognized that our test is not a simple measure of activity when reaction starts at -195°C. For example, in a test of a Shell 405 catalyst where the hydrogen-oxygen feed was passed over the catalyst for 5 minutes while the reactor was cooled in liquid nitrogen, instead of the usual 1 minute, before removing the liquid nitrogen bath to start the warming period, activity was not detected until -150°C. In routine tests, with the 1-minute "feed on - liquid $N_2$ up" period, the Shell 405 catalyst shows

 Figures 8 and 9 follow

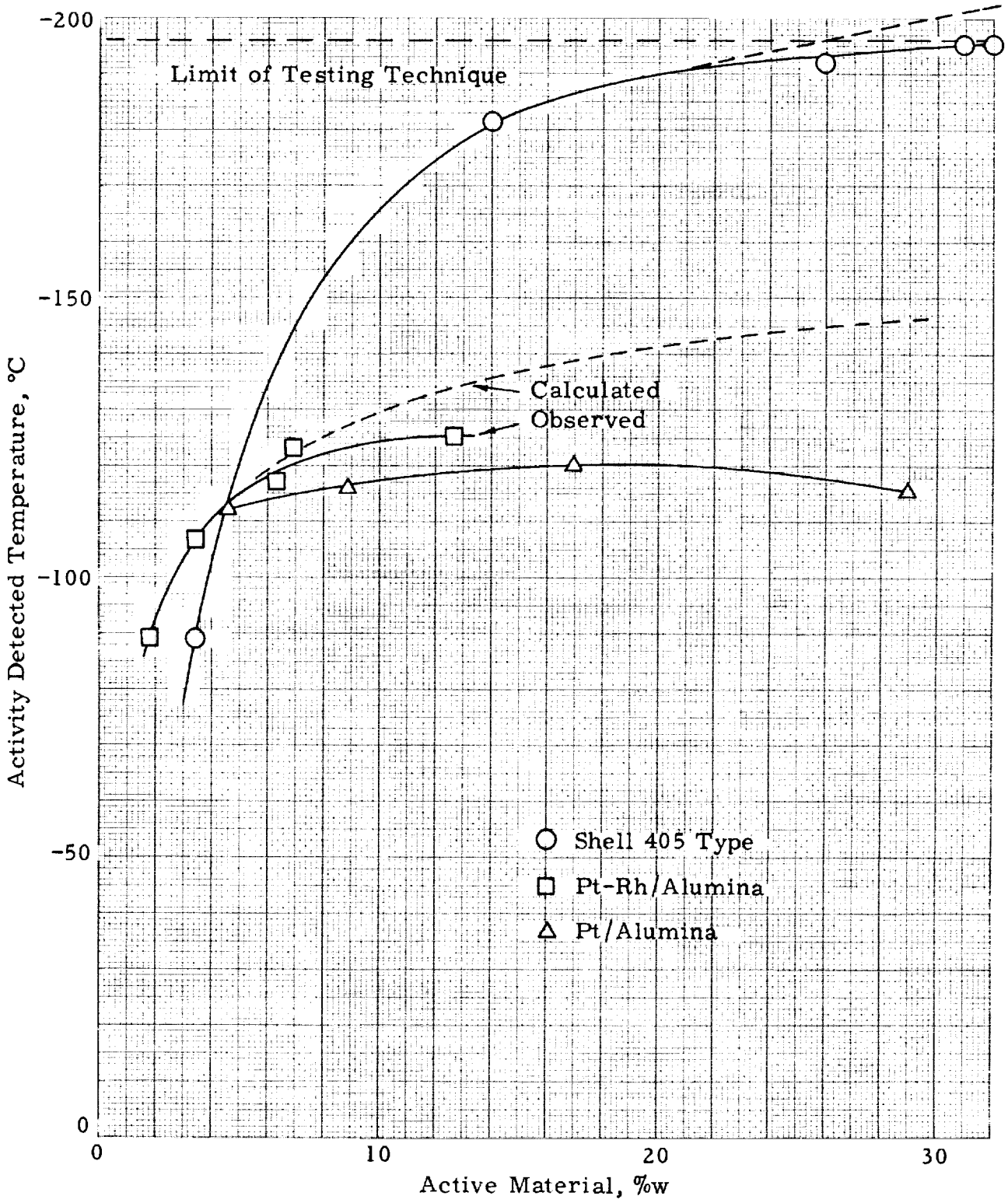


Figure 8. VARIATION OF CATALYST ACTIVITY WITH ACTIVE MATERIAL CONTENT

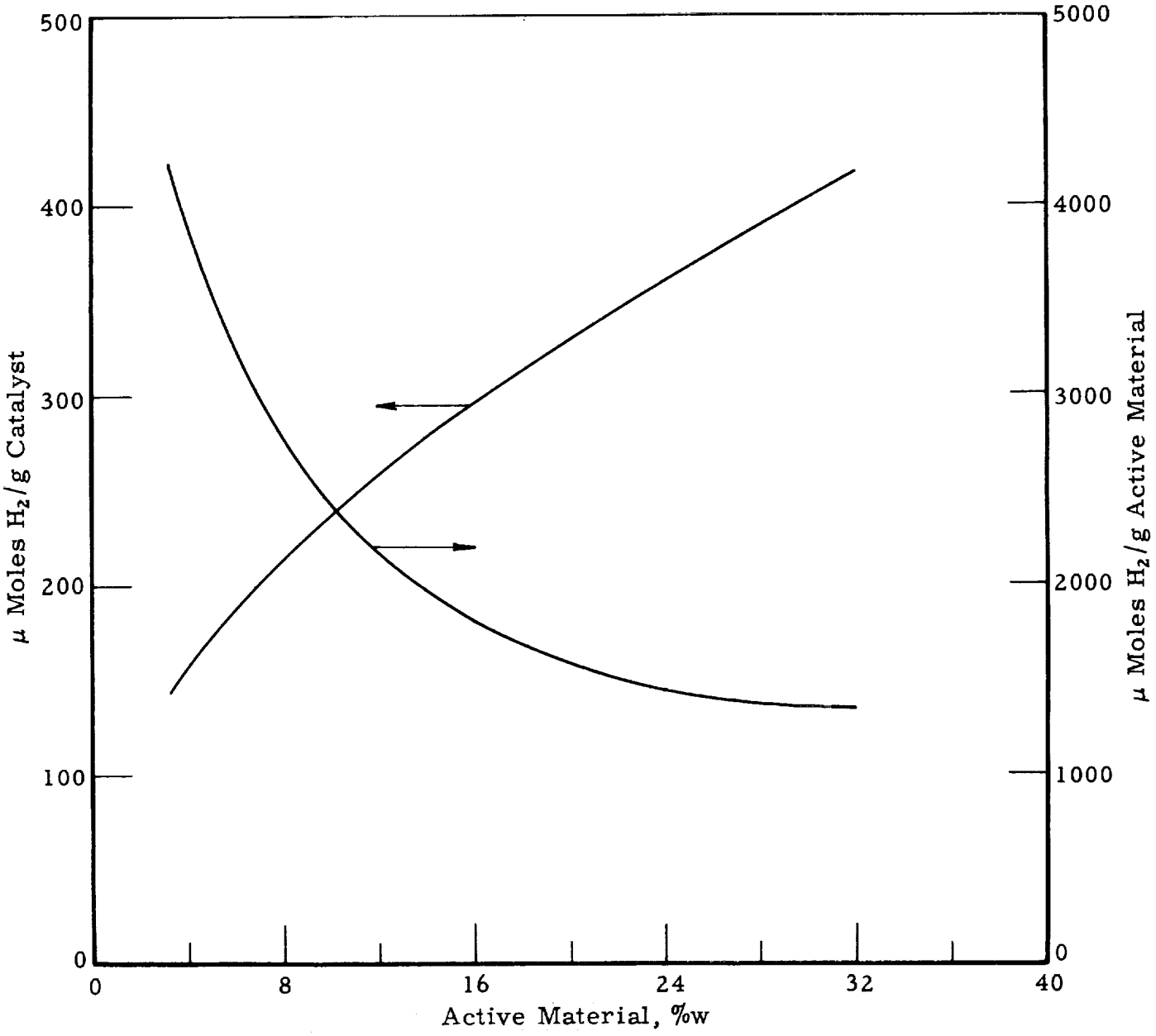


Figure 9. HYDROGEN CHEMISORPTION ON SHELL 405 TYPE CATALYSTS

activity very shortly after replacement of the liquid nitrogen bath with the cold air bath. (See Appendix for technique details.) In view of this behavior, it is thought that the activity of the Shell 405 catalyst at -195°C is probably due partly to chemisorption of oxygen onto the hydrogen-covered active material while cooled by liquid nitrogen; then on early replacement of the liquid nitrogen bath, the heat losses from the catalyst are slower and the catalyst temperature rises. This increases the rate of chemisorption, with its corresponding heat of adsorption release, and the temperature of the active surface is boosted to a temperature where the hydrogen-oxygen reaction can proceed rapidly. When the catalyst was cooled efficiently at -195°C for the longer 5-minute period, the heat of chemisorption of oxygen onto the active surface was removed before the warming period began, and the "true" activity of this catalyst for the hydrogen-oxygen reaction was observed at -150°C.

Another interpretation of this decreased activity after extended "feed-on cooling" is possible, however. It may be that the proposed chemisorption of oxygen is also accompanied by slow interaction of adsorbed oxygen with the pre-adsorbed hydrogen, and that water so formed poisons the active surface for further reaction, so making determination of a "true" activity impossible by this technique.

Further consideration along these lines raises doubts as to exactly what properties of the catalyst were being measured by this rising temperature technique. Only with the Shell 405 catalysts was any indication of a temperature rise observed on first contacting the catalyst with the hydrogen-oxygen feed while cooled in liquid nitrogen. It is possible that chemisorption of oxygen on the hydrogen-covered metal surfaces occurred so slowly at about -195°C that the rate of heat liberation was insufficient to boost the catalyst temperature to a point where continuous reaction could occur. Alternatively, it may be that very little chemisorption of oxygen onto the hydrogen-covered surface occurred at -195°C, and that liberation of adsorption heat became appreciable only at the temperature at which activity was detected on each particular catalyst.

Varying combinations of the above possible degrees of involvement of the heat of oxygen chemisorption in giving detectable catalytic activity would explain the great differences in acceleration rates and transient activity behavior observed in testing different catalysts.

Further support for a slow oxygen chemisorption onto a hydrogen-covered Shell 405 type catalyst comes from a series in which only oxygen, 4% in helium, was admitted to the catalyst with no hydrogen in the feed. When this catalyst was pretreated in the normal manner and cooled from 400°C to -195°C in a 50% hydrogen-50% helium atmosphere, then flushed with helium for 2 minutes before admitting oxygen, only about 3°C temperature rise was observed while held in a liquid $N_2$ bath, with a 51°C jump to -143°C shortly after removing the liquid $N_2$. When this same catalyst sample was flushed with helium for 10 minutes at 400°C and cooled in helium to -195°C following the hydrogen reduction, however, a temperature rise of 18°C was observed on admitting oxygen even while still held in liquid $N_2$. This suggests that these catalysts would probably perform better under outer-space vacuum conditions than after being stored in a hydrogen gas atmosphere, and further emphasizes the sensitivity of the observed activity of the catalyst to the heat capacity of the system in this temperature range.

## Relationship of Activity With Physical Properties

There are many reports in the literature of catalytic activity of supported metal catalysts being directly proportional to the active metal surface area, as measured by hydrogen chemisorption. In general, the as-prepared activity of catalysts on similar support materials also followed closely the hydrogen chemisorption values as shown in Tables 17 and 19. However, many large deviations were observed on attempting to extend this correlation to different support compositions, and to catalysts on supports of the same composition but different pore texture.

The most striking deviation from a direct correlation of increasing activity with increasing hydrogen chemisorption, however, was shown by catalysts of low binary metal content on steaming. In many cases the observed activity of the catalyst actually improved on hydrogen-steam treating at 1000 or 1100°C for 30 minutes, while the hydrogen chemisorption and total surface area values decreased continuously with increasing severity of such treatments. Data for several such cases are shown in Table 19. In some instances, a several-fold decrease in active metal area resulted in a catalyst apparently many times (10 to 30°C) more active. Nevertheless, catalysts showing greatest activity, with reaction detected at -150°C or lower, showed the largest hydrogen chemisorption values (80 μmoles or more).

Such variations of activity and corresponding metal area are difficult to explain. Studies of the effect of the support composition and pore texture on the operation of supported metals have suggested that runaway reaction temperatures occur more readily with catalysts of high diffusivity and low thermal conductivity.[35] Since the first is more likely with larger pores, activity variation with pore texture can be expected. High temperature steaming favors retention and possible development of large pores at the expense of smaller ones. Other effects, such as removal of poisons from the catalyst surface, migration of a more active component to the surface, or compound formation in binary alloys to give lower activation energies, could also help account for the increase in activity on hydrogen-steam treatment.

Highly enhanced activity of several metals following high temperature baking has been reported for several other reactions, with no satisfactory explanation of this phenomena being found.[36] In most of these cases the enhanced activity was temporary only, and decreased to its original value on storage, sometimes quite rapidly. In this work, no loss in activity of the more active hydrogen-steamed catalysts was observed over several days, but no long-term comparison was made.

Table 19. EFFECTS OF STEAMING ON SURFACE AREA, HYDROGEN CHEMISORPTION, AND ACTIVITY

| Catalyst | | Steam-$H_2$ Treatment, °C | Surface Area, $m^2/g$ | Chemisorption, µmoles $H_2/g$ | Activity Detected, °C |
|---|---|---|---|---|---|
| No. 9418- | Composition, %w | | | | |
| 65C | MFSA-4X (Pt-Rh) | None | 231 | 25 | -115 |
| | | 1100 | 38 | 7 | -125 |
| | | 1200 | 11 | 5 | -116 |
| 90C[a)] | 8.6% Pt, 4.4% Ru/RA-1 (700) $Al_2O_3$ | None | 19 | 32 | -137 |
| | | 1100 | 17 | 20 | -132 |
| | | 1200 | 12 | 13 | -129 |
| 90D[a)] | 8.5% Pt, 8.5% Ir/RA-1 (700) $Al_2O_3$ | None | 21 | 80 | -150 |
| | | 1100 | 19 | 53 | -132 |
| | | 1200 | 14 | 40 | -123 |
| 106B | .76% Pt, 2.0% Ru/RA-1 (700) $Al_2O_3$ | None | 70 | 26 | -89 |
| | | 1100 | 29 | 8 | -120 to -138 |
| 17A | 2.3% Pt, 1.2% Rh/RA-1 (1000) $Al_2O_3$ | None | 29 | 37 | -114 |
| | | 1100 | 22 | 14 | -112 |
| 9F | 2.2% Pt, 1.2% Rh/RA-1 (700) $Al_2O_3$ | None | 118 | 67 | -107 |
| | | 1100 | 56 | 11,20 | -113 |
| 12A | 1.1% Pt, 0.6% Rh/RA-1 (700) $Al_2O_3$ | None | - | 41 | -89 |
| 9F | 2.2% Pt, 1.2% Rh/RA-1 (700) $Al_2O_3$ | None | - | 67 | -107 |
| 12B | 4.5% Pt, 2.4% Rh/RA-1 (700) $Al_2O_3$ | None | - | 107 | -123 |

a) Calcination temperature of support used for 9418-90 series catalysts in doubt. Surface area data suggests 1100°C rather than 700°C (see Table 15).

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|---|---|---|---|---|---|
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| | | 1100 | 38 | 7 | -125 |
| | | 1200 | 11 | 5 | -116 |
| 90C[a)] | 8.6% Pt, 4.4% Ru/RA-1 (700) $Al_2O_3$ | None | 19 | 32 | -137 |
| | | 1100 | 17 | 20 | -132 |
| | | 1200 | 12 | 13 | -129 |
| 90D[a)] | 8.5% Pt, 8.5% Ir/RA-1 (700) $Al_2O_3$ | None | 21 | 80 | -150 |
| | | 1100 | 19 | 53 | -132 |
| | | 1200 | 14 | 40 | -123 |
| 106B | .76% Pt, 2.0% Ru/RA-1 (700) $Al_2O_3$ | None | 70 | 26 | -89 |
| | | 1100 | 29 | 8 | -120 to -138 |
| 17A | 2.3% Pt, 1.2% Rh/RA-1 (1000) $Al_2O_3$ | None | 29 | 37 | -114 |
| | | 1100 | 22 | 14 | -112 |
| 9F | 2.2% Pt, 1.2% Rh/RA-1 (700) $Al_2O_3$ | None | 118 | 67 | -107 |
| | | 1100 | 56 | 11,20 | -113 |
| 12A | 1.1% Pt, 0.6% Rh/RA-1 (700) $Al_2O_3$ | None | - | 41 | -89 |
| 9F | 2.2% Pt, 1.2% Rh/RA-1 (700) $Al_2O_3$ | None | - | 67 | -107 |
| 12B | 4.5% Pt, 2.4% Rh/RA-1 (700) $Al_2O_3$ | None | - | 107 | -123 |

a) Calcination temperature of support used for 9418-90 series catalysts in doubt. Surface area data suggests 1100°C rather than 700°C (see Table 15).

## Miscellaneous Catalyst Preparations

Table 20 gives the results of various miscellaneous preparations. These catalysts were prepared to check on preparative variables or to determine effects not covered in other portions of this report. Platinum-containing catalysts were prepared from the tetrammine platinous chloride salt which is a cationic complex of the platinum metal in contrast to the chloroplatinate anion used for most of the catalysts. Decomposition appeared to occur sooner with the tetrammine salt and a metallic film was deposited on the decomposition vessel indicating poor adsorption by the alumina. Although the platinum content of these catalysts (9418-89A and -B) was 16%, their activity was lower than a 5% Pt catalyst prepared with chloroplatinic acid (chloroplatinate ion). The adsorption of chloroplatinate ion from excess chloroplatinic acid by RA-1 alumina, followed by rinsing with water to remove the chloroplatinate ion in solution from the pores of the alumina, was carried out several times with a decomposition step between each adsorption. About 5% Pt was adsorbed which gave a reasonable but not improved catalyst (9418-99). This is a tedious procedure so no further work was done in this direction.

Reduction in hydrogen instead of decomposition in air between normal impregnation with chloroplatinic acid gave a defintely inferior catalyst 9418-100.

A recent patent[37)] claimed that platinum metal ions would migrate to the surface of moist alumina where they could be reduced in a humid stream of hydrogen at temperatures less than 100°C and so deposit platinum crystallites at the exterior surface of the alumina. At 0-75° on silica-alumina the crystallite size was reported to have a maximum dimension of less than 50 A. Catalyst 9418-150A was prepared by this technique on Harshaw 1404 1/8 inch pellets. The resulting catalyst had visible flecks of platinum metal near and on the surface of the pellets. The platinum appeared to form discrete "islands" of metal. This catalyst was quite inactive but a second catalyst (150B) prepared by directly decomposing in air a portion of the similarly impregnated pellets was active.

High ruthenium on alumina (9223-94A) was inactive as found earlier with low ruthenium content. The same catalyst promoted with 4.4% Pt (9418-170A) had good activity and was stable at 1100°C with both runs detecting activity at about -147°C. In contrast, promotion of Pt on the highly active 405 type catalyst raised the detection temperature from -195 to -175 (Catalyst No. 9418-170C).

The effect of adding Pt and Ru chlorides together or first $RuCl_3$ and then $H_2PtCl_6$ is seen in the 9418-171 series. While putting on Ru first gave a less active catalyst as prepared, steaming improved the activity greatly. This could result from interaction of the Pt and Ru at the high temperature. Finally pure platinum "sponge" was prepared by the thermal decomposition of ammonium chloroplatinate followed by reduction in hydrogen. This material (9418-177) showed activity at -90°C. It would not be expected to be thermally stable.

Table 20. MISCELLANEOUS PREPARATIONS

| Catalyst | | Activity Detected, °C | |
|---|---|---|---|
| Number | Composition, %w[a] | As Prepared | Steamed 1100°C |
| 9418- 89A | 16% Pt from tetramine platinous chloride on RA-1 (700) | -95 | -99 |
| - 89B | 16% Pt from tetramine platinous chloride on 1100°C calcined RA-1 (700) | -105 | -96 |
| - 99 | About 5% Pt adsorbed from excess $H_2PtCl_6$ solution on RA-1 (700) | -121 | -105 |
| -100 | 4.4% Pt from $H_2PtCl_6$ but reduced instead of decomposed between impregnations on RA-1, Al (700) | -64 | -54 |
| -150A | 2% Pt from $H_2PtCl_6$, reduced at 50°C while still damp on Al-1404 (700) | >0 | - |
| -150B | 2% Pt from $H_2PtCl_6$, decomposed in air then reduced in hydrogen on Al-1404 (700) | -109 | - |
| -170A | 4.4% Pt on 9223-94A | -146 | -148 |
| -170C | 4.6% Pt on 405 type (32%) | -176 | -175 |
| -171A | 1.5% Pt, 2% Ru on RA-1 (700) | -123 | -122 |
| -171B | 2.9% Pt, 3.8% Ru on RA-1 (700) | -110 | -125 |
| -171C | 1.9% Pt, 2.0% Ru on RA-1 (700) Ru on first | -101 | -142 |
| -171D | 3.7% Pt, 3.8% Ru on RA-1 (700) Ru on first | -111 | -138 |
| -177 | 100% Pt sponge from $(NH_4)_2$ $PtCl_6$ | -90 | - |
| 9223- 94A | 30% Ru/Al-1404 | >0 | - |

a) See Table 14 for description of support materials.

## Conclusions

1. Research was done to investigate the preparation and thermal stability of catalysts for the hydrogen-oxygen reaction. With this object, catalysts were tested using a rising temperature technique and dilute hydrogen-oxygen mixtures. Several important features of the reaction at low temperatures were observed which probably apply under firing conditions. From these observations, the literature, and past experience, a model for the phenomena occurring during initiation of reaction was derived. Some observations are:

a) Ignition is possible down to at least -195°C.

b) Catalyst pre-conditioning is highly important. Heating in hydrogen-rich gas to above 300°C for several minutes removes adsorbed oxygen and water vapor, and gives great improvement in activity.

c) The heat of adsorption of oxygen onto bare catalyst (cooled in He or evacuated) gives large, rapid heat release which can boost the catalyst temperature by 100°C. Oxygen chemisorption is slowed by pre-adsorbed hydrogen on the surface at liquid nitrogen temperature, however, and the slower heat release gives a smaller temperature rise.

d) Rates of chemisorption and reaction are highly sensitive to small variations in temperature at the low temperatures considered, -196°C (77°K) and -253°C (20°K). Feeding the reactants as liquids at these low temperatures will give a large heat sink since the liquids need vaporizing before temperatures can rise. High initial liquid flows will tend to absorb heat liberated, and so probably quench the reaction.

e) High flows of gaseous reactants to the catalyst, however, to the extent studied, have no effect on the temperature at which activity is detected. This observation suggests that greater reliability of ignition will be obtained with gaseous feeds during this initial stage.

f) The concentration of reactants or their ratio in the feed gases has no definite effect on the temperature at which activity is first detected, provided that adsorption heat is removed prior to reaction. Increasing reactant concentration does increase the rate of reaction acceleration, however, and probably also increases the rate of oxygen chemisorption on a hydrogen-covered surface. Thus higher reactant concentrations will favor initiation under practical conditions.

2. The tests made in this study indicate that the best catalysts, the Shell 405 type catalysts, are much more active than the MFSA catalysts tested in previous programs. The 405 catalysts will ignite at -195°C when fresh or after 30 minutes steam-$H_2$ exposure at 1100°C (2012°F). After 15 minutes exposure to steam-hydrogen at 1200°C (2192°F), however, several catalysts show similar or better activity than the steamed Shell 405 catalyst which then ignites at -137°C. Of these, Pt-Ru on RA-P "super-pure alumina" and on 80 $ZrO_2$-20 $ThO_2$ supports are slightly superior to others (see Table 10).

3. Many questions regarding the physical chemistry of catalyst preparation, catalyst aging, and catalytic ignition remain unanswered. However, before further work is undertaken, it would be preferable to confirm the conclusions and catalyst activities obtained in this program by actual test firing in a larger reactor with undiluted feeds. In such testing close attention should be given to the catalyst condition immediately prior to each test. Ideally, an ignition catalyst should be sealed in vacuum or helium until the time of ignition, and for best re-ignition it should be shut down with hydrogen lag.

4. Further advances in improving catalyst activity and, more especially, high temperature stability appear feasible. Such advances will probably be gradual and will require development of improved, high surface area, supports. The present study has provided a basis for further improvements and has given a better understanding of the requirements needed to obtain initiation of reaction at low temperatures.

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## APPENDIX


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Temperature Rise Due to Heat of Initial Adsorption

As mentioned earlier in this report, the initial adsorption of oxygen onto the catalyst would be expected to liberate a considerable amount of heat over a short period of time, and so give an initial rise in the catalyst temperature. No reliable values could be found in the literature for the heat of adsorption of oxygen onto hydrogen covered surfaces of the platinum series metals. However, since oxygen adsorption on a clean platinum surface releases about 65 kcal/mole, the heat of adsorption on a hydrogen covered surface would probably exceed the difference between this value and the 30 kcal/mole heat of adsorption of hydrogen on a clean platinum surface.

A catalyst containing about 25%w platinum, well dispersed, would adsorb about 400 μ moles of hydrogen or oxygen per g catalyst, and assuming a heat of chemisorption of 30 kcal/mole oxygen adsorbed, would liberate 12 cal/g catalyst. The specific heats of platinum and alumina are low at the low temperatures being considered, and vary with temperature as described by Figure 10.

From these data

$$\begin{aligned} \text{Catalyst } C_p &= \text{platinum part } C_p + \text{alumina part } C_p \\ &= 0.25\ (0.03) + 0.75\ (0.00082T - 0.049) \\ &= 0.000615T - 0.0293 \end{aligned}$$

and if the feed reaching the catalyst is at -183°C then

$$\int_{90}^{T} C_p = 0.000308T^2 - 0.0293T + 0.13$$

in calories per gram catalyst per °K (absolute temperature). Assuming there is no heat loss from the catalyst to the flowing gases (instantaneous heat liberation), then the 12 calories heat of chemisorption would raise the catalyst temperature 160°C from -183°C to -23°C.

Such large initial temperature jumps were not found in practice with a 4% oxygen in helium feed to the catalyst. The maximum temperature rise due to chemisorption of oxygen was observed on a Shell 405 type catalyst. This catalyst after the usual 400°C hydrogen reduction and cooling to -196°C pretreatment showed only a slight slow temperature rise at the central thermocouple while still cooled by a liquid nitrogen bath for a 1 minute "oxygen only, feed on" period. Almost immediately on replacing the liquid nitrogen bath with the cold air bath (at -196°C) the thermocouple temperature rapidly rose from -196°C to a maximum of -142°C before dropping again, indicating that at liquid nitrogen temperature oxygen chemisorption onto a hydrogen covered surface was slow. This behavior further emphasizes the great sensitivity of the system to heat transfer. While the reactor was liquid nitrogen cooled heat losses were sufficiently great to prevent any rapid temperature rise, and oxygen chemisorption sufficiently slow that it was still continuing at the end of the one minute period. Higher oxygen concentrations would be expected to give more rapid chemisorption and heat liberation.

 Figure 10 follows

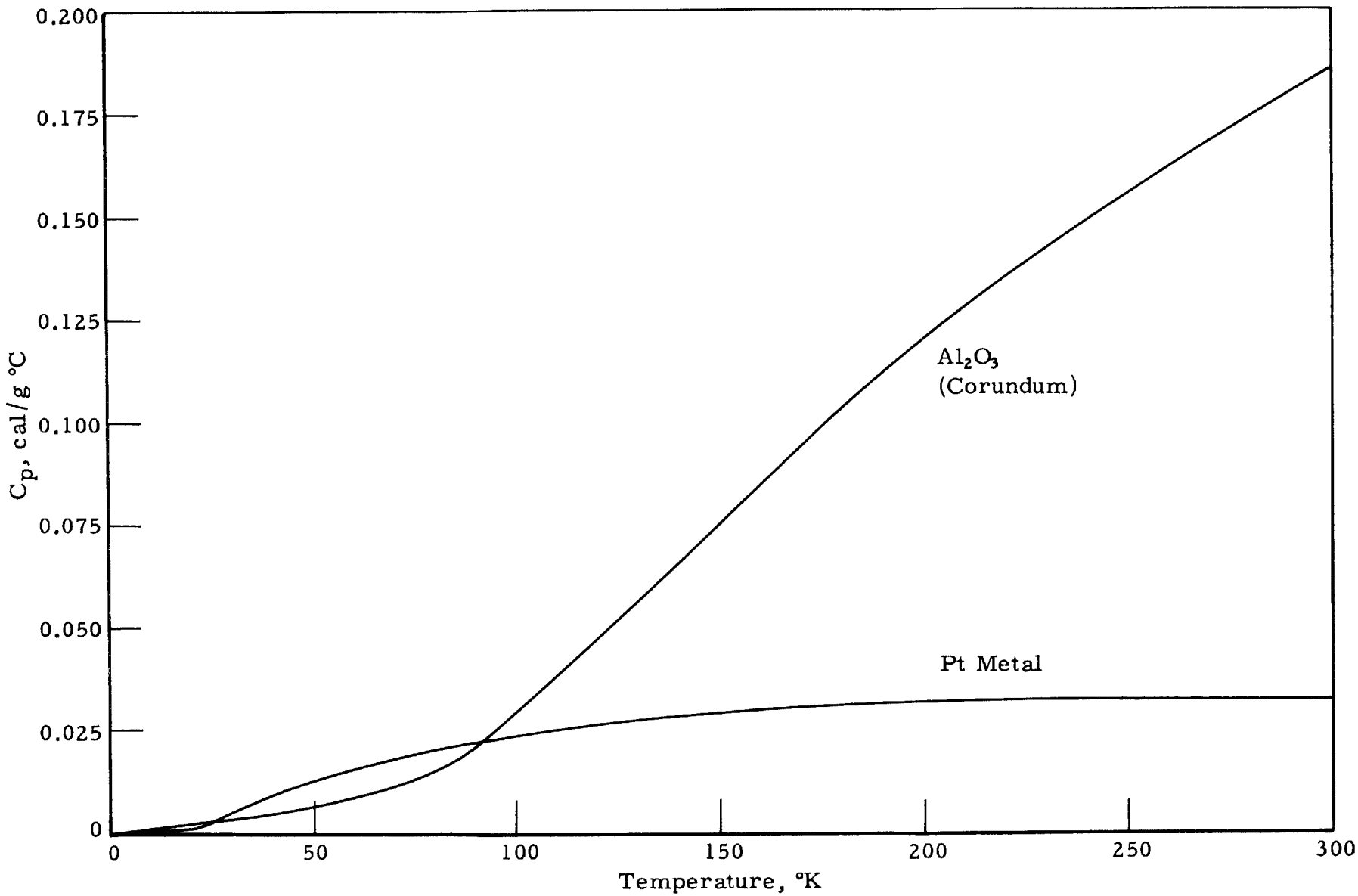


Figure 10. SPECIFIC HEATS OF ALUMINA [34] AND PLATINUM

## The Apparent Activation Energy for Reaction

The Arrhenius equation for the temperature dependence of the rate of a chemical reaction is

$$\text{Rate} = r = A \exp(-E/RT)$$

where E is the activation energy, R the gas constant, T the absolute temperature in °K, and A a constant. If now it is assumed that the rate of reaction which is first detected by the routine testing of this study is the same at least for a given series on the same support material, and that at detection the central thermocouple is recording the catalyst temperature, then we can write

$$r_D = A \exp(E/RT_D)$$

The constant A, often called the frequency factor, is a function of the number of molecules involved in reaction per gram of catalyst, and should be closely proportional to the active metal surface area, so that

$$r_D = BS \exp(-E/RT_D)$$

where B is a constant and S is the active surface per gram catalyst.

Using this relationship with the "as prepared" data for catalysts 9418-12A, -9F, and -12B of Table 16 gives three equations with only two unknowns if it is assumed that the active surface per gram catalyst is directly proportional to the total active metal content for a given metal composition. Pairing these equations gave values of 2.1 and 2.3 kcal/mole for the apparent activation energy of the hydrogen-oxygen reaction on Pt-Rh catalysts.

$$r_D = BS_1 \exp(-E/RT_{D1}) \qquad (1)$$

$$r_D = BS_2 \exp(-E/RT_{D2}) \qquad (2)$$

Dividing Equation 1 by Equation 2 gives

$$1 = S_1/S_2 \exp(E/RT_{D2} - E/RT_{D1})$$

taking logs gives

$$0 = \ln\left(\frac{S_1}{S_2}\right) + \frac{E}{RT_{D2}} - \frac{E}{RT_{D1}}$$

$$\ln\left(\frac{S_2}{S_1}\right) = \frac{E}{R}\left(\frac{T_{D1} - T_{D2}}{T_{D1} \cdot T_{D2}}\right)$$

and E can readily be calculated.

## Maximum Rate of Reaction Possible at Low Temperatures

Using the kinetic theory of gases and assuming values for the activation energy of the slowest step, the maximum possible rates of reaction of hydrogen with oxygen can easily be calculated as follows.

The kinetic theory of gases gives the number of molecules of a gas striking the surface/sec as being

$$V = \frac{kT}{(2\pi kT)^{1/2}} \frac{C_g}{m^{1/2}}$$

$$= 36.35 \frac{C_g T^{1/2}}{M^{1/2}} \times 10^3$$

where M = molecular weight, T is the absolute temperature °K, and $C_g$ is the number of molecules of gas per cc and

$$C_g = 9.65 \times 10^{17} \frac{P_g}{T}$$

where $P_g$ is the gas partial pressure in mm Hg.

For oxygen at -252°C (21°K), $V = 13.5 \times 10^{20} P_g$,

at -196°C (77°K), $V = 7.08 \times 10^{20} P_g$,

and at -78°C (195°K), $V = 4.44 \times 10^{20} P_g$ molecules/sec/cm$^2$.

Substituting these values into the Arrhenius equation gives the maximum possible rate of reaction

$$r_{max} = V \exp(-E/RT) \text{ molecules/sec/cm}^2$$

where E is the activation energy of the rate controlling step in the reaction, and R is the gas constant.

Values calculated from this equation for several assumed values of E are shown in Table 21. As can readily be seen from these results, with a catalyst of metal area of 50 m$^2$/g, an appreciable rate of reaction at temperatures in the region of -160°C can only occur if the activation energy of the reaction is 5 kcal/mole or less.

## Temperature Dependence of the Reaction Rate

The temperature dependence of a chemical reaction approximates to

$$\text{Rate} = r = A \exp(-E/RT)$$

where E is the apparent activation energy, R is the gas constant and T is the absolute temperature, °K. As the temperature falls and T becomes small, the rate r becomes increasingly sensitive to small changes in temperature.

Table 21. CALCULATED MAXIMUM POSSIBLE RATES

$P_g$ = 250 mm, V = ~4 x $10^{20}$
1 cc gas at -183°C and 250 mm Hg
contains 2.7 x $10^{18}$ molecules

| Temperature | | Rate, molecules/sec/$m^2$ | | |
|---|---|---|---|---|
| | | Activation Energy, E, kcal/mole | | |
| °C | °K | 10 | 5 | 2 |
| -196 | 77 | 2 x $10^{-2}$ | 6 x $10^{12}$ | 2 x $10^{21}$ |
| -183 | 90 | 5 x $10^{2}$ | 6 x $10^{14}$ | 1 x $10^{22}$ |
| -160 | 113 | 5 x $10^{7}$ | 2 x $10^{17}$ | 1 x $10^{23}$ |
| -130 | 143 | 5 x $10^{11}$ | 2 x $10^{19}$ | 9 x $10^{23}$ |
| -78 | 195 | 5 x $10^{15}$ | 2 x $10^{21}$ | 6 x $10^{24}$ |

For a small increase in temperature, $\Delta T$, the rate increases from $r_1$ to $r_2$ and

$$\frac{r_2}{r_1} = \exp\left[-\frac{E}{R}\left(\frac{1}{T + \Delta T} - \frac{1}{T}\right)\right]$$

$$\ln \frac{r_2}{r_1} = \frac{E}{R} \frac{\Delta T}{T_1(T_1 + \Delta T)}$$

The increase in rate expected from a 1°C and 10°C rise in temperature at temperatures down to that of liquid nitrogen are shown in Table 22. Even greater rate decreases would be expected for similar temperature decreases. The high sensitivity of the reaction rate to small variations in temperature at temperatures below that of liquid oxygen (-183°C) can readily be seen. These considerations also apply to rates of chemisorption, and unless chemisorption of the reactants occurs with extremely low activation energies, the possibility of obtaining catalytic reaction starting at liquid hydrogen temperature seems unfeasible.

Table 22. TEMPERATURE DEPENDENCE OF REACTION RATE

Activation energy E in kcal/mole

| Temperature | | | Increase in Rate, $r_2/r_1$ | | |
|---|---|---|---|---|---|
| °C | °K | $\Delta T$ | E = 0.5 | E = 2 | E = 5 |
| -153 | 120 | 1 | 1.02 | 1.1 | 1.2 |
| -153 | 120 | 10 | 1.2 | 2.0 | 5.4 |
| -183 | 90 | 1 | 1.04 | 1.1 | 1.4 |
| -183 | 90 | 10 | 1.3 | 3.2 | 18.5 |
| -253 | 20 | 1 | 1.9 | 7.4 | 513 |
| -253 | 20 | 10 | 81 | $\sim 6 \times 10^7$ | $\sim 10^{19}$ |

## The Rising Temperature Reactor

The same reactor design was used for both the isothermal and rising temperature reactions, and was of W-tube design of Pyrex glass as shown in Figure 3. The feed gases first passed through a pre-cooling limb before reaching the reactor proper, where they flowed down through the catalyst bed. Two different sized reactors were used and had the dimensions given in the figure. In the smaller reactor, 1 cc samples of 20-30 mesh catalyst granules were tested, while the larger reactor was used to test 2 cc samples of all catalysts having larger particles or pellets.

In early tests, slow poisoning of several catalysts on repeated testing was very apparent. The main cause of poisoning was finally traced to the presence of very small traces (<0.1%) of carbon dioxide in the He, 4% $H_2$ mixture (Matheson Company) which probably gave carbon monoxide on reduction over the catalyst during the 400°C pretreatment period. Carbon monoxide is a

known poison of Pt metal catalysts. Following this, the contaminated cylinders were evacuated overnight and fresh gas mixtures of 4% $H_2$ in He and 4% $O_2$ in He were made up using "Airco" helium, oxygen and hydrogen, and gas purification trains were installed in the gas lines to the test system.

Oxygen and helium-4% oxygen gases were first passed through a "Permasorb" filter-drier (M5-44 McIntire Company, Livingston, New Jersey), then through a 1-in. ID x 6-in. tube of 0.5% Pd/alumina at 100°C, and finally through a 1/2-in. ID x 12-in. tube of Ascarite (8-20 mesh, A. H. Thomas Co., Philadelphia) to remove carbon dioxide and water vapor. Hydrogen and helium-4% hydrogen gases were passed through a filter-drier, a tube of Ascarite, then through a 1/2-in. ID x 24-in. tube of active charcoal (baked out at 200°C) and finally through a 1/2-in. ID x 12-in. tube of 5% Pd/alumina at 100°C. Pure helium was passed through a filter-drier, active charcoal and 5% Pd/alumina at 100°C to remove water vapor, carbon dioxide, and other possible contaminants. These purified gas streams were then separately fed to the test apparatus and metered (Dwyer Magnehelic gages) to provide pre-treatment and feed mixture streams which were completely independent of each other. Both streams were flowed simultaneously, and could be switched through the reactor or to bypass using a four-way valve. The gas stream flowing to the reactor was further purified by passing through short 1/2-in. ID x 2-in. beds of indicating Drierite (10-20 mesh, Hammond Drierite Co., Xenia, Ohio) and Ascarite, then through a 1/2-in. ID x 18-in. tube of molecular sieve. Even so, traces of water vapor could still be detected in the gases reaching the reactor in the early tests, but slowly decreased as testing continued.

The reactor temperature was measured by an iron-constantan 30 B and S gauge thermocouple located at a level about 2 mm below the top of the catalyst bed in the central thermowell of the reactor. This thermocouple was connected through a reference ice temperature junction and switched to either a potentiomer (Rubicon Company) or a 0-10 mv, 11 in. scale potentiometric recorder (Honeywell-Brown). During each test the potentiometer was used to calibrate the recorder, and accuracies of better than ±0.5°C were obtained from the recorder reading at -190°C, and improved at higher temperatures. Any temperature difference between the catalyst bed and the incoming gases was detected by a differential thermocouple with both junctions located in the central thermowell as shown in Figure 3, and the potential measured on a 0-1 mv, 11-in. scale potentiometric recorder (Honeywell-Brown).

The standard routine test procedure adopted consisted of loading 1 cc of a catalyst having granules smaller than 10 mesh into the small reactor, flushing with 200 cc/min helium, then heating to 400°C for 10 minutes in 400 cc/min of helium, 50% hydrogen. During this pretreatment, the catalyst temperature was at 400°C for about 8 minutes. Following this, the reactor was cooled to -196°C in the same gas stream by liquid nitrogen over a period of about 5 minutes. At this temperature the feed mixture of 400 cc/min helium, 3% hydrogen, 1% oxygen was switched through the reactor, then exactly one minute later the liquid nitrogen bath was quickly replaced by a poorly insulated air bath which had been pre-cooled to -195°C with liquid nitrogen. This one minute delay was designed to absorb the heat of adsorption of oxygen on the catalyst, and to obtain a uniform temperature through the bed. It is now doubted that this was completed with the most active catalysts.

In the case of catalysts of medium activity, a few seconds after changeover the recorder readings would indicate a slowly rising temperature at about 10°C/min average which was almost linear with time. Reaction was detected first usually by deviation of the more sensitive differential couple recording from its almost constant reading, indicating a temperature increase in the bed over that of the incoming gases. Shortly after that, the temperature record would begin to rise more rapidly than its previously almost linear increase with time, and this acceleration would vary from catalyst to catalyst. Most error in determining catalyst activity occurred with catalysts having such slow accelerations that it was extremely difficult to exactly determine the temperature at which such acceleration began. The reason for this variation in catalyst behavior was not resolved but fortunately most catalysts gave rapid reaction acceleration.

Catalyst Stability Testing

The method used to test a catalyst's stability for use in a hydrogen-oxygen reactor consisted simply of exposing the catalyst for various periods of time to constant high temperatures in an atmosphere of about 85% hydrogen, 15% steam. This mixture is similar to that which would be formed from reaction of a fuel-rich hydrogen-oxygen mixture to give about 1000°C.

The furnace tube used to obtain the high temperatures was of "fused quartz" and mounted vertically with 12 in. in the furnace and 3 in. above the furnace. At the top was a 34/45 standard taper joint into which fitted a 6-in. Pyrex tube, narrowed at the top and having a narrow side arm through which nitrogen sweep gas could be flowed. Nitrogen or hydrogen were flowed through a thermostatted water saturator then up through the furnace tube.

Temperatures were measured using Pt/Pt-10% Rh thermocouples with a Rubicon potentiometer, and the furnace thermostatted by Celectray controller with Chromel-Alumel thermocouple.

The technique used consisted simply of loading a 1-2 cc sample of the catalyst into a fine mesh platinum gauze bucket (approximately 1 cm ID x 2 cm) and suspending it in the upper Pyrex tube from the thermocouple, which passed down through the narrow upper length of this tube. After sweeping out first with nitrogen, then with hydrogen-steam, and adjusting the furnace temperature, the sample was lowered into the center of the heated section of the furnace tube for an accurately controlled period of time. At the end of this period, the sample was quickly raised into the Pyrex section, swept with nitrogen and removed for testing in the rising temperature reactor. The delay between treating in this manner and testing varied greatly from several minutes to several days, but no appreciable change in activity was observed on repeat testing after being stored several days in small screw-capped bottles.

The temperature at the point in the region of the sample cycled ±5°C about the controlled temperatures of 1000, 1100, or 1200°C, and the sample was at furnace temperature in less than two minutes after lowering into position.

After prolonged use at 1200°C, crystallization and cracking of the silica tube became a problem. For any future work, impervious fused alumina tubes would be preferred.

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