JOURNAL OF CATALYSIS 4, 239-247 (1965)

The Catalyzed Low-Temperature Hydrogen–Oxygen Reaction

MICHAEL LADACKI, THOMAS J. HOUSER, AND ROBERT W. ROBERTS

*From Rocketdyne, A Division of North American Aviation, Inc.,
Canoga Park, California*

Received August 17, 1964; revised October 13, 1964

The activity of various metallic catalysts for the hydrogen–oxygen reaction at ambient and low temperatures (down to −196°C) was studied. The effects of various catalyst pretreatments, and of the changes of gas flow parameters, on the yield of water were examined. Nineteen custom-made and commercial supported catalysts were screened. The effective metals were palladium, platinum, and rhodium, while nickel gave disappointing results. The best combination for the low temperatures proved to be Pt–Rh–Pb on alumina. It was found that a high surface area and thorough drying of catalysts prior to runs at low temperatures were essential, and that the nature of the catalyst support was also important. The yields at low temperatures were sensitive to changes in the flow rates of gases. The results suggested that at low temperatures the catalyzed H_2–O_2 reaction may require a higher activation energy than the reportedly similarly catalyzed H–D isotopic exchange reaction studied by Boreskov.

INTRODUCTION

In contrast to other hydrogenation processes, the heterogeneously catalyzed H_2–O_2 reaction has been relatively unexplored. The metal-catalyzed H_2–O_2 interaction found some utilization in the purification of effluent gas streams at ambient or elevated temperatures. Otherwise there has been very little incentive for investigation of the industrially unprofitable H_2–O_2 process.

The space age has brought a new significance to the H_2–O_2 interaction, i.e., rocket propulsion. The reaction has to be triggered since the hydrogen-oxygen mixtures do not ignite on contact. Suitable catalysts for accelerating the reaction to the point of ignition are desirable. These catalysts have to be effective under severe environmental conditions, particularly low temperatures and high rates of gas flow.

The objective of the present investigation was to find and test effective catalysts under the above conditions. A large number of commercial and custom-made catalysts were to be evaluated for this purpose by some simple criteria of effectiveness. A practical approach was adopted, and the work involved simple comparative tests of moderate accuracy.

EXPERIMENTAL

Catalysts

Nineteen catalysts, obtained from various manufacturers, were selected for evaluation. These catalysts are listed in Table 1. Understandably, little information on these proprietory products was obtained. Several samples of greater interest were characterized in the laboratory, but many features, particularly methods of preparation, remained unknown.

Apparatus and Procedures

A simple flow system was adopted for comparisons of catalytic activity. Appropriate gas blends were introduced into an evacuated all-glass apparatus, passed through a catalyst layer in the U-tube reactor and then through a water absorber (Drierite) tube, and finally vented. The

TABLE 1
CATALYSTS TESTED

Code	Metal	Carrier	Size and shape	Color	Remarks
A-1	Pd	Alumina	1/8-inch spheres	Black	See Table 4
A-2	Pd	Alumina	1/8-inch spheres	Black	See Table 4
A-3	Pt-Rh	Alumina	1/8-inch sph. & cyl.	Black	See Table 4
A-4	Pt-Rh-Pb	Alumina	1/8-inch spheres	Black	See Table 4
B-1	Pt-Ni	Refractory	1/4-inch tablets	Grey	Reportedly 0.1% Pt, 3% Ni
B-2	Pd	Alumina	3/16-inch tablets	Light grey	Reportedly 0.05% Pd
B-3	Prom. Pd	Alumina	1/8-inch tablets	Yellow	Reportedly 0.03% Pd
B-4	Pd	Alumina	3/16-inch tablets	Light grey	Reportedly 0.05% Pd
B-5	Prom. Pd	Alumina	1/8-inch tablets	Orange	Reportedly 0.50% Pd
C-1	Pd	Alumina	3/16-inch tablets	Black	—
D-1	Ni	Mineral	1/8-inch tablets	Black	—
E-1	Pt	Ni-alloy	Metallic ribbon	Black	—
F-1	Pt	γ Alumina	1/8-inch cyl.	Light grey	Lower surface area than F-2
F-2	Pt	γ Alumina	3/16-inch cyl.	Grey	See Table 4
F-3	Cr	Alumina	1/8 × 1/4 extr.	Green	—
F-4	Pd	γ Alumina	1/8-inch cyl.	Light pink	—
F-5	Pd	Kaolin	0.15-inch cyl.	Grey	Reportedly 0.5% Pd
G-1	Pt	Silica gel	Irreg. particles	Black	Reportedly 6% Pt
G-2	Pt	Silica gel	Irreg. particles	Black	Reportedly 0.6% Pt

apparatus was fitted with a differential manometer and gas sampling tubes on the inlet and exit sides, and with a series of suitable bypasses. After each run, the system was purged with an inert gas or with one reactant only; the glass tubing was heated during the purge. Both the water absorber and the reactor were weighed before and after the run. The amount of water collected, expressed as per cent conversion, served as a criterion of catalytic effectiveness. Identical experimental conditions (rate of gas flow, ratio of reactants, duration of run, weight of catalyst, initial catalyst temperature) were used in each series, making the comparisons of catalytic activity possible.

In the preliminary runs, a small cylinder of premixed hydrogen and oxygen gases (2% O_2, 4% He, 94% H_2) was used, while helium served as a purging gas. This arrangement proved to be rather inflexible and somewhat hazardous. Therefore, the majority of experiments were performed using two cylinders of gas, 4% O_2 in nitrogen and 4% H_2 in nitrogen. The hydrogen–oxygen ratio was varied through the use of a gas proportioner. The apparatus was purged with the hydrogen–nitrogen mixture. The total amount of oxygen introduced served as a basis for calculations, except for one run in which hydrogen was in an amount less than stoichiometric (see Table 5).

The reproducibility of results was checked by several duplicate experiments, as shown in Table 2.

TABLE 2
TEST OF REPRODUCIBILITY

Catalyst	Catalyst temp. (°C)	Amt of H_2O collected (g)	% Conversion
A-3, 5 g	25°	0.363	91.7
A-3, 5 g	25°	0.365	92.2
A-4, 5 g	−196°	0.252	63.7
A-4, 5 g	−196°	0.244	61.5
A-4, 1 g	25°	0.344	87.4
A-4, 1 g	25°	0.330	83.5

Although some water might remain in the line, it could not exceed 1–2% since some runs yielded water corresponding to 98–99% conversion. To minimize any possible losses, the experiments were usually run for 10 min at relatively high flow rates, the amount of water corresponding to the complete conversion being rather large (usually 0.396 g). Consistency of results in various series indicated a satisfactory accuracy (±2%) of the method adopted.

For surface characterization of the catalysts, the Engelhard Isorpta Analyzer was used. This analyzer permits development of complete adsorption isotherms in a relatively short time with moderate accuracy, sufficient for most industrial applications. The nitrogen adsorption isotherm obtained provides information on surface area, total pore volume, and average pore diameter. In addition, pore-size distribution curves are obtainable, provided the number of steps taken in developing the isotherm is sufficiently large. The surface area is calculated by the usual BET method, while the BJH procedure (*1*) or newer methods, such as that of Anderson (*2*), can be utilized for the pore-size distribution. In this work, 12–14 steps were usually taken to reach $p/p_o = 0.93$, which corresponds to a pore diameter of 300 Å. The procedure, including the preliminary "degassing" of the sample (heating at approximately 300°C for at least 4 hr, while passing dry helium), required about 8 hr for one isotherm. The number of steps taken and the nature of information sought did not justify the laborious corrections used in the BJH procedure. However, the simple derivative curves, $\Delta V/\Delta d$ vs. d, which represented, somewhat crudely, the pore-size distributions, proved to be quite informative.

RESULTS

Initially, the activity of all the catalysts was compared under identical experimental conditions at ambient temperature. As a result, several catalysts appeared particularly promising. Further differentiation was effected in runs at low temperatures. Finally, the most interesting catalysts were used in series of tests examining the effect of various parameters.

(*i*) *Activity of Nontreated Catalysts*

The activity of nontreated catalysts at ambient and low temperatures is presented in Table 3; "nontreated" refers to catalysts as received and only vacuum-dried.

Ambient temperature. Runs conducted at 25°C separated the catalysts into effective and ineffective classes, there being practically no intermediate cases. The effective catalysts (except for G-1) were submitted to an independent outside laboratory for the spectrographic analysis, and the semiquantitative results (main components) are given in Table 4. The G-1 catalyst, according to the manufacturer, contained 6% platinum on silica gel. The effective catalysts contained Pd, Pt, or Pt-Rh and Pt-Rh-Pb combinations. They all had high surface areas and porosity. The disappointing ineffectiveness of the all-metallic catalyst E-1 was probably associated with its small surface area. The requirement of the high surface area is best illustrated by the catalysts F-1 and F-2 which reportedly had the same content of Pt and the same type of carrier, and differed only in their surface properties. The F-2 catalyst, having the surface area 238 m^2/g, was quite active, whereas the F-1 catalyst, with the surface area reduced by a factor of 2, proved to be ineffective under the test conditions. Of course, high surface area is only a prerequisite. Thus, the catalyst B-3 possessed favorable surface characteristics but proved to be ineffective, having nominally only 0.03% Pd. The pair of catalysts based on silica gel, G-1 and G-2, also serve as an example. These two catalysts had the same substrate and practically identical surface characteristics. The platinum-rich (6%) catalyst G-1 gave the quantitative conversion, whereas the G-2 catalyst, even at 0.6% Pt level, showed low activity.

Low temperatures. In this series, involving only effective catalysts, the long reactor tube was kept immersed in an appropriate cooling bath, ensuring that both the catalyst and the incoming gas were maintained at the desired temperature. Conversions at the dry ice temperature were not much different from those at ambient temperature. Runs at −196°C, however, provided a clear differentiation between the catalysts. Some surprisingly high conversions were obtained. The accumulation of ice crystals in the voids between the catalyst pellets was clearly visible. The water formed was prac-

TABLE 3
CATALYTIC ACTIVITY[a]

Catalyst	Pretreatment	Surface features (Isorpta): Surface area (m^2/g)	Pore volume (ml/g)	Average pore diam (Å)	% Conversion: 25°C	−80°C	−196°C
A-1	None	230	0.24	42	93.5	86.3	19.0
A-1	Repeated use	—	—	—	93.1	—	—
A-2	None	224	0.30	54	94.5	92.7	22.7
A-2	Repeated use	—	—	—	91.8	—	—
A-2	Thermal shock	—	—	—	83.0	3.7	2.7
A-3	None	251	0.28	44	92.2	87.5	24.2
A-3	Activation *in situ*	—	—	—	92.8	76.2	24.5
A-3	Repeated use	191	0.21	44	83.6	—	—
A-3	Thermal shock	—	—	—	94.6	83.1	8.2
A-4	None	460	0.58	50	95.7	87.4	63.7
A-4	Calcination	243	0.25	42	97.0	96.0	78.3
A-4	Thermal shock	172	0.22	51	94.5	64.2	17.7
B-1	None	—	—	—	2.0	—	—
B-2	None	—	—	—	2.3	—	—
B-3	None	288	0.38	52	3.8	—	—
B-3	Calcination	—	—	—	5.6	—	—
B-4	None	—	—	—	0.6	—	—
B-5	None	290	0.36	49	1.8	—	—
B-5	Calcination	216	0.30	56	67.0	19.8	3.3
C-1	None	—	—	—	0.9	—	—
D-1	None	189	0.14	29	2.5	—	—
D-1	Activation *in situ*	—	—	—	2.5	—	—
D-1	Calcination	—	—	—	2.5	—	—
E-1	None	18	0.007	—	6.8	—	—
E-1	Activation *in situ*	—	—	—	6.6	—	—
F-1	None	120	0.13	43	3.3	—	—
F-2	None	238	0.32	53	85.6	66.0	9.6
F-2	Thermal shock	142	0.22	62	63.6	19.5	5.9
F-3	None	—	—	—	2.3	—	—
F-3	Calcination	—	—	—	1.0	—	—
F-4	None	—	—	—	2.7	—	—
F-5	None	141	0.18	51	1.9	—	—
F-5	Calcination	—	—	—	2.0	—	—
G-1	None	566	0.25	18	99.9	34.4	12.2
G-2	None	542	0.22	16	8.8	—	—

[a] Experimental conditions: Catalyst, 5 g; Reactants, 4% H_2 in nitrogen and 4% O_2 in nitrogen, H_2/O_2 molar ratio 3:1, total gas flow rate 2330 cc/min, linear velocity 41 cm/sec; duration of run, 10 min, preceded by 2-min hydrogen lead; theoretical yield, 0.396 g water.

tically all retained in the reactor, the Drierite tube serving mainly for collection of vapor from the connecting tubing which was heated and purged following the run. It was found that, whereas the gradual accumulation of ice and moisture on catalyst pellets during the run had relatively little effect on the reaction except for physical blocking, evidenced by rising back-pressure, the initial presence of moisture at the start of the low-temperature run was very detrimental to activity. Apparently, a different degree of blocking of inner pores or active sites was involved in these two cases. Therefore, a thorough drying of the catalyst before each run at low temperature became absolutely essential.

One practical expedient was found useful:

TABLE 4

SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF SOME CATALYSTS

	A-1	A-2	A-3	A-4	F-2
Aluminum	47	48	48	52	52
Silicon	4.0	3.6	4.0	0.096	0.035
Palladium	0.29	0.27	0.001	Nil	Nil
Platinum	Nil	Nil	0.26	0.13	0.14
Rhodium	Nil	Nil	0.58	0.14	Nil
Sodium	0.61	0.92	0.23	Trace	Trace
Calcium	0.023	0.021	0.027	0.001	0.003
Lead	Nil	Nil	Nil	0.13	Nil

The final drying of a catalyst could be done by passing the reactant gases through it at ambient temperature for a few minutes (the moisture formed being vented through a bypass). It was found that no water was retained by the catalyst under these conditions. Also, it was found beneficial to alternate runs between ambient and low temperatures when working with the same catalyst sample.

The runs at low temperatures demonstrated the superiority of the A-4 catalyst, i.e., the Pt-Rh-Pb combination. Singly, palladium appeared to perform better than the platinum metal. The silica-gel-based G-1 catalyst exhibited only a mediocre performance at low temperatures, despite its inordinately high content of platinum (6%) and a large surface area. Although one might associate this mediocre activity with the small average pore diameter in the catalyst, it is more likely that the effect was simply due to the avidity of silica gel for water and the early permeation with moisture of small particles of the carrier.

(ii) *Effects of Catalyst Pretreatments*

The effects of various treatments of catalysts prior to the runs are shown in Table 3. The pretreatments were carried out on many catalysts, including some originally ineffective ones. In view of the unknown history of catalysts, the results of these treatments are mainly of practical interest.

Activation in situ. Several catalysts were "activated" *in situ* prior to tests, by heating at 300–320° for 2 hr in a hydrogen atmosphere. Table 3 indicates that this treatment essentially brought no improvement. Apparently, the 2-min lead of hydrogen in normal runs was already sufficient to remove adsorbed oxygen from the noble metal catalysts. One manufacturer indicated that any attempts to activate his catalysts would be not only redundant but possibly detrimental.

Calcination. It was noted that some catalysts changed color on roasting in air. In the case of catalysts containing "promoted palladium" as a coating, the color change was dramatic (Catalyst B-3 from yellow to white, Catalyst B-5 from orange to black) indicating volatilization or modification of the promoter. The effects of such "calcination" (heating in air at 600°C for 2 hr) on catalytic activity and surface characteristics of several catalysts were, therefore, examined. Table 3 shows the activity of some nontreated and calcined samples differed considerably, while others remained inactive even after the treatment. The burst of activity of the B-5 catalyst (promoted Pd) can be attributed to the removal of a promoter and uncovering of the latent active noble metal (nominal 0.5% Pd). The enhancement of activity of the A-4 catalyst will be tentatively discussed later. The calcination resulted in a decrease of surface areas. Figure 1, comparing the pore-size distribution of the nontreated and calcined B-5 catalyst, shows this decrease of surface area occurred at the expense of small pores, while the proportion of larger pores actually increased.

Thermal shock treatment. In this test (also termed the "sauna treatment") the catalyst pellets were chilled with liquid nitrogen, placed in a muffle furnace at

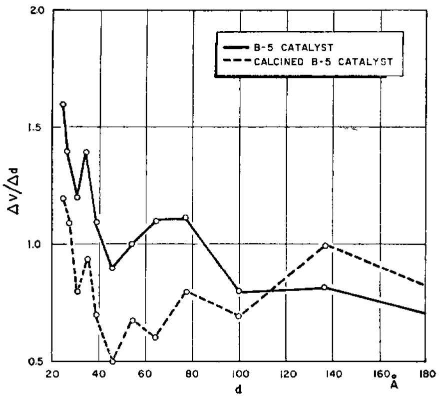

FIG. 1. Pore-size distribution. For Catalyst B-5.

1000°C for 10 min, and then plunged into liquid nitrogen. Essentially, this drastic treatment tested the mechanical stability of carriers. As anticipated, smaller pellets (⅛ inch) performed better than the larger ones (¼ inch). Table 3 shows that the catalytic activity of treated samples decreased considerably, particularly at low temperatures. Moreover, there was a different pattern of this decrease for each catalyst tested (compare A-2 with A-3 and F-2).

Repeated use. The results from samples of three catalysts which had been repeatedly used in larger-scale field tests and subjected to high temperatures and mechanical attrition, were compared with those obtained from fresh ones. The Catalyst A-3 had been used particularly extensively; it contained some broken pellets and a powdery, partly fused material. Table 3 shows the effect was relatively small; the catalysts tested exhibited a good retention of their effectiveness. Figure 2 compares the pore-size distribution of the fresh and the used A-3 catalyst. The curve for the used sample, although lower (corresponding to the reduced surface area), retains the original shape, indicating no permanent changes occurred due to a possible preferential utilization of some specific pore range. This behavior could be expected from the gaseous reactants and the volatile product.

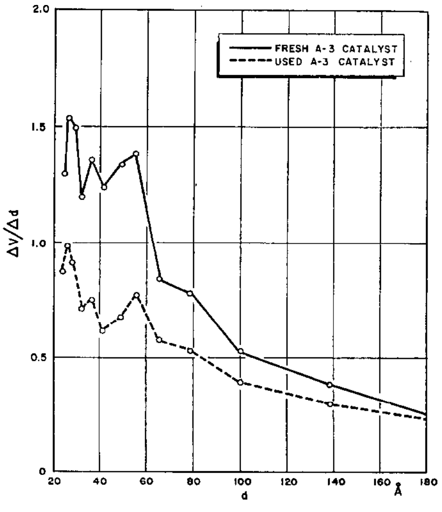

FIG. 2. Pore-size distribution. For Catalyst A-3.

(*iii*) *Effects of Other Parameters*

Hydrogen/oxygen ratio. The gas proportioner used permitted the molar hydrogen/oxygen ratio to vary; the effect is shown in Table 5. Actually, the results are not strictly comparable, since the gas flow rates varied somewhat in these runs. Nevertheless, the expected trend is noted. The best results are obtained at ratios near stoichiometric, otherwise the excess component gas acts as an extra diluent and coolant.

TABLE 5
EFFECT OF THE MOLAR HYDROGEN/OXYGEN RATIO

Catalyst	H_2/O_2 ratio	Gas flow rate (cc/min)	Linear velocity (cm/sec)	% Conversion (25°C)
A-4, 1 g	3:1	2330	41	87.4
A-4, 1 g	1:1	1220	23	85.6[a]
A-3, 5 g	3:1	2330	41	92.2
A-3, 5 g	47:1	3030	53	80.0
A-1, 5 g	3:1	2330	41	93.5
A-1, 5 g	47:1	3030	53	88.7

[a] Conversion calculated on the basis of the amount of H_2 supplied.

Velocity of gases. In several experiments the linear velocity of gases (based on the empty reactor) was varied, from 16 to 51 cm/sec (corresponding to the variation of the contact time from 0.3 to 0.1 sec, respectively). Parallel runs were carried out at ambient temperature and at −196°C, and the results are collected in Table 6. At ambient temperature the conversions were somewhat higher at lower gas velocities, i.e., at longer contact times, as expected. Runs at −196°C, however, showed the opposite effect. The fast-moving gases gave high conversions. The conversions dropped considerably when the gas stream was slowed down, apparently due to a more efficient precooling of the gas, and also possibly to a more localized blocking of pores.

TABLE 6
EFFECT OF THE VELOCITY OF GASES[a]

Flow rate (cc/min)	Linear velocity (cm/sec)	% Conversion	
		25°C	−196°C
3020	51	96.7	90.7
2330	41	97.0	78.3
1430	25	99.8	70.9
886	16	98.4	25.4

[a] Catalyst, calcined A-4, 5 g; H_2/O_2 ratio, 3:1; duration of run, 10 min.

Conversion vs. time. To extend runs to longer times, lower flow rates of gases had to be adopted. The results are shown in Table 7. Runs at ambient temperature gave practically quantitative conversions. Experiments at −196°C were plagued by rising back-pressure, and drops in yields were pronounced. No permanent deactivation was observed; redried catalysts exhibited the original activity.

TABLE 7
CONVERSION VS. TIME[a]

Duration of run (min)	Linear velocity (cm/sec)	% Conversion	
		25°C	−196°C
5	16	97.6	36.5
10	16	98.4	25.4
20	16	99.9	—
40	16	99.8	—
10	25	99.8	70.9
30	25	—	50.2

[a] Catalyst, calcined A-4, 5 g; molar ratio H_2/O_2, 3:1.

(iv) *Other Tests*

Upon heating in a drying oven at 250°C for 4 hr, the nontreated A-4 catalyst registered 10.8% weight loss, in contrast to other catalysts for which the weight losses were in the order of 2–4%. It was also found after a nonisothermal run at ambient temperature that the A-4 sample in the reactor suffered a 10.1% weight loss, while the corresponding weight was additionally gained in the water absorber. These facts suggest the A-4 catalyst was originally in the form of alumina trihydrate (gibbsite) which changes to the dihydrate at 200°C, the theoretical weight loss being 11.5%. It can be inferred also that the catalyst in the reactor reached 200°C temperature during this 10-min run started at the room temperature.

DISCUSSION

Perhaps the studies most relevant to this work are those by G. K. Boreskov and coworkers in Russia in the period 1952–57. Boreskov (*3*) investigated the effectiveness of Fe, Co, Ni, Cu, Rh, Pd, Pt, Ag, and Au as catalysts in the H_2–O_2 reaction. Pure metals (wire, foil, sponge) were studied in a circulatory flow system at elevated temperatures, and the "specific catalytic activity" (activity per unit of surface) was determined from the reaction rates. The best catalysts were Pd, Pt, and Ni, and also some Pt-Au and Pt-Ag alloys. The specific activity was independent of the method of preparation, crystal size, surface area, or thermal treatment. In a later paper, Boreskov (*4*) modified his conclusion on the effect of heat treatment: Heating of catalysts in hydrogen was beneficial and heating in air detrimental to the initial activity. With use, however, the activity converged asymptotically to a stationary value. Independence of the specific activity on the surface area was confirmed. This time, a supported Pt catalyst (0.2% Pt on silica gel) was examined, in addition to Pt wire and foil, and conformed to the general conclusions.

Although the concept of "specific catalytic activity" may be fundamental for the choice of metals, it has to be supplemented by comparisons of the actual activity of practical catalysts. In the present work, Pd and Pt showed high activity. In addition, rhodium emerged as a particularly effective metal. The best combination proved to be Pt-Rh-Pb; although some of these metals might have been used to improve deposition of the main component (Rh) on the carrier, synergistic effects should not be excluded. It is significant that in Boreskov's work the alloys Pt-Au and Pt-Ag proved to be more effective than the single components; thus synergistic effects are evidenced.

Rhodium showed no outstanding activity in Boreskov's work at elevated temperatures. However, Rh is an excellent catalyst for the hydrogenation of ethylene (better than either Pt or Pd), as shown by Beeck (*5*). Furthermore, Rh is selectively effective in the hydrogenation of benzene and heterocyclics in the liquid phase. A recent patent (*6*) claims specifically that the Pt–Rh combination is useful for the ignition of jet fuels. The effectiveness of the Pt–Rh combination in this work was not entirely unexpected.

Nickel stands high among the Boreskov's effective catalysts. In addition, Beeck (*7*) found a high mobility of chemisorbed H atoms on Ni at very low temperatures. However, limited experiments with the Ni-containing catalysts in this work gave disappointing results.

The prerequisite of the high surface area, demonstrated in this work, is consistent with Boreskov's conclusion on independence of the "specific catalytic activity" on surface area. Our findings on the effect of calcination are in variance with his conclusion on the immediate effects of heating in air. However, the presence of a carrier, and the unknown past history of the catalyst introduce complications. The observed enhancement of actual activity of the A-4 catalyst after calcination cannot be attributed to changes in surface characteristics, which are unfavorable. Other changes pertaining to the carrier (a more efficient drying, expulsion of the water of hydration, etc.) might be overriding. Nonetheless, some favorable changes in the nature of the metallic coating could have also occurred. Chu (*8*) finds that the prolonged heating in air at 600°C of supported platinum (on alumina) considerably increases its content of metallic crystallites.

The mechanism of the H_2–O_2 reaction at low temperatures may differ from that at high temperatures. Avdeenko, Boreskov, and Slin'ko (*9*) studied the mechanism of the catalyzed H–D isotopic exchange reaction at both high and low temperatures. That investigation is of particular interest since it stressed a direct parallelism (at high temperature) of the H–D exchange with the previously studied H_2–O_2 reaction. Figure 3, quoted from that work, compares the behavior of the Pt-Au alloys in both cases, and demonstrates the previously mentioned synergistic effects.

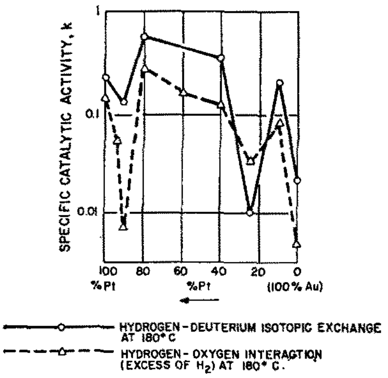

FIG. 3. Parallelism in rates; from Avdeenko, Boreskov, and Slinko (ref. *9*).

Avdeenko *et al.* postulate two mechanisms for the H–D exchange reaction:

(1) The Rideal-Eley mechanism (chain reaction involving a positively charged complex with catalyst) at low temperatures, 90–200°K, the activation energy being only 0.3 kcal/mole.

(2) The Bonhoeffer-Farkas mechanism (adsorption–desorption) at higher temperatures, 293–473°K, with the activation energy of 7.5 kcal/mole.

The present results (Table 3) show that the low-temperature performance of effective catalysts was not entirely predictable from their high-temperature behavior.

Hence, the nature of the low-temperature H_2–O_2 reaction may differ from that at elevated temperatures. Attempts to elucidate a mechanism would require separate extended studies and a more sophisticated experimental setup; this was outside the scope of our work. The observed pronounced dependence of rates on the velocity of gases (hence on variations in their actual temperature, within small range) in the low-temperature runs is inconsistent with the low activation energy postulated for the reportedly parallel H–D reaction. We can only conclude the extension of the analogy between the H–D and the H_2–O_2 reactions to low temperatures may not be valid, and indicate the necessity for a more systematic basic study.

ACKNOWLEDGMENTS

The assistance of E. Gross for the determination of the surface areas and pore volumes is gratefully acknowledged.

This project was sponsored by NASA Office of Advanced Research and Technology (Contract NAS 3-2565), and coordinated through Mr. J. Gregory, ARTB, Lewis Research Center, Cleveland, Ohio.

REFERENCES

1. BARRETT, E. P., JOYNER, L. G., AND HALENDA, P. P., *J. Am. Chem. Soc.* **73**, 373 (1951).
2. ANDERSON, R. B., *J. Catalysis* **3**, 50 (1964).
3. BORESKOV, G. K., *J. Chim. Phys.* **51**, 759 (1954); *Chem. Abstr.* **49**, 7350 (1955).
4. BORESKOV, G. K., SLIN'KO, M. G., AND CHESALOVA, V. S., *Zh. Fiz. Khim.* **30**, 2787 (1956); *Chem. Abstr.* **51**, 13539 (1957).
5. BEECK, O., *Advan. Catalysis* **2**, 151 (1950).
6. ANDERSON, E. P., U.S. Patent 3,085,402, April, 1963 (to Engelhard Industries, Inc.).
7. BEECK, O., *Rev. Mod. Phys.* **20**, 127 (1948); quoted in "Catalysis" (P. H. Emmett, ed.), Vol. V, p. 309. Reinhold, New York, 1957.
8. CHU, B., *J. Phys. Chem.* **67**, 1916 (1963).
9. AVDEENKO, M. A., BORESKOV, G. K., AND SLIN'KO, M. G., *Probl. Kinetiki i Kataliza* **9**, 61 (1957); *Chem. Abstr.* **53**, 7740 (1959).