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On the Reduction of Tungsten Trioxide Accelerated by Platinum and Water

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The reduction of WO_3 by H_2 to a blue form proceeds readily above 400°C. If the WO_3 powder is mixed with platinum black, reduction will start below 100°C. But if this mixture is made to adsorb water, reduction takes place rapidly at room temperature. The catalysis by platinum is apparently due to the dissociation of molecular hydrogen on the metal, followed by diffusion of adsorbed hydrogen atoms across the metal–oxide interface. The acceleration by water is ascribed to a marked increase in the rate of diffusion of the reducing species.

INTRODUCTION

Since the early experiments of Kobosew and Nekrassow (*1*) in 1930, the reduction of tungsten trioxide, WO_3, to a blue form in the presence of metals has been studied under a variety of experimental conditions, an excellent summary of which may be found in a paper by Foresti and Musumeci (*2*). More recently Khoobiar (*3*) and Kohn and Boudart (*4*) have reported that the blue reaction may be obtained by passing hydrogen at room temperature over WO_3 mixed with a catalyst consisting of platinum supported on alumina.

In all of these studies no measurement of the rate and amount of hydrogen uptake was made during the reduction of the oxide. Preliminary experiments by us with WO_3-Pt-Al_2O_3 mixtures at room temperature indicated that *the visible reduction is accompanied by a very rapid and massive consumption of hydrogen.* However, when these experiments were repeated under carefully controlled conditions in a high-vacuum apparatus, we experienced considerable difficulty in reproducing the effects, in agreement with observations of Hartog and Pitkethly (*5*), and we soon concluded that *water has a profound and favorable effect on the reaction.* To study this phenomenon, we eliminated the alumina, which made it difficult to control the amount of water present in the reaction system, and most subsequent studies were carried out with mixtures of platinum black and tungsten trioxide.

The work reported here was undertaken to study in some detail and under a variety of controlled experimental conditions the rate and extent of reduction of WO_3, which proceeds without oxygen elimination to form hydrogen analogs of tungsten bronzes with a gross molar composition of $H_{0.35}WO_3$. Emphasis was placed on the rapid reduction at room temperature.

EXPERIMENTAL

A conventional gas volumetric system in the modification of Krieger (*6*) was used to prepare gas mixtures and to measure the constant-volume hydrogen uptakes. Auxiliary equipment consisted of a mercury diffusion pump backed by a mechanical pump and isolated from the adsorption apparatus by a liquid nitrogen trap. The samples were protected from mercury vapor by means of a small trap filled with gold powder and were held in place with a mini-

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mum amount of Pyrex glass wool which had been boiled in concentrated nitric acid to remove oils. Portable furnaces and liquid baths were used to obtain the desired temperatures. The low-volume sample chambers had separate capillary stopcock connections to the gas burette and to a water reservoir so that water vapor could be added to the samples to a known pressure before admitting hydrogen. This pressure will be referred to as initial P_{H_2O} (see Table 3).

Matheson electrolytic hydrogen was purified by passage through a Milton Roy Company palladium purifier. Matheson extra-dry oxygen was dried further by passage through a Dry Ice-acetone trap. Matheson helium, used for dead-space determinations, was passed through a liquid nitrogen trap; the dead space was always determined at the end of an experiment to minimize contamination of the surfaces with traces of oils. Distilled water was freed of dissolved gases by boiling, freezing three times in liquid nitrogen, and pumping while the ice melted.

A powder of WO_3 was prepared from Matheson, Coleman and Bell reagent H_2WO_4. After boiling in distilled water and filtering while hot to remove soluble substance, the H_2WO_4 was dried in an oven for 5 hr at 150°C and then dehydrated by evacuation with the diffusion pump for 12 hr at 250°C. The resultant oxide, which was partially reduced to a greenish form, was reoxidized to yellow WO_3 by heating in O_2 at 400°C for 4 hr. Two preparations of WO_3 had surface areas of 11.1 and 17.4 m^2/g, as determined with nitrogen by a Perkin-Elmer Model 212C Sorptometer. In the preparation of samples which contained H_2WO_4, Matheson, Coleman and Bell reagent grade H_2WO_4 was used as received. Platinum black from Engelhard Industries, Inc., stated to be 100% pure, was used as received; its surface area, determined by the Sorptometer, was 23 m^2/g, and it took up 760 μmoles H_2/g by the method described by Benson and Boudart (7).

Data on the samples and their preparations are summarized in Table 1. Sample No. 3, prepared by shaking the components in a vial, was very nonuniform and contained coherent lumps of WO_3. Sample weights from 0.3 to 5 g were used in individual runs. The pretreatment used in each case is described in detail in the next section.

TABLE 1
PREPARATIONS OF SAMPLES

Sample No.	% Pt by Wt	Support	Preparation
1	2.5	WO_3	Components ground in a mortar for 30 min
2	2.5	H_2WO_4	Components ground in a mortar for 30 min
3	2.5	WO_3	Components shaken in a glass vial for 10 min
4	~0.1	WO_3	Impregnation of WO_3 with H_2PtCl_6 followed by calcination in air for 10 hr at 425°C and then for 3 hr at 600°C

RESULTS

A yellow powder of WO_3 which had been degassed at 250°C for 12 hr took up no detectable amount of hydrogen at temperatures below 200°C; after raising the temperature over a period of 7½ hr to 425°C in about 300 Torr H_2, the powder was noticeably darker and had taken up 110 μmoles H_2/g, an amount which therefore may be regarded as the critical amount that makes the reduction just visually detectable. Above 425°C the reduction to a blue oxide proceeded quite rapidly. When WO_3 was exposed to around 300 Torr H_2 containing 2.5% H_2O, essentially the same behavior as that above was observed; no significant reduction occurred at temperatures below 400°C. A thick paste of WO_3 and water also exhibited no uptake of hydrogen up to 117°C, when the experiment was discontinued.

The dramatic difference between pure WO_3 and mixtures of WO_3 with platinum is evident from the qualitative data in Table 2. These data were taken on portions of Sample No. 1 exposed to approximately 300 Torr of dry H_2 at room temperature. This table clearly shows the effect of varying amounts of water on the rate of H_2 uptake. We have verified many times this effect of water; so long as water is carefully removed from the sample, such as by outgassing for

TABLE 2
EFFECT OF TIME AND TEMPERATURE OF OUTGASSING ON UPTAKE OF HYDROGEN AT ROOM TEMPERATURE BY Pt-WO_3 (No. 1)

Temperature of outgassing (°C)	Time of outgassing (minutes)	Contact time (minutes)	Total uptake (μmoles H_2/g mixture)
23	5	20	330
23	2	5	350
25	720	60	120
105	60	60	16[a]

[a] Corresponds closely to 19 μmoles H_2/g mixture, calculated from 760 μmoles H_2/g Pt black.

2 hr at 105°C, no H_2 uptake is observed at room temperature even over long times, except for the small amount which reacts immediately with the Pt black present. Furthermore, the manner in which water is introduced has a profound effect on the rate of H_2 uptake. For example, if about 300 Torr H_2 containing 4% H_2O vapor or 0.7% O_2 is added at room temperature to thoroughly outgassed portions of Sample No. 1, no rapid uptake of H_2 is observed. If, however, the outgassed Pt-WO_3 is first equilibrated with water at about 20 Torr and then about 300 Torr H_2 added, the sample takes up large amounts of H_2 rapidly at room temperature and turns intensely blue in a manner similar to that reported by Khoobiar (*3*) for a mixture of WO_3 and platinum-alumina.

From the preliminary observations above we adopted two standard procedures of outgassing. (1) Outgassing for 2 hr at 105°C left the platinum surface in the oxidized form and was sufficient to prevent any significantly large uptake of hydrogen at room temperature when the samples were exposed to around 300 Torr H_2 in the absence of water vapor. (2) In some experiments we removed oxygen from the platinum surface by the method of Aston (*8*). After a standard 2-hr outgassing at 105°C, the sample was treated with dry H_2 at around 300 Torr at room temperature for 30 min, followed by another standard 2-hr outgassing at 105°C.

These outgassing procedures enabled us to conduct semiquantitative experiments on the effect of such factors as dispersion and content of metal, state of the platinum surface, water vapor pressure, extent of contact between platinum and WO_3, and the presence of inert diluents as heat sinks.

Portions of Sample No. 1 that had been given pretreatments (1) or (2) and then heated in 300 Torr of dry H_2 began to take up significant amounts of H_2 slowly at around 90°C, the rate of the reduction increasing as the temperature continued to rise. We were unable to make meaningful measurements of the rate of this process, but it was evident that dried Pt-WO_3 could be reduced at temperatures lower than for WO_3 alone and higher than wet Pt-WO_3.

The conditions and results of the rate experiments on Pt-WO_3 and Pt-H_2WO_4 are given in Table 3 and Fig. 1. The final H_2 uptakes are given at the far right of Fig. 1; these values were taken when further uptake was almost undetectable.

In spite of uncertainty as to the amount of water present in the vapor phase and the consequently semiquantitative nature of the calculations, the results were surprisingly reproducible in duplicate runs. The one exception was for the sample prepared by shaking Pt black with WO_3; this probably was due to the inhomogeneity of the preparation, which made it impossible to perform the experiment with the same inhomogeneous sample in duplicate runs.

The adsorption of water on WO_3 (17.4 $m/^2g$) was estimated by weighing samples of WO_3 before and after exposure at room temperature to water vapor at 20 Torr. In three experiments the weights adsorbed per gram of WO_3 and the times of contact with water vapor were 7 mg in 2 min (approximately the time of contact with water vapor before uptakes of hydrogen were measured), 13 mg in 30 min, and 11 mg in 30 min. With 10^{19} adsorption sites/m^2 WO_3, the smallest coverage of WO_3 by water in these experiments corresponds roughly to the ratio $(7 \times 10^{-3}/18)\ (6 \times 10^{23})/(17.4)\ (10^{19}) \cong 1.3$ water molecules/site. We conclude that WO_3 is covered with at least a monolayer of water at 20 Torr; possibly only a partial monolayer is attained at 10 Torr H_2O.

X-ray powder patterns were taken on some of the samples. Dry WO_3 and WO_3 which had been exposed to 20 Torr of water vapor showed identical patterns with all

TABLE 3

Conditions of Experiments in Fig. 1[a]

Curve	Data points	Sample[b]	Pretreatment[c]	Initial P_{H_2O} (Torr)	Initial P_{H_2} (Torr)
A	⊙	No. 1	(1) (oxidized Pt)	24	318
A	+	9 parts by wt powdered Al to 1 part by wt No. 1	(1) (oxidized Pt)	22	298
A	⊡	No. 1 pelleted at 3000 psi	(1) (oxidized Pt)	25	250
B	⊙	No. 1	(2) (reduced Pt)	21	308
B	×	7.5 parts by wt powdered glass to 1 part by wt No. 1	(2) (reduced Pt)	19	301
C	⊙	No. 1	(2) (reduced Pt)	10	297
D	⊙	No. 3	(1) (oxidized Pt)	24	283
E	◈	No. 2	(1) (oxidized Pt)	19	296
F	⊙	No. 2	(1) (oxidized Pt)	0	316
G	⊙	No. 4	(2) (reduced Pt)	24	279

[a] All at room temperature.

[b] See Experimental Section.

[c] See Results Section.

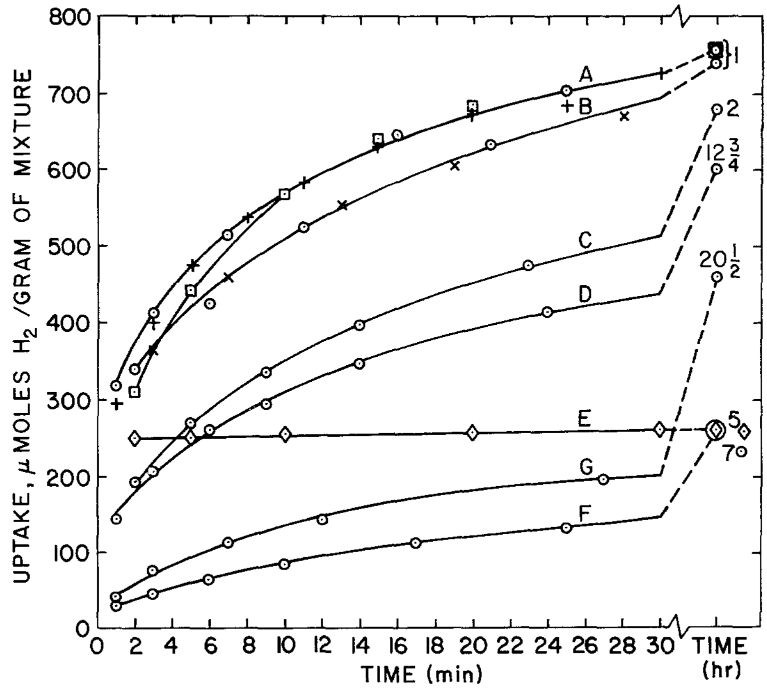

Fig. 1. Hydrogen uptakes for runs described in Table 3.

of the peaks assignable to WO_3; there was no evidence of H_2WO_4 in the patterns, and line-broadening indicated crystallites of about 1000-Å diameter. Powders of Pt-WO_3 which had been treated with hydrogen to form the blue reduced form showed patterns characteristic of $H_{0.33}WO_3$ and/or $H_{0.5}WO_3$ as reported by Glemser and Naumann (*9*). Although it was not possible to distinguish between these, the line intensities indicated that reduction in depth had occurred to form these hydrogen analogs of tungsten bronzes.

DISCUSSION

In the presence of an amount of platinum sufficient to adsorb less than 20 μmoles of hydrogen, a powder of WO_3 with enough water to form a little over a monolayer on its surface is able to take up, at room temperature, 375 μmoles of hydrogen in 2 min and another 375 μmoles over an hour.

These are very large amounts and correspond to a gross molar composition $H_{0.35}WO_3$ for the reduced blue powder. Reduction in bulk is indicated by the X-ray patterns taken on Sample No. 1; these showed, after exposure to hydrogen, the existence of the phases $H_{0.33}WO_3$ and/or $H_{0.5}WO_3$ in a depth adequate to give sharp X-ray lines.

The speed and extent of this bulk reduction at room temperature are the characteristic novel findings which differentiate the present work from previous observations (*3*, *4*) that relied on a visual change of color. It is now clear that both platinum and water are necessary for the rapid reduction at low temperature; indeed, a powder of WO_3, dry or wet, is reduced only above 400°C, and a mixture of platinum and tungsten trioxide, which has been dried but may still contain traces of water, is reduced only around 100°C at a slow rate. It appears therefore that platinum is required to dissociate molecular hydrogen into "active" forms which must then be transported away to the tungsten oxide particles, the rate of transport being accelerated by water.

First consider the production of the "active" species. The near coincidence of Curves A (upper branch) and B (Fig. 1) establishes that the rate and extent of reduction do not depend significantly on whether oxygen is initially present on the platinum surface or not. The slightly higher amounts taken up indicated by the upper branch of curve A are probably due to the reaction of H_2 with the surface PtO present. If a correction is made for the 19 μmoles H_2/g of mixture which reacted with surface PtO, the two curves are in quite good agreement. In particular, the final amounts taken up in both sets of data coincide if this correction is made.

It will also be noted on Fig. 1 that in both cases A and B the rate and extent of reduction are not affected at all by diluting the mixture with an inert material in large excess, aluminum or powdered glass. This point is particularly valuable for the A runs where the exothermic reaction taking place initially between H_2 and surface PtO might have distorted the results. It can be concluded that the phenomena observed are not artifacts due to eventual heating of the mixtures.

It has been argued recently by Kohn and Boudart (*4*), following previous arguments of Taylor (*10*), that the release of hydrogen atoms into the gas phase from a platinum surface cannot take place at low temperature unless oxygen atoms are preadsorbed on the platinum surface. While such a phenomenon remains entirely possible, the close correspondence between the runs represented by Curves A (upper branch) and B leads us to conclude that under our experimental conditions reduction is not occurring by mass transfer of free hydrogen atoms through the gas phase. Another reason for believing that preadsorbed oxygen on platinum is not required for the reduction of WO_3 at room temperature is the fact that most of the massive uptake proceeds long after the surface PtO has reacted with the large excess of hydrogen in the system.

The main argument against the release of hydrogen atoms into the gas phase in order to explain the reduction is, however, quantitative. The release of 1500 μmoles of free H atoms (i.e., 30 cc NTP) into the gas phase from 25 mg of platinum in contact for 1 hr with hydrogen at room temperature, with or without adsorbed oxygen, is simply unthinkable.

If the role of platinum were to generate a few free atoms into the gas phase, it would be necessary to postulate *in addition* a chain reaction at the surface of WO_3 through which *many* hydrogen molecules would be able to participate on a site that would have been "activated" by atomic hydrogen. Intriguing as this concept of chain reaction may be, we have not observed any fact in its favor. Thus, we have found no evidence that the rapid reduction of tungsten trioxide with molecular hydrogen could be triggered at high temperature (around 400°C), or as an electrical discharge is passed through the gas, or as the sample is exposed to γ rays from a Co^{60} source.

If then the adsorbed hydrogen atoms at the surface of the platinum are unable to leave the surface in any significant quantity, there must be contact between the particles of platinum and of tungsten oxide so that the atoms can diffuse across the interface between these two solid phases. Mixing both powders mechanically by grinding them together in a mortar brings about such a contact. In fact, as shown by data points on Curve A, compressing the mixture in a pelletizing machine made no difference in the uptake of hydrogen except at the beginning (lower part of Curve A) where the compacted material took up hydrogen less rapidly than the loose mixture, probably because of diffusional limitations.

A much more efficient way to achieve better contacting between both phases would be to support platinum on the tungsten oxide powder by impregnating the latter with chloroplatinic acid. This expectation is borne out by the data shown in curve G, taken on a sample containing 25 times less platinum than those of Curves A, B, C, and D. When allowance is made for this difference, it is apparent that the impregnated WO_3 is being reduced very rapidly. The final uptake of the impregnated sample is more than half the final uptake of these other samples containing so much more metal.

The very good contact achieved by shaking the two powders gently in a vial, as indicated by the rapid uptake and high final extent of reduction shown by Curve D, is surprising. It appears that the transport of adsorbed hydrogen atoms away from the interface is a very rapid process requiring a very efficient surface diffusion. In view of the transport of hydrogen atoms, the lack of reproducibility (see Results section) on such inhomogeneous samples prepared by shaking, is readily understood.

What makes this surface diffusion possible appears to be water, which we have discovered to be essential in the Pt-WO_3 system for the fast reduction at room temperature. As indicated by X-rays, the role of water is not to rehydrate WO_3 to H_2WO_4. As a matter of fact, the mode of reduction of H_2WO_4 is quite different from that of WO_3, as shown by Curve E in the presence of water and Curve F in its absence. In spite of the obvious differences between the Pt-WO_3 and Pt-H_2WO_4 systems, it is of particular interest for the present discussion that the reduction of Pt-H_2WO_4 is also accelerated very appreciably by water.

As reported in an earlier section, although the amount of water on the samples was not accurately known, it appeared to be in the range of a monolayer and not of capillary condensation. In that case, the value of the water vapor pressure with which the sample is equilibrated prior to the admission of hydrogen may well have an effect on the rate of transport of adsorbed hydrogen atoms away from the platinum centers. That this is so can be seen by comparing Curves B and C. The rate of reduction is slower for the run corresponding to the smaller pressure of water vapor, everything else being the same. That the function of adsorbed water is to accelerate the diffusion of reducing species is further shown by the fact that the final uptake is practically the same for both Curves B and C, although the rates are substantially different.

The rapid transport of hydrogen atoms in an adsorbed layer of water, perhaps as H_3O with exchange migration of a hydrogen atom between adjacent water molecules, or as some other hydrated reducing species, is therefore suggested by our results. It may well be a phenomenon of widespread significance. In the absence of water, the penetration of hydrogen atoms through the particles of tungsten oxide becomes so slow that extensive reduction takes place only around 100°C instead of room temperature and then only at a much smaller rate.

CONCLUSION

The difficulty of reproducing results obtained by Khoobiar (*3*) and by Kohn and Boudart (*4*) with mixtures of platinum-alumina and tungsten oxide, is due to the lack of control by these authors of one variable, namely water, the role of which has been clearly defined in the present investigation. This has been made possible by a quantitative study of the fast and extensive reduction of WO_3 taking place at room temperature in the presence of *both* platinum and water. An examination of the literature has convinced us that where WO_3 was observed to be reduced rapidly at room temperature in the presence of platinum, water was either introduced deliberately (*1*, *2*, *11*, *12*) or may have been present because of insufficient drying (*1*, *3*, *4*, *5*) before exposure to hydrogen.

Moreover, this study presents another example of the possible role of surface diffusion. Well-recognized in crystal growth since the classical work of Volmer, this phenomenon has received little attention in connection with phenomena of adsorption and catalysis. Discussed by Patterson (*13*), by Tsu and Boudart (*14*), and by Taylor (*15*), who coined the name of "portholes" for what corresponds in our work to the platinum centers, the phenomenon has been studied more recently by Robell and Boudart (*16*), who investigated the chemisorption of hydrogen by carbon, after its dissociation on supported platinum centers.

The example studied here is the most striking yet. The amount of hydrogen leaking in through the platinum "portholes" and being transported swiftly with the aid of water to reduce tungsten oxide in depth is in more than 35-fold excess over the amount picked up by the platinum centers separately. The magnitude of the effect and the low temperature at which it is observed are due to the assistance by water, which succeeds in spreading the reducing species rapidly over the entire internal surface of the tungsten oxide particles.

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