[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, FORDHAM UNIVERSITY]

# Application of Palladium- and Platinum-Polyvinyl Alcohol-Vanadium Catalysts

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In previous papers from this Laboratory the preparation[2] of highly active palladium- and platinum-synthetic high polymer catalysts and their application[3] to catalytic hydrogenations has been described. It was also found that the particle size of polyvinyl alcohol (PVA) exerts a definite effect on the efficiency of the catalysts.

The present communication describes the preparation and use of Pd- and Pt-PVA catalysts in which the noble metal has been reduced by divalent vanadium. The application of these catalysts has brought out significant results which also have bearing on the question whether oxygen is essential in catalytic hydrogenations.[4] Electrolytic hydrogen, freed of all but measured traces of oxygen, and also that resulting from the reaction $CO + H_2O \rightarrow CO_2 + H_2$, were used for the hydrogenations.

**Materials.**—Electrolytic hydrogen was freed of oxygen as directed by Meyer and Ronge[5] and was likewise tested for content of oxygen by the phosphorescence of a trypaflavine–silica gel preparation. The hydrogen and nitrogen so purified contained less than $4 \times 10^{-5}\%$ of oxygen.[6] Pure carbon monoxide was prepared as before.[2] Purified benzaldehyde after being shaken with dilute sodium carbonate solution was washed with water. After drying it was fractionally distilled in an atmosphere of nitrogen. Cinnamic aldehyde was purified as described before.[3]

**Preparation of Catalysts.**—The Pd- and Pt-PVA catalysts were prepared as previously[2] described. The vanadium solution was obtained by partially dissolving 5 g. of vanadium pentoxide in 250 cc. of hot 3 *N* sulfuric acid, passing sulfur dioxide in the boiling solution until the vanadium pentoxide was completely converted to vanadyl sulfate, $VOSO_4$, and then removing the sulfur dioxide by bubbling in carbon dioxide. The blue solution was shaken with amalgamated zinc until the lavender color of divalent vanadium ion was produced.[7] This solution was employed for the reduction of the noble metal.

**Procedure.**—To the unreduced Pd- or Pt-PVA catalyst contained in an atmosphere of purified nitrogen a solution of divalent vanadium was added and after the nitrogen had been displaced by hydrogen or carbon monoxide, the substance to be hydrogenated was introduced. In some cases the vanadium solution was added after the catalyst had been reduced by hydrogen.

**Discussion of Results.**—The rates observed when the hydrogen from the reaction $CO + H_2O \rightarrow CO_2 + H_2$ was utilized as the source of hydrogen for the hydrogenation of nitrobenzene[8] in which the palladium was reduced by purified hydrogen, by carbon monoxide and by divalent vanadium, indicate that the manner of reduction does not cause an appreciable difference (within the experimental error).

The course of hydrogenations, in which purified hydrogen has been employed with Pd- and Pt-PVA catalysts with varying amounts of vanadium signified that the rate is not measurably affected even by large excess of vanadous solution. Moreover, reductions performed with purified and unpurified electrolytic hydrogen give the same rate.

These methods were also applied to the reduction of maleic acid and benzaldehyde.

Maleic acid (2 g.) was reduced by purified hydrogen in twenty minutes by a Pd-PVA catalyst (10 mg. Pd, 250 mg. PVA, du Pont RH—391), the metal being reduced by divalent vanadium equivalent to 29.3 mg. of vanadium pentoxide. A parallel experiment in which no vanadium was present showed that the time of reduction was the same.

On the other hand, the two-step hydrogenation of benzaldehyde by a Pd-PVA catalyst reduced with a vanadous solution is quite interesting, as shown in Fig. 1. The vanadium reduced palladium (curve 2) not only converts benzaldehyde to benzyl alcohol at five times the rate of a hydrogen reduced Pd-PVA catalyst but is also able to carry the reduction to toluene. If the vanadium is introduced after the catalyst has been reduced with hydrogen (curve 3) the rate is the same as the vanadium reduced catalyst only up to the benzyl alcohol stage. The reduction to toluene proceeds extremely slowly as is the case with the hydrogen reduced catalyst (curve 1).

With Pt-PVA the reduction of 1 cc. of benzaldehyde was 25% complete in one and one-half hours. The same catalyst in the presence of vanadium gave only a 60% reduction

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[1] From part of a thesis submitted to the Graduate School of Fordham University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.—The contents of this work was presented at the Spring meeting of the American Chemical Society, St. Louis, Mo., 1941.

[2] Louis D. Rampino and F. F. Nord, THIS JOURNAL, **63**, 2745 (1941).

[3] Rampino and Nord, *ibid.*, **63**, 3268 (1941).

[4] For a literature survey and references, see the dissertation of L. D. R.; *cf.* however: R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, **54**, 113 (1921); A. Skita, *ibid.*, **55**, 139 (1922); W. H. Carothers with Roger Adams, THIS JOURNAL, **45**, 1071 (1923); R. L. Shriner with Roger Adams, *ibid.*, **46**, 1683 (1924); M. Bodenstein, *Ann.*, **440**, 177 (1924); K. A. Hofmann, *Ber.*, **55**, 573 (1922); H. Gall and W. Manchot, *ibid.*, **58**, 485 (1925).

[5] F. R. Meyer and G. Ronge, *Angew. Chem.*, **52**, 637 (1939).

[6] These data were corroborated by experiments in which K. Kavanagh succeeded in hydrogenating iodine quantitatively to hydrogen iodide; 1 g. of resublimed iodine was dissolved in 50 cc. of 50% alcohol and as catalysts both PVA-Pd (containing 40 mg. of Pd), as well as PVA-VPd (containing 40 mg. of Pd + vanadium equivalent to 20 mg. of $V_2O_5$), were used. The hydrogenations were completed in about sixty and eighty-five hours, respectively. The sensitive starch test carried out at the end of the reductions was negative in all cases. If measurable amounts of oxygen had been present in the system, then the reduction could not have been completed, and some iodine should have been formed again.

[7] H. E. Roscoe, *Ann. Suppl.*, **6**, 77 (1868).

[8] F. F. Nord, *Ber.*, **52**, 1705 (1919).

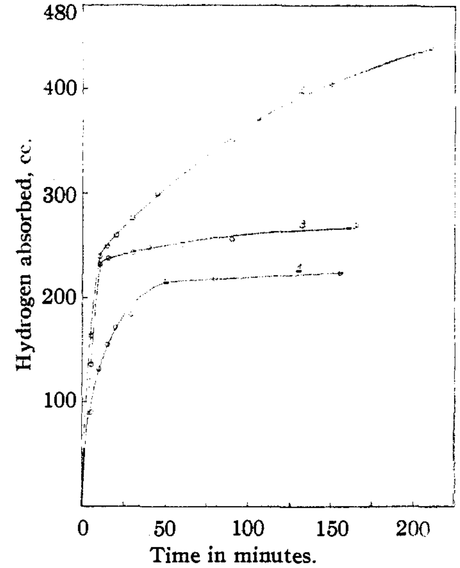

Fig. 1.—Reduction of benzaldehyde by Pd–PVA and Pd–PVA–V catalysts: reaction mixture is, one cc. of benzaldehyde in 50 cc. of 50% alcohol, 10 mg. of Pd, 250 mg. of PVA (du Pont RH-391): Curve 1, neutral medium; 2, $V^{++} \cong 29.3$ mg. $V_2O_5$; 3, $V^{++} \cong 29.3$ mg. $V_2O_5$.

in thirteen hours. If the vanadium was added to the same catalyst after it had been reduced with hydrogen, the reduction was one-half as fast, 30% of the benzaldehyde being reduced in thirteen hours.

It was reported previously[3] that in the reduction of 2 cc. of cinnamic aldehyde with a Pd-PVA catalyst (10 mg. Pd, 250 mg. PVA, 50 cc. of 50% alcohol) 1.39 moles of hydrogen per mole of compound was absorbed in 120 minutes. With the same catalyst reduced by 3 cc. of divalent vanadium solution equivalent to 29.3 mg. of vanadium pentoxide the absorption of 1.68 moles required only fifty minutes. The rate also was doubled when vanadium was applied to a Pd-PAME catalyst. With 1 cc. of cinnamic aldehyde in 50 cc. of glacial acetic acid (10 mg. Pd, 400 mg. methyl ester of polyacrylic acid) 2.19 moles of hydrogen was absorbed in eighty minutes.[2] However, the same catalyst reduced by 1.2 cc. of divalent vanadium equivalent to 11.6 mg. of vanadium pentoxide required for the absorption of 2.08 moles of hydrogen forty minutes.

An over-all increase in the rate of reduction of quinone[3] also has been observed in the presence of vanadium. The depressing effect on the rate with increasing acidity is seen in Fig. 2 from curves 1, 2 and 3. Notwithstanding the increased acidity over that prevailing in curve 1 due to the introduction of vanadium, the reduction proceeds at a much faster rate (curves 4, 5 and 6) and shows no tendency to diminish as in curves 1 and 2. In addition, in the vanadium experiments a change in color of the colloidal catalyst solution from dark brown to a lighter brown was observed at the point where the quinone had taken up one-half of the theoretical amount of hydrogen for conversion to hydroquinone and a change of color again to dark brown on complete reduction to hydroquinone.

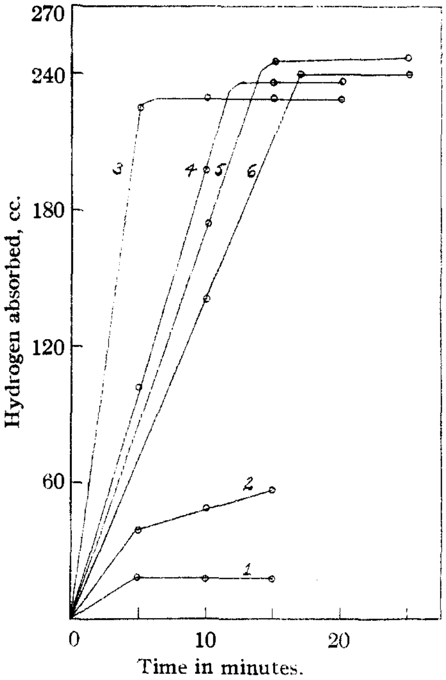

Fig. 2.—Application of Pd–PVA and Pd–PVA–V catalysts to the reduction of quinone: reaction mixture is, quinone (1.08 g.) in 50 cc. of 50% alcohol, 10 mg. of Pd, 250 mg. PVA (I. G.): Curve 1, 0.5 cc. of concd. hydrochloric acid; 2, 0.25 cc. of concd. hydrochloric acid; 3, neutral medium; 4, Pd reduced by 5 cc. of $V^{++} \cong 48.9$ mg. $V_2O_5$, 0.25 concd. hydrochloric acid; 5, Pd reduced by 1 cc. of $V^{++} \cong 9.4$ mg. $V_2O_5$, 0.25 cc. of concd. hydrochloric acid; 6, 5 cc. of $V^{++} \cong 26.8$ mg. of $V_2O_5$, 0.2 cc. of concd. hydrochloric acid.

## Discussion

It appears from the experiments recorded that the presence of oxygen is dispensable in the hydrogenations carried out with colloidal noble metal catalysts. The carbon monoxide obtained by the dehydration of formic acid through phosphoric acid supplied the hydrogen for reduction by reacting with water. It is presumed that in these reactions, carried out with due precautions, the absence of measurable amounts of oxygen is secured. The constancy of the course of the reactions observed in the carbon monoxide reductions is paralleled in those experiments effected by purified and unpurified electrolytic hydrogen. Due to the possibility that, in spite of the precautions taken, traces of oxygen might have been present, both the carbon monoxide and hydrogen reductions were carried out in the presence of divalent vanadium in excess of that needed to reduce the metal. The demonstrative force of the vanadium experiments depends, of course, both on the concentration of oxygen at equilibrium and also on the rate at which oxygen is removed by the reagent. However, it is certain that in the presence of a manifold excess of the strongly reducing, divalent vanadium, the equilibrium concentration of oxygen would be negligible, and according to the observed color change the removal of oxygen is instantaneous.

In the case of the reduction of quinone in the presence of vanadium, the color changes cited previously, and the constancy of the slope of the curves obtained, indicate that in the absence of vanadium the quinone–semiquinone equilibrium is such that with the *p*H prevalent in the medium, the reduction of the free radical is hindered. In the presence of reduced vanadium the semiquinone can be easily taken over into hydroquinone even at a much lower *p*H.[9]

Since quinone can be reduced in acid solution by unpurified hydrogen with the Pd-PVA catalyst the explanation offered by Neunhoeffer and Pelz[10] in regard to the inability of their palladium catalyst to hydrogenate quinone in acid media is meaningless.

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## Summary

1. Highly active Pd-PVA-V catalysts were prepared and applied to the reduction of benzaldehyde, cinnamic aldehyde, maleic acid, quinone and iodine.

2. Experiments are presented indicating that hydrogenations with colloidal noble metal catalysts can be performed in the absence of oxygen.

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[9] L. Michaelis, *Annals N. Y. Acad. Science*, **40**, 39 (1940).

[10] O. Neunhoeffer and W. Pelz, *Ber.*, **72**, 433 (1939).

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[CONTRIBUTION FROM THE RESEARCH DIVISION OF THE NEW JERSEY ZINC COMPANY OF PA.]

# Zinc Oxide Pigments. The Surface Area and Catalytic Activity

BY C. W. SILLER

The properties of paints and rubber compounds are strongly influenced by the extent of the surface and the physical and chemical nature of the surface of the pigments used in their formulation. The *extent* of the surface determines the size of the interface with the binding medium. The extent of the interface affects the extent and rate of physical and chemical interaction which, in turn, determine many of the mechanical properties of the resulting materials. The *condition* of the surface determines wetting, strength of bond, and, possibly, the nature of the reaction products which may materially alter the properties of paint films and rubber stocks. It is desirable to know the role played by each one of these two factors.

Attempts to study the effects produced by one or the other of these factors usually yield inconclusive results because it is quite difficult to vary one without affecting the other. The purpose of this paper is to describe the preparation and the testing of a series of zinc oxide pigments which varied in surface area but had similar surface characteristics as judged by the results of catalysis experiments.

The surface of zinc oxide particles is quite active and hence subject to contamination, which can markedly affect the surface characteristics. Taylor and Kistiakowsky[1] found that the adsorption of hydrogen and carbon monoxide was very sensitive to the cleanness of the surface of the oxide particles. The adsorption results correlated well with the known activity of zinc oxide in the methanol decomposition. It is also known[2,3] that the presence of alkaline and acid ions on the surface of zinc oxide affects the characteristics when the material is used as a catalyst. Hüttig and Feher[4] studied the catalytic activity of many samples of zinc oxide prepared by different precipitation methods. They concluded that the catalytic activity of an oxide for a given reaction may be used to define the oxide when its properties depend upon the previous history and the method of preparation.

The observations cited above indicate that the

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[1] Taylor and Kistiakowsky, THIS JOURNAL, **49**, 2468 (1927).

[2] Taylor, "Fourth Report of the Committee on Contact Catalysis," *J. Phys. Chem.*, **30**, 185 (1926).

[3] Taylor, "Fourth National Colloid Symposium," Chemical Catalog Co., Inc., N. Y., 1926, p. 25.

[4] Hüttig and Feher, *Z. anorg. allgem. Chem.*, **197**, 129 (1931).