the tray. This suggests greater curvature and a shorter focal length. It may be that the drop of benzene was forced out of contact with the water to a position on top of the stearic acid. No sudden change in appearance, other than that noted in regard to the focal length, was observed. Of course more stearic acid would be expected to dissolve in the benzene at higher film pressures and this would slow down the rate of evaporation. One would hardly expect a sudden and large increase in life of drop to result from this cause.

The pressure at which this second increase took place was not as definite and reproducible as the spreading pressure. At the present time it is not possible to enumerate the factors which determine the pressure at which the increase in time of evaporation occurs.

At the higher pressures it was noted frequently that the film pressure after evaporation was not as great as the initial pressure before the drop was added. This difference, larger than the normal, slow decrease which occurs with films under such pressures, indicates loss of film material. This was probably due to the failure of some of the dissolved stearic acid to take its place in the film as the benzene evaporated. Deposits of film material were visible as the three values plotted in curve A of Fig. 1 above 20 dynes per centimeter were obtained.

Attempts were made to measure the minimum pressure at which appreciable solution of stearic acid in the benzene took place. As the film pressure was gradually increased, added drops of benzene were blown to the edge of the tray with a current of air. Observations were then made to discover whether or not a loss of film material had occurred. The critical film solution pressures thus measured were not very reproducible, but in a number of trials values between 10.8 and 11.4 dynes per cm. were indicated.

Summary

The times required for uniform drops of benzene to evaporate from monomolecular films of stearic acid in different states of compression on water have been measured.

The changes in pressure of the monomolecular films due to these spreading and evaporating drops have been determined.

Attempts have been made to explain some of the rather interesting observations in terms of changes in shape and condition of the drops, and in terms of solution of film in the drops and its subsequent redeposition.

LINCOLN, NEBRASKA RECEIVED JULY 18, 1941

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

Preparation of Palladium and Platinum Synthetic High Polymer Catalysts and the Relationship between Particle Size and Rate of Hydrogenation

BY LOUIS D. RAMPINO* AND F. F. NORD

Investigations in the field of catalytic hydrogenation have led to the development of a new type of colloidal catalyst. The present paper describes the preparation of palladium and platinum catalysts in which synthetic high polymers are used as protective colloids. The particle size of the protective colloid and the rate of hydrogenation have been related by studies of polyvinyl alcohol (PVA) in various degress of polymerization as the protecting agent. Also, studies have been made of catalysts with PVA solutions which have been subjected to freezing to determine their activities in relation to the change of particle size deduced from earlier work.[1] Gold numbers of the various preparations have been determined. The use of PVA and polyacrylic acid as protective colloids is limited to water and water–alcohol mixtures. For hydrogenations in organic solvents we have therefore applied the polymer of methyl methacrylate (MMA) and that of the methyl ester of polyacrylic acid (PAME).

Apparatus.—The apparatus consisted essentially of a system of burets, a specially constructed hydrogenation

* 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, 1941. (Present address, Frick Chemical Laboratory, Princeton University.) A report on this work was presented at the St. Louis meeting of the American Chemical Society, April, 1941.

(1) F. F. Nord, *Naturwissenschaften.*, **24**, 481 (1936); L. Holzapfel and F. F. Nord, *Ber.*, **71**, 1217 (1938); *Biodynamica*, **3**, No. 57 (1940); F. F. Nord, *Ergebn. Enzymforschung*, **2**, 23 (1933).

flask and a machine which shook the vessels at a speed of 250 times a minute with an eccentricity of $1^3/_4$". The hydrogen and nitrogen used were purified by passage over heated copper.[2] Carbon monoxide was prepared by dropping formic acid on hot phosphoric acid.[3] The special hydrogenation flasks were provided with a separatory funnel attachment to permit the introduction of the colloidal catalyst. Provision was also made for the introduction of solids by means of a 7-mm. glass-stoppered opening. The flasks also had two two-way stopcocks, one at each end, so that gas could be supplied to or let out of the system.

Purification of Materials.—Absolute ethyl alcohol was prepared by refluxing 95% ethyl alcohol over calcium oxide for several days. It was then distilled and following treatment with aluminum amalgam[4] it was fractionated; b. p. 78.2°. Glacial acetic acid was refluxed for ten hours over chromium trioxide (1% by weight) and then treated with triacetyl borate.[5] The fraction, b. p. 117.6°, was taken. Acetone (U. S. P.) was treated with silver oxide and then dried with calcium chloride.[6] The fraction, b. p. 56.1°, was collected. Thiophene-free benzene was dried over sodium and distilled, b. p. 80.0°. Commercial cyclohexane was freed of thiophene by shaking with fuming sulfuric acid. After being successively washed with sodium hydroxide solution and water it was dried first with calcium chloride and then sodium. The fraction b. p. 80.2–80.5° was collected. Eastman Kodak Co. best grade of nitrobenzene[6a] was fractionated; b. p. 210.2°.

Preparation of the Catalysts.—A typical Pd-PVA catalyst was prepared in the following manner. To 12.5 cc. of a 2% aqueous solution of PVA was added 11 cc. of water. One cc. of a palladium chloride solution (1% Pd) was introduced followed by the addition drop by drop of 0.5 cc. of a 4% solution of sodium carbonate, which was sufficient to convert the palladium to the hydroxide and to neutralize the hydrochloric acid present in the palladium chloride solution. Absolute alcohol was now added to give a 50% alcohol–water mixture or alternatively more water was introduced and the catalyst used in a purely aqueous medium. The brown colloid was introduced into the hydrogenation flask and shaken with hydrogen in order to reduce the palladium to the metal, after which the compound to be hydrogenated was added and the course of hydrogenation followed by measuring the hydrogen uptake at definite time intervals.

The Pt-PVA catalyst was prepared in a similar manner. The platinum was incorporated in the form of a potassium platinous chloride (K_2PtCl_4) solution (0.5% Pt). In order to convert the platinum to the hydroxide it was found necessary to boil the solution for a few minutes with the required amount of sodium hydroxide solution.

A Pd-MMA catalyst was prepared by adding to 20 cc. of a 2% glacial acetic acid solution of methyl methacrylate, 29 cc. of glacial acetic acid and then 1 cc. of a palladium chloride solution (1% Pd). When a mixed solvent was employed the catalyst was prepared as just described and after reduction with hydrogen for five minutes, the second solvent in varying amounts was added to the Pd-MMA or Pd-PAME in glacial acetic acid.

Figure 1 records the activities of the Pd-PVA catalysts in comparison with two other colloidal catalysts and with two supported catalysts whose efficiency in hydrogenations is conceded to be of the highest magnitude. Curve 3 is drawn from data supplied by Baker and Company. Curves 4 and 5 represent the rates obtained with their Pd-C catalyst. If the absorption of hydrogen at the end of five minutes is taken as the standard for comparison, then the Pd-PVA catalyst is almost 5 times as efficient as the Pd-C catalyst. The Pd-PVA catalyst contains 10 mg. of palladium whereas the Pd–barium sulfate catalyst[7] has twice as much. Notwithstanding this fact, the Pd-PVA catalyst is more efficient (compare curves 1 and 2). If curves 6 and 7 are examined it can be seen readily that the Pd-PVA catalyst is again almost 5 times as efficient as the Pd-gum arabic catalyst. Curves 8, 9 and 10 show the comparative activities of PVA-, gum arabic- and gum tragacanth-Pd catalysts. The activity of gum arabic in acid solution (curve 11) compares more favorably with that of the Pd-PVA catalyst. The reproducibility of the absorptions of hydrogen was about ±10% at the end of five minutes which was the time interval generally used for comparing catalyst efficiencies.

The gold numbers[8] of PVA, gum arabic, and gum tragacanth are summarized in Table I. It can be seen readily that even though PVA possesses a higher gold number (1.6–1.4) than gum arabic with a gold number of 0.1–0.12, it produces a much more efficient catalyst. On the basis of these data the implication of a statement made in a recent work,[9] "The sodium salts of protal-

TABLE I

EFFECTIVENESS OF VARIOUS COLLOIDS IN TERMS OF HYDROGEN ABSORBED AND THEIR GOLD NUMBERS

Pd, mg.	Colloid	Colloid, mg.	Absorption of H_2 in 5 min.[a]	Gold no.
20	Polyvinyl alcohol	100	370	1.4–1.6
20	Gum arabic	100	135	0.1–0.12
20	Gum tragacanth	100	140	*ca.* 2

[a] Cc. at 25° and 760 mm.

(2) F. R. Meyer and G. Ronge, *Angew. Chem.*, **52**, 637 (1939).
(3) J. G. Thompson, *Ind. Eng. Chem.*, **21**, 389 (1929).
(4) P. Walden, H. Ulich and F. Laun, *Z. physik. Chem.*, **A114**, 275 (1925).
(5) W. Eichelberger and V. K. LaMer, THIS JOURNAL, **55**, 3633 (1933).
(6) E. A. Werner, *Analyst*, **58**, 335 (1933).
(6a) F. F. Nord, *Ber.*, **52**, 1705 (1919).
(7) C. Paal and W. Poethke, *ibid.*, **59**, 1511 (1926).
(8) R. Zsigmondy, *Z. anal. Chem.*, **40**, 718 (1901).
(9) S. Berkman, J. C. Morrell and G. Egloff, "Catalysis," Reinhold Publishing Co., New York, N. Y., 1940, p. 247.

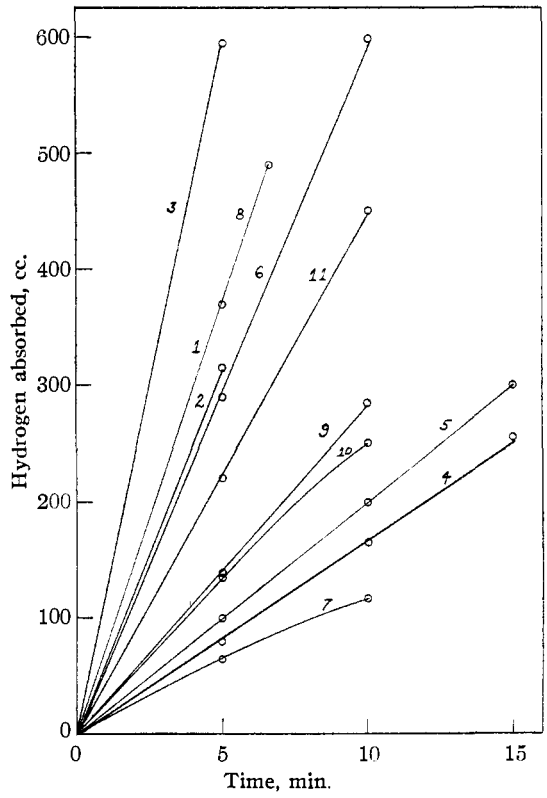

Fig. 1.—Comparison of Pd-PVA and other catalysts—reaction mixture: 1 cc. nitrobenzene, 50 cc. 50% alcohol, 2% sodium hydroxide. Curve (1) 10 mg. Pd, 250 mg. PVA; (2) 20 mg. Pd in 2 g. Pd-$BaSO_4$; (3) 50 mg. Pd in 1 g. Pd-Charcoal (data by Baker and Co.); (4) 10 mg. Pd in 200 mg. Pd-Charcoal (Baker); (5) 10 mg. Pd in 200 mg. Pd-Charcoal (neutral medium); (6) 10 mg. Pd, 100 mg. PVA; (7) 10 mg. Pd, 100 mg. gum arabic; (8) 20 mg. Pd, 100 mg. PVA; (9) 20 mg. Pd, 100 mg. gum tragacanth; (10) 20 mg. Pd, 100 mg. gum arabic; (11) 10 mg. Pd, 100 mg. gum arabic, 1.6% HCl. The PVA in these experiments was a specially purified I. G. Product.

binic and lysalbinic acids are excellent protective colloids as indicated by their gold number which is about 0.05; gelatin ranges from 0.005 to 0.01 and that of gum arabic is about 0.02," is certainly untenable.

The Pd-PVA and Pt-PVA catalysts possess the practical advantage of being equally effective in acid, neutral and alkaline media. In Fig. 2, curves 1, 2, 3, 4 and 5 show the activity of the catalyst for the reaction $CO + H_2O \rightarrow CO_2 + H_2$ as the source of hydrogen[10] as compared with other palladium preparations. The superiority of the Pd–PVA catalyst over the Pd–gum arabic catalyst is indicated by curves 2 and 4. Even though the Pd–gum arabic catalyst contains 30

(10) H. Wieland, *Ber.*, **45**, 679 (1912); O. Neunhoeffer and W. Pelz, *ibid.*, **72**, 433 (1939).

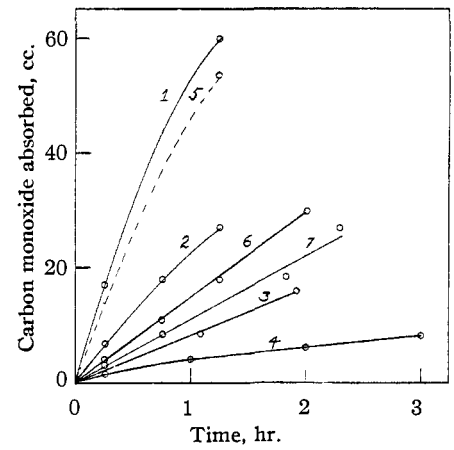

Fig. 2.—Comparison of Pd-PVA catalyst with other catalysts for reductions with carbon monoxide—reaction mixture: 1 cc. nitrobenzene, 50 cc. 50% alcohol, 2% sodium hydroxide. Curve (1) 20 mg. Pd in 2 g. Pd-$BaSO_4$; (2) 10 mg. Pd, 250 mg. PVA (I. G.); (3) 250 mg. Pd prepared by reducing palladousammine chloride ($Pd(NH_3)_2Cl_2$) at 150°. Acceptor: 2 g. *o*-nitrobenzaldehyde; (4) 300 mg. Pd, 500 mg. gum arabic; (5) 20 mg. Pd, hypothetical curve (twice curve 2); (6) 10 mg. Pd, 100 mg. PVA (I. G.). Pd reduced by hydrogen; (7) 10 mg. Pd, 100 mg. PVA (I. G.). Pd reduced by carbon monoxide.

times as much Pd as the Pd–PVA catalyst it has an activity which is less then one-fifth of that of the Pd-PVA catalyst. On the other hand, the Pd–barium sulfate catalyst compares very favorably with the Pd–PVA catalyst. Figure 3 shows the comparison of the efficiencies of both the Pd-PVA (curves 1, 2, 3 and 4) and Pt–PVA catalysts (curves 5, 6 and 7) prepared by using different PVA concentrations. It can be seen readily that both with palladium and platinum the PVA exhibits a maximum effect at a definite concentration, with 250 mg. of PVA to 10 mg. of Pd, and with 100 mg. of PVA to 10 mg. of Pt.

The same concentration effect was also observed with palladium in organic solvents. With MMA and with the methyl ester of polyacrylic acid (PAME) the optimum concentration is obtained at 400 mg. as shown in Fig. 4, curves 1 and 6. That the Pd–MMA and also the Pd–PAME catalyst are efficient when acetone, curve 2, or when mixed solvents, curves 3, and 4 are used is also shown in Fig. 4. The effect of adding small amounts of acetone is striking as shown by curves 5 and 1 and curves 6 and 7. However, with increasing amounts of acetone the activity is diminished. It may be said that PAME exerts a better protective action than MMA. Although Pd–PAME catalysts show a short induction

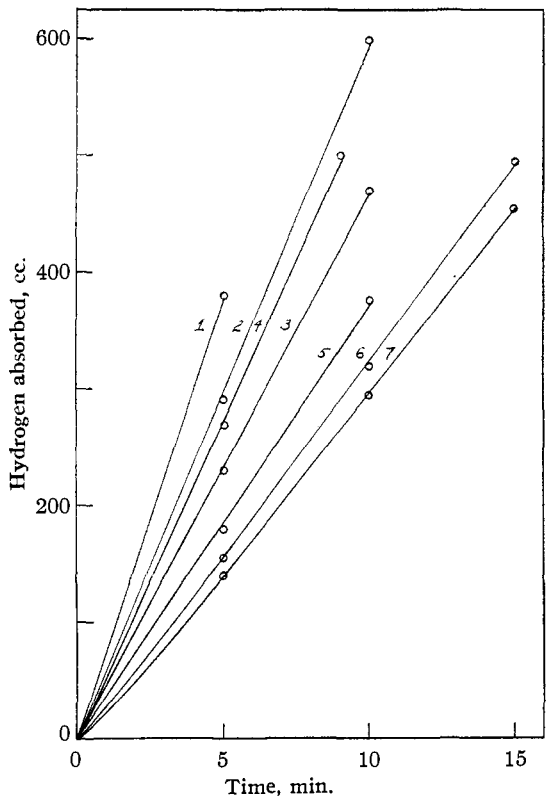

Fig. 3.—Efficiencies of Pd-PVA and Pt-PVA catalysts at various PVA concentrations—reaction mixture: 1 cc. nitrobenzene, 50 cc. 50% alcohol; Pd catalysts prepared with I. G. PVA and used in 2% sodium hydroxide; Pt catalysts prepared with du Pont RH-391 PVA and used in neutral media. Curve (1) 10 mg. Pd, 250 mg. PVA; (2) 10 mg. Pd, 100 mg. PVA; (3) 10 mg. Pd, 25 mg. PVA; (4) 10 mg. Pd, 300 mg. PVA; (5) 10 mg. Pt, 100 mg. PVA; (6) 10 mg. Pt, 250 mg. PVA; (7) 10 mg. Pt, 50 mg. PVA.

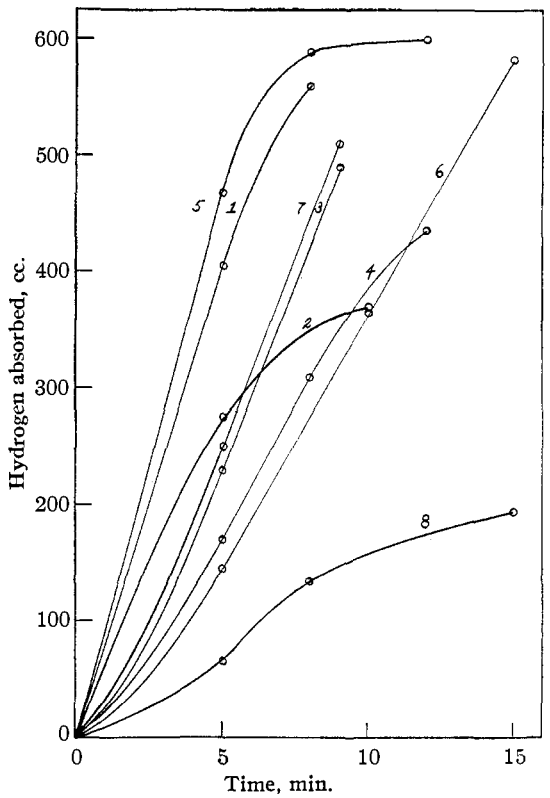

Fig. 4.—Rates with Pd-MMA and Pd-PAME catalysts in organic solvents. Reaction mixture: 1 cc. nitrobenzene, 10 mg. Pd. Curve (1) 400 mg. MMA, 50 cc. glacial acetic acid; (2) 250 mg. MMA, 50 cc. acetone; (3) 400 mg. MMA, 50 cc. glacial acetic acid, 10 cc. cyclohexane; (4) 400 mg. MMA, 50 cc. glacial acetic acid, 10 cc. benzene; (5) 400 mg. MMA, 50 cc. glacial acetic acid, 10 cc. acetone; (6) 400 mg. PAME, 50 cc. glacial acetic acid; (7) 400 mg. PAME, 50 cc. glacial acetic acid, 5 cc. acetone; (8) 250 mg. MMA (monomeric), 50 cc. acetone.

period, they possess a better sustained rate of hydrogenation, curve 6, whereas the rates obtained with the Pd–MMA catalysts although showing a higher initial rate have a tendency to fall off, curve 1.

Experiments carried out with monomeric MMA in acetone show that even here some protective action is in effect, curve 8. It is interesting to note in these experiments that even though the PAME solution is colloidal, it is uncertain whether the Pd–PAME or –MMA catalysts are completely colloidal. Notwithstanding this fact the catalysts so produced possess the same efficiency as the Pd–PVA catalysts which are completely colloidal.

In order to establish what effect a change in the particle size of PVA would have on efficiency, catalysts were prepared with the various grades of du Pont PVA and with a product, specially freed of electrolytes, of the I. G. Farbenindustrie, A. G. Höchst. The results obtained are shown in Table II.

TABLE II

COMPARISON OF TRANSFERRED AMOUNTS OF H_2 AND OF GOLD NUMBERS OF VARIOUS PVA'S[a]

Polyvinyl alcohol	Time, min.	Hydrogen,[b] cc.	Gold numbers Unfrozen	Gold numbers Frozen
I. G.[c]	5	345	1.4–1.6	1.2–1.4
	8	510		
du Pont RH-391 (55)[d]	5	265	1.8–2.0	2.4–2.6
	8	433		
du Pont RH-623 (5)[d]	5	221	1.0–1.2	1.3–1,5
	8	315		

[a] Catalyst prepared as described previously, 10 mg. Pd, 150 mg. PVA used with 1 cc. $C_6H_5NO_2$. [b] Volumes at 25° and 160 mm. [c] Degree of polymerization, 300. [d] Degree of polymerization in terms of viscosity.

It can be seen that a high polymer appears to be more efficient than one of lower degree of polymerization.[11] Since earlier work[1] has shown that a change of particle size of PVA can be effected by subjecting an aqueous solution of it to freezing, this technique was also applied. Aqueous solutions, 2 and 0.1% PVA, were frozen for two hours at −15°. The solutions were then thawed out at room temperature and used to prepare the colloidal catalysts. The effect produced by freezing on the rate of hydrogenation was within the range of experimental error. However, in the case of du Pont PVA, RH-623, the aggregation caused by freezing a 2% solution was sufficient to induce a coagulation of the catalyst on reduction, which was not observed when the unfrozen colloidal solution was used to prepare the catalyst. The gold numbers of both the frozen and unfrozen solutions, which indicate the changes taking place on freezing, are shown in Table II. It is also evident that, in the unfrozen solutions, the gold numbers give an index as to the degree of polymerization. Recent consideration[12] on the meaning to be attached to gold numbers are consistent with the data in Table II.

Hydrogenation of Oils.—The Pd–PVA catalyst was also applied to the hydrogenation of both castor oil and fish oil in order to compare the progress made with the present catalyst operating at room temperature and slight pressure over that of a previously applied Pd catalyst used at approximately 75° and 8 atmospheres of pressure.[13]

The experimental procedure followed in the preparation was the same as that described previously. The PVA used was du Pont RH-391. After the palladium had been reduced with hydrogen, weighed quantities of the oils (1.78 g. castor oil and 1.77 g. fish oil) were introduced into the reaction vessel. The experiments were terminated at the end of three hours and the iodine numbers of both the unhydrogenated and the hydrogenated oils were determined. The hydrogenated products were both solids, that of castor oil being harder than that of the fish oil, which had lost its fishy odor during the process of reduction. The castor oil had an iodine number of 84.0 before, and 43.5 after, reduction. With fish oil the iodine number was changed from 129.5 to 57.4.

Effect of Concentration of Noble Metal.—The amount of palladium or platinum normally used was 10 mg. Experiments with 20 mg. of noble metal and varying amounts of protective colloid gave rates of hydrogen absorption not much greater than those in which 10 mg. was used. Experiments with still higher amounts of noble metal indicated that rate of hydrogenation may be governed by factors such as volume, shape and shaking of the vessel.

These new catalysts have the advantage of being equally useful in acid, neutral and alkaline media; they suggest also the possibility of an extended use of water gas for hydrogenations, and of their use in catalytic reactions now carried out under high pressures and temperatures.

Acknowledgments.—This investigation has been assisted in part by a grant from the Penrose Fund of the American Philosophical Society to one of us (F. F. N.) and is being continued. We acknowledge the generous assistance in supplying materials of Abbott Laboratories, Inc., New York, N. Y., Baker and Company, Inc., Newark, N. J., E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware, I. G. Farbenindustrie A.-G., Frankfurt a/M.-Höchst, Germany, Röhm and Haas Co., Inc., Philadelphia, Pa., The Dow Chemical Co., Midland, Mich.

Summary

1. Directions are given for the preparation of Pd- and Pt–polyvinyl alcohol catalysts which have high hydrogenation efficiencies in water and water–alcohol mixtures.

2. Directions are given for the preparation of Pd–methyl methacrylate and Pd–methyl ester of polyacrylic acid catalysts of high activity, useful in organic solvents.

3. The particle size of polyvinyl alcohol is found to exert a definite effect on the efficiency of the catalyst.

4. The fact that the catalysts are efficient for the reaction $CO + H_2O \rightarrow CO_2 + H_2$ and also for the reduction of oils suggests an extended use of these catalysts.

NEW YORK, N. Y. RECEIVED JULY 14, 1941

(11) Recent measurements by L. D. Rampino, K. Kavanagh, R. W. G. Wyckoff (Lederle Laboratories, Pearl River, N. Y.) and F. F. Nord have been made on Pd–PVA catalysts submitted to ultracentrifuging for one hour at 500 and 200 r. p. s. At 500 r. p. s., 2.64 mg. palladium out of 12.13 mg. in 32 cc. of solution remained in the supernatant liquid, and had approximately 10 times the activity of the sedimented catalyst per unit weight of palladium. At 200 r. p. s. 5.11 mg. remained with an activity 5-fold that of the sedimented material. Absorption measurements on Pd-PVA and Pd-gum arabic (Pd-GA) catalysts indicate that the former require the amount of hydrogen theoretically necessary for reduction and that Pd-GA catalysts require approximately twice this amount. Further work is planned to decide the relative contributions of smaller particle size and palladium distribution to activity.

(12) H. M. Cassel, *J. Phys. Chem.*, **42**, 955 (1938).

(13) F. F. Nord, *Z. angew. Chem.*, **32**, 305 (1919).