

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 pH 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 pH .⁹

Since quinone can be reduced in acid solution by unpurified hydrogen with the Pd-PVA catalyst the explanation offered by Neunhoeffer and Pelz¹⁰

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

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

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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Zinc Oxide Pigments. The Surface Area and Catalytic Activity

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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 Kistiakowsky¹ 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 Feher⁴ 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

(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 (1921).

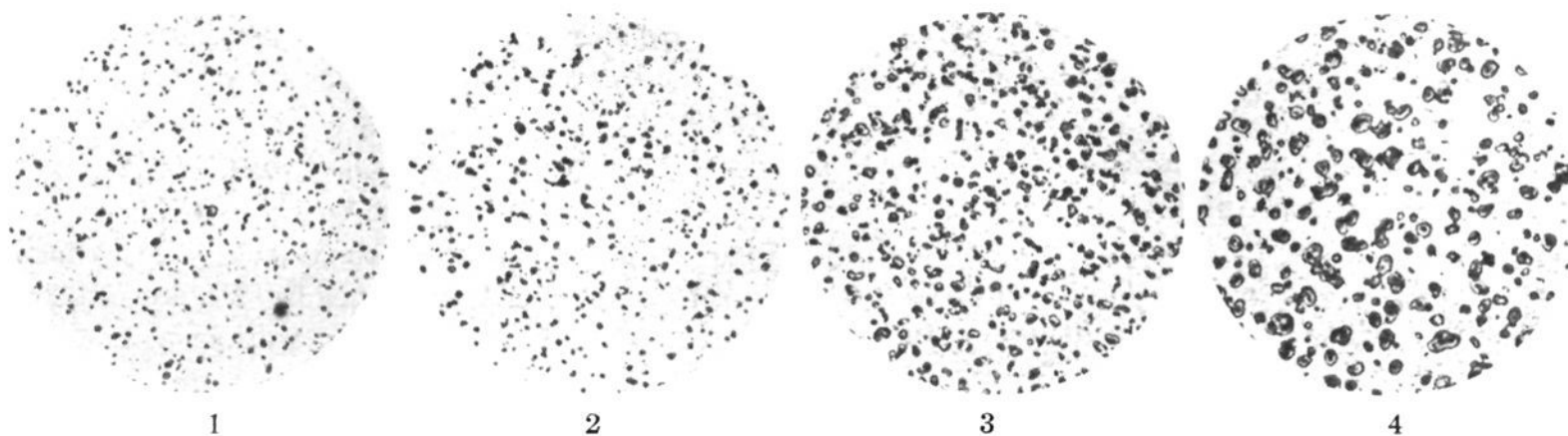


Fig. 1.—Photomicrographs (X1285).

surface characteristics of zinc oxide are strongly reflected in its catalytic activity. For this reason the catalytic activity was chosen as a criterion of the surface condition of the pigments.

Experimental

The Preparation of the Samples.—A master batch of fine zinc oxide was prepared by vaporizing zinc in an electrically heated crucible and oxidizing the vapor in air. Three portions of the master batch were reheated in an electrically heated rotary muffle furnace employing different times and temperatures necessary to give a series of samples which contained increasingly larger particles. The particle size of the original and the three reheated samples was determined by a direct microscopic method.⁵ The surface area per gram was calculated from these results (see Table I).

TABLE I

THE PARTICLE SIZE, SURFACE AREA AND APPARENT VOLUMES OF THE SAMPLES

Sample number	Particle size ^a		Sp. surf., sq. m./g.	App. vol., ^b cc./g.
	d_1	d_2		
1	0.25	0.40	2.72	2.62
2	.35	.54	1.98	2.37
3	.65	.87	1.21	1.57
4	.92	1.25	0.84	0.987

^a d_1 = Average mathematical mean particle diameter, microns. d_2 = Average "surface" diameter. This is the size, in microns, of a pigment of uniform particle size having the same specific surface as the material in question.

^b Measured on a Scott volumeter apparatus; the amount of sample necessary to fill a given volume under standardized conditions.

Photomicrographs (X1285) of the samples are presented in Fig. 1.

The Catalysis Apparatus.—The apparatus and procedure were quite similar to those used by Frolich, Fenske and Quiggle.⁶ A few changes were made to facilitate the operation of the apparatus. The methanol bulb was thermally insulated to reduce the rate of vaporization to 1.5 cc. of liquid in ninety minutes. The apparatus was so designed as to allow the introduction of methanol without containing it with stopcock grease. The boat was introduced through a ground glass joint, thus eliminating the

litharge-glycerol seal; the joint was lubricated with a heavy rubber base grease. No special procedure was used in putting the catalyst into the porcelain boat, which had a capacity of 1.5 cc. All of the experiments were performed with the catalyst at 360°. The methanol was "Baker's Analyzed"; it was not further purified. The progress of the experiment was followed by observing the volume of the gaseous decomposition products at definite intervals of time. The decomposition products were not analyzed.

The Results

The Results of the Catalysis Experiments.—Preliminary experiments showed that the catalytic activity per gram and per sq. m. depended to some extent upon the weight of the catalyst exposed to the methanol. For this reason, the first series of experiments was performed with equal weights (0.5 g.) of the samples. The results are presented in Fig. 2. The curves do not pass through the origin because the time at which the methanol was placed in the apparatus was taken as zero time and consequently some time was necessary to bring the methanol to temperature.

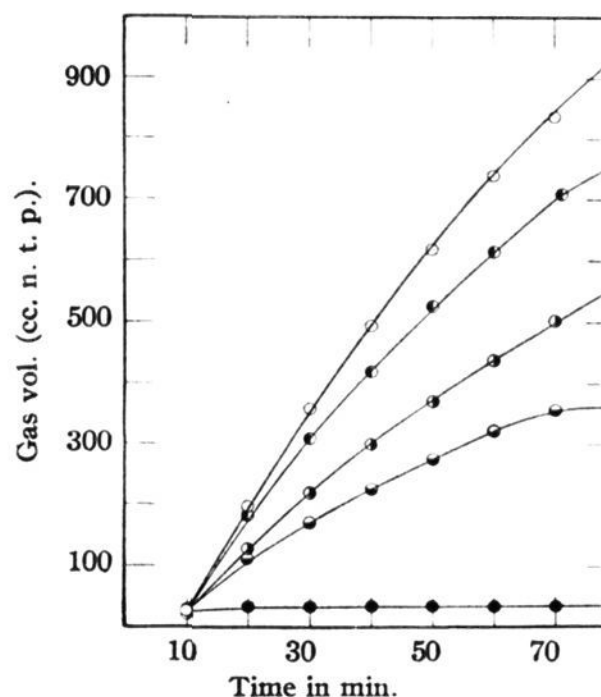


Fig. 2.—O, no. 1; ○, no. 2; ○, no. 3; ○, no. 4; ●, control, empty boat.

(5) Green, *J. Franklin Inst.*, **192**, 637 (1921).

(6) Frolich, Fenske and Quiggle, *Ind. Eng. Chem.*, **20**, 694 (1928).

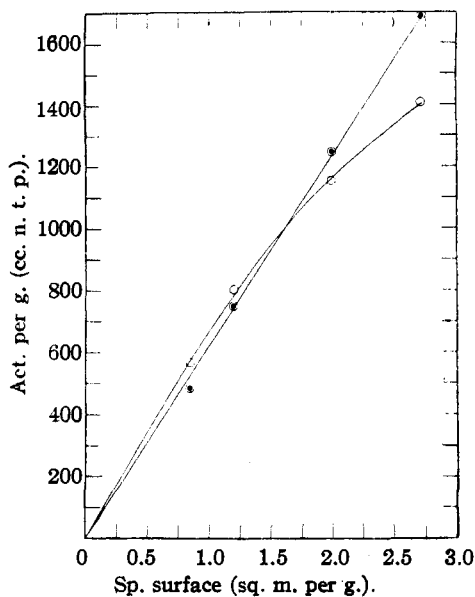


Fig. 3.—O, 0.5 g. samples; ●, samples having 1 sq. m. surface.

These data allow the calculation on two quantities: namely, the activity per gram and the activity per sq. m. The activity per gram is arbitrarily defined as the volume of gas evolved after one hour divided by the weight of the catalyst; the activity per sq. m. is arbitrarily defined as the volume of gas evolved after one hour divided by the surface area of the catalyst. These results are presented in Table II (see also Fig. 3).

TABLE II
THE ACTIVITY PER G. AND PER SQ. M. FOR 0.5-G. SAMPLES

Sample number	App. vol. of catalyst, cc.	Surf. area, sq. m.	Act. per g., cc. per g.	Act. per sq. m., cc. per sq. m.
1	1.31	1.36	1408	518
2	1.18	0.99	1154	582
3	0.78	.605	804	664
4	.49	.42	568	676

Another series of experiments was performed in which equal surfaces, and incidentally approximately equal apparent volumes, of the samples were tested (see Fig. 4). The activity per gram

TABLE III
THE ACTIVITY PER G. AND PER SQ. M. FOR SAMPLES HAVING ONE SQ. M. SURFACE AREA

Sample number	Catalyst, g.	App. vol. of catalyst, cc.	Act. per g., cc. per g.	Act. per sq. m., cc. per sq. m.
1	0.368	1.0	1690	623
2	.505	1.2	1250	631
3	.827	1.3	750	621
4	1.19	1.2	485	576

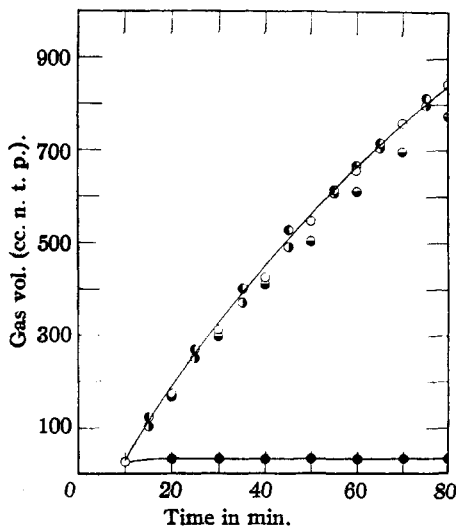


Fig. 4.—O, no. 1; ◐, no. 2; ◑, no. 3; ◒, no. 4; ●, control, empty boat.

and per sq. m. were calculated in the manner described before.

From these results it is evident that the activity per sq. m. was about equal except for sample no. 4. A possible explanation of the behavior of this sample will be given later in the paper. The curve for the activity per gram *versus* the specific surface (see Fig. 3, partially shaded circles) was linear, indicating that the surface characteristics of the various samples were similar. It would have been highly coincidental if the heat treatment given the second, third, and fourth samples to grow the particles to the sizes indicated had altered the surface condition just enough to compensate for the change in the surface area.

Discussion of the Results

Before entering into a discussion of the results it should be recorded that each catalysis experiment was repeated at least once; the catalysis experiment involving sample no. 4 was repeated three times. The results of the check runs agreed to within 3% of the original results. Average values were used in the construction of the graphs.

When 0.5-g. portions of the pigments were tested for catalytic activity, it was found that the activity per gram was not a linear function of the specific surface (see Fig. 3, open circles). The following reasons for explaining this effect are suggested: (1) a change in surface characteristics brought about by the heat treatment of the samples, (2) variations in the partial pressure of methanol in the gas stream brought about by the

different catalytic efficiencies of the samples, (3) increasing rate of diffusion of the various gases through the catalyst because of the decreasing apparent volume. The second and third possibilities were eliminated by testing portions of the pigments having both approximate equal apparent volumes and equal surface areas. The results of these experiments showed definitely that the surfaces of the pigment were similar as judged from the catalytic activity.

It was shown that sample no. 4 had a somewhat lower catalytic activity per gram than the other samples. This sample had received the most severe heat treatment (fifteen minutes at 900°), and it is believed some sintering could have taken place. This condition would cause the pigment to have a smaller surface area than indicated by the microscopical measurements. The mechanical work done on the sample in the course of mounting it for microscopical study probably disintegrated the sintered aggregates. Emmett and DeWitt⁷ explained a discrepancy between the surface area of a severely reheated sample of zinc oxide measured microscopically and by gas adsorption in a similar manner.

Hüttig and Feher⁴ define the "catalytic efficiency" as the weight of methanol decomposed per unit time divided by the weight of the catalyst. They report that this value has the character of a constant. The results of the present investigation indicate that catalysts should be compared by determining the amount of catalyst which has an arbitrarily chosen catalytic activity.

Graue and Köppen⁸ and Schleede, Richter and Schmidt⁹ observed that the catalytic activity increased with increasing surface area. The results of the present work confirm these observations.

(7) Emmett and DeWitt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 28 (1941).

(8) Graue and Köppen, *Z. anorg. allgem. Chem.*, **228**, 49 (1936).

(9) Schleede, Richter and Schmidt, *ibid.*, **223**, 49 (1935).

The results of Emmett and DeWitt⁷ and Ewing¹⁰ indicate that the direct microscopic method gives low values for the surface area of pigments. These observations seem reasonable when it is remembered that the particles are not spherical, the so-called "inner" or "capillary" surface cannot be measured by the direct microscopic method, and that submicroscopic particles might be present. The results of this research indicate that, at least, the samples were properly classified as to surface area. The uniformity of the samples with respect to particle size (see Fig. 1) and the reported observation⁹ that zinc oxide pigments made by the oxidation of zinc vapor do not possess an appreciable amount of "inner" surface might have contributed substantially to the accuracy of the direct microscopical measurements.

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Summary

1. A series of zinc oxide pigments was prepared which varied in particle size but had similar surface characteristics as judged from the results of catalysis experiments.

2. The catalytic activity was shown to be directly proportional to the surface area of the zinc oxide pigments.

3. It is believed that catalysts should be compared by determining the amount of catalyst which has an arbitrarily chosen catalytic activity. The experiments should be conducted in such a manner that the rates of diffusion of the gases through the catalyst are unimportant.

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(10) Ewing, *THIS JOURNAL*, **61**, 1317 (1939).