ment, in particular Professor R. C. Tolman and Dr. M. E. Nordberg. The very excellent rock salt windows used were kindly furnished by Mr. Rene Engel of the Geology Department of this Institute.

Summary

1. It has been suggested that the maintenance of rate in the decomposition of nitrogen pentoxide may be due to assistance from radiation, which becomes important only at low pressures.

2. It has been found experimentally, however, that radiation of wave length less than 5μ is not able to increase the reaction rate even at low pressures.

3. It is concluded that the important region, if there is any, will probably lie between 5 and 10μ, but that it is hard to see how enough radiation can be absorbed to maintain the rate. An experiment which might detect this activity, if it exists, has been suggested.

4. The other possible escapes from the nitrogen pentoxide dilemma have been considered. No definite conclusion has been reached.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

STUDIES OF COPPER CATALYSTS PREPARED FROM PRECIPITATED HYDROXIDE. I.
ACTIVITY AS A FUNCTION OF THE TEMPERATURE OF PRECIPITATION

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In the course of a study of the high pressure synthesis of methanol undertaken by this Laboratory some three years ago, it was observed that certain catalysts prepared from precipitated hydrates showed variations in activity which might be attributed to differences in the temperatures at which the hydrates had been precipitated from the corresponding nitrate solutions. To obtain more quantitative information concerning this temperature effect, a series of experiments was made with copper catalysts under carefully controlled conditions in order to eliminate in so far as possible the effect of variables other than the temperature of precipitation. The copper hydroxide was precipitated with ammonium hydroxide from aqueous solution of one of the standard makes of high purity (c. p.) copper nitrate. Since any occluded ammonium hydroxide or nitrate was easily volatilized in subsequent operations, the resulting catalysts might be expected to be of identical chemical composition.

Six different temperatures of precipitation were used, *viz.*, 0, 10, 22, 55, 85 and 100°.

Preparation of Catalyst and Experimental Procedure.—One hundred grams of copper nitrate crystals ($Cu(NO)_3 \cdot 3H_2O$) was dissolved in 1500 cc. of water and heated or cooled to the temperature chosen for precipitation. An ammonia solution containing one part by volume of concentrated ammonia (sp. gr. 0.89) to two parts of water, was brought to the same temperature and added to the nitrate solution at a constant rate of 20 cc. per minute until a faintly alkaline reaction was obtained. During the precipitation the solution was continuously agitated by a motor-driven stirrer. The hydroxide was allowed to settle and then washed three times by decantation, each time using one liter of distilled water at the same temperature as that used in the precipitation. In some cases the third settling was very slow and the gel was therefore placed on the suction filter. After washing on the filter with a fourth liter of water at the same temperature, the gel was transferred to an electric oven and dried at 110°. In order to remove any occluded ammonia salts, the hydroxide was then heated at 220° for four hours in a stream of nitrogen. By this procedure the hydroxide was converted into copper oxide.

The apparatus was exactly the same as that employed in previous studies on methanol catalysts and described in detail elsewhere.[1] It consisted essentially of an electrically heated pyrex tube in which the catalysts were exposed to methanol vapor supplied at a constant rate of flow. At the exit end of the apparatus means were provided for collecting the products of reaction, that is, formaldehyde, methyl formate and gaseous products.

A fixed amount of copper oxide, 0.43 g., prepared as above by heating at 220°, was reduced by passing over it 0.0462 mole of methanol at the lowest temperature at which reduction could be made to take place, varying between 190 and 210°. The resulting catalyst was then raised to operating temperature, 360°, and 0.1156 mole of methanol vapor passed over it at a constant rate of flow for a period of ninety-three minutes. Formaldehyde and methyl formate were absorbed in low-head scrubbers containing water and methanol, while the gaseous products, consisting of hydrogen, carbon monoxide, carbon dioxide and methane, were collected in a graduated gasometer. All analyses were made according to standard methods.[1]

Discussion of Results.—The percentage of methanol decomposed as a function of temperature of precipitation is shown in Fig. 1, plotted from the data in Table I. It is seen that the maximum decomposition occurs with the catalyst prepared by precipitating the hydroxide at 22° and that this point stands out markedly from the others, corresponding to a five-

TABLE I

RESULTS OF EXPERIMENTS

Precip. temp., °C.	Methanol decomposed, %	Methanol decomposed occurring as Formaldehyde, %	Methyl formate, %	Carbon monoxide, %
0	2.5	83.2	15.9	0.2
10	5.3	77.8	19.8	.5
22	12.3	45.5	51.2	1.2
55	6.9	75.0	23.8	0.5
85	8.8	55.0	41.2	2.0
100	8.4	61.2	36.2	1.0

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[1] Frolich, Fenske and Quiggle, *Ind. Eng. Chem.*, **20**, 694 (1928).

fold increase in activity over the catalyst resulting from precipitation at 0°. Another catalyst prepared by the same procedure gives a perfect check of the 22° point, and the entire general shape of the curve is checked in another series of experiments using smaller amounts of catalyst.[2]

As already mentioned above, these results were obtained with constant weights of catalyst. However, the specific volumes of the copper oxide samples and of the resulting catalysts were rather constant throughout, and hence the shape of the decomposition curve in Fig. 1 cannot be explained on the basis of variations in the time of contact of methanol vapor with the catalysts. Furthermore, it was observed that the more active the catalyst the lower the temperature required to start reduction. This initial reduction temperature is an inherent property of the copper oxide; it seems to be the result of the catalytic activity of the substance in question, rather than the cause, although it is of course impossible to distinguish completely between the two effects. The variation in the temperature of reduction is undoubtedly closely associated with the chemical composition and physical structure of the gels from which the catalysts are prepared. That the gels precipitated at various temperatures vary profoundly in these respects, is apparent from the following observations. The low temperature hydroxides are blue, while those precipitated at higher temperature are black, with a gradual transition in color between the two extremes. The gels resulting from low temperature precipitation

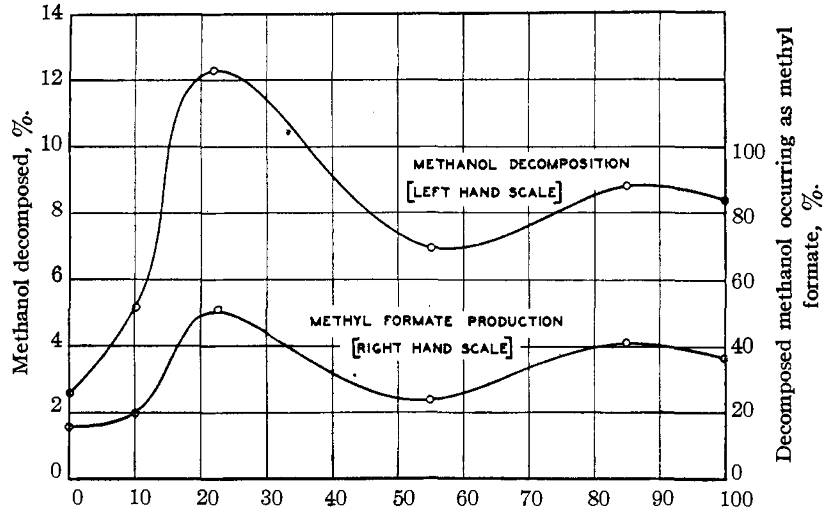

Fig. 1.—Data on copper catalysts prepared from the ammonia precipitated hydroxides, showing activity as a function of temperature of precipitation.

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[2] G. L. MacLaughlin, M. I. T. "Thesis," 1927.

are also much more hydrated and bulky than those obtained at high temperature.[3]

Interesting light is also thrown upon the character of the gels by means of x-ray analysis. The gels precipitated at 85° and higher temperatures consist essentially of copper oxide with only small amounts of hydroxide. As the temperature of precipitation decreases, the amount of copper hydroxide present in the dried gels increases, until finally the material obtained by precipitation at 30°, or lower, shows only faint indications of copper oxide. The particle size of the dried gels is quite small and, in a qualitative way, the x-ray pictures indicate smaller gel particle size to be associated with the more active catalysts.

Based on these admittedly qualitative data on particle size, an explanation of the decomposition curve in Fig. 1 may be offered. Thus it seems that the particle size of the hydroxides decreases with decreasing temperature of precipitation, but at the same time the degree of hydration increases markedly. When the resulting gels are subsequently dried at 110° there is a tendency for the particle size to increase, as is commonly observed in analytical chemistry when highly insoluble precipitates as, for instance, barium sulfate and calcium oxalate, etc., are left wet for a few hours at 80 to 100°. However, since it takes a longer time for the water to be removed from the highly hydrated low temperature gels, these particles will have more chance to grow than will the particles precipitated at the higher temperature and containing practically no water of hydration. The result is that the final particle size of the dried gel is determined by two opposing factors: (1) the tendency for the initial particle size to decrease with decreasing temperature of precipitation, and (2) the tendency for the initially formed particles to grow while the drying proceeds at 110°. This might well explain the occurrence of a minimum particle size corresponding to a temperature of precipitation of about 22°. It may then be assumed that the particle size of the dried gel determines the activity of the catalysts resulting from subsequent reduction, either by determining the size of the catalyst particles or their form. This line of reasoning is further substantiated by the work of MacLaughlin,[2] showing that the most active catalyst results by precipitation at 0° when the gels are dried at room temperature (25°), rather than at 110°, as was done in this series of experiments.

The particle size of the metallic copper catalysts, in contrast to the gel from which they are prepared, is relatively large, a result which might be expected because there is no foreign material present to interfere with growth of crystals during the reduction process. However, x-rays fail to

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[3] An interesting discussion of the various hydrated copper oxides or hydroxides is given by H. B. Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, **1926**, p. 134.

disclose any perceptible difference in particle size of the individual catalysts.

From the data in Table I it will be seen that these catalysts decompose methanol largely into formaldehyde, but that considerable methyl formate is produced simultaneously. The more active the catalyst the larger is the percentage of decomposed methanol occurring as methyl formate, as shown in Fig. 1.[4] Apparently this effect of the active catalysts producing mainly methyl formate is characteristic of promoted copper, as has already been demonstrated to be the case for mixtures of copper and zinc oxide.[1] A similar effect is observed when alkali is used as a promoter, as will be shown in the second paper of this series.

Acknowledgment.—The data presented here are abstracted from a considerable amount of experimental work conducted in the Research Laboratory of Applied Chemistry during the past years. The writers are indebted to Messrs. G. L. MacLaughlin and R. O. Spurdle for preparation of some of the catalysts discussed, and to Mr. W. C. Asbury who obtained the x-ray data in coöperation with Dr. G. L. Clark.

Summary

The activity of copper catalysts prepared from the ammonia precipitated hydrate varies markedly with the temperature of precipitation. There appears to be a maximum in activity corresponding to a temperature of precipitation in the neighborhood of 22°.

On the basis of x-ray examination of the dried gels prior to reduction, it is suggested that the activity is determined by the particle size at this stage in the catalyst preparation. An explanation is also attempted to account for the apparent minimum in particle size of the gels precipitated at about 22°.

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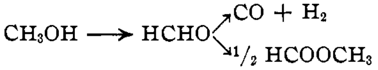
[4] Roughly, the methyl formate curve runs parallel to the activity curve, the curve for formaldehyde (not plotted) being the reverse of the methyl formate curve. No doubt the methyl formate is a polymer of formaldehyde formed in accordance with the following scheme for the decomposition of methanol



$$CH_3OH \longrightarrow HCHO \begin{array}{l} \nearrow CO + H_2 \\ \searrow \tfrac{1}{2}\, HCOOCH_3 \end{array}$$

That aldehydes can polymerize to form esters is well known [Mannich and Geilmann, *Ber.*, **49**, 585 (1916)] and this same type of reaction is apparently employed for the production of butyl butyrate by dehydrogenation of butyl alcohol by means of copper catalysts [U. S. Patent 1,580,143, April 13, 1926].