5. The free energy of formation from the elements of liquid methyl alcohol at 298°K. was obtained as $-44,000$ cal. per mole.

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

STUDIES OF COPPER CATALYSTS PREPARED FROM PRECIPITATED HYDROXIDE.

II. COMPARISON OF SODIUM HYDROXIDE AND AMMONIA AS A PRECIPITATING AGENT

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RECEIVED SEPTEMBER 24, 1928 PUBLISHED JANUARY 8, 1929

In order to obtain copper of the highest purity, the catalysts discussed in the preceding paper were prepared from the hydroxide precipitated from copper nitrate with ammonia. While this method of preparation was useful for a study of the temperature effect, it was apparent that the resulting copper catalysts, on the whole, possessed very low activity.[1] In this respect, as well as in appearance, they resembled the clear, red, very compact metal with low catalytic power which Sabatier[2] prepared by calcination of copper nitrate and subsequent reduction with hydrogen. No doubt both these types of catalysts owe their large particle size and low activity to their high purity, which does not leave any foreign matter to interfere with the crystallization of the metal during reduction.

Reduction of the ammonia precipitated product with hydrogen gave the same low activity that was obtained when using methanol vapor. On the other hand, highly active catalysts were prepared by reduction of the tetra cupric hydroxide precipitated from a boiling copper nitrate solution with sodium hydroxide.[2] This copper, in contrast to that resulting from precipitation with ammonia, was a light violet-colored metal with all the appearance of possessing a smaller particle size.

Experimental Work

These observations pointed to a promoter effect of the small amount of sodium salts which undoubtedly were occluded in the copper hydroxide precipitated with sodium hydroxide. To test this supposition the experiments reported in Table I were made.

Two hundred grams of copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) was dissolved in 1500 cc. of water and from this solution the hydroxide was precipitated either with ammonium hydroxide or with sodium hydroxide, as indicated in the table. In each case the hydroxides were heated at 220° in a stream of nitrogen for four hours prior to reduction

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[1] Frolich, Fenske and Quiggle, THIS JOURNAL, 51, 61 (1929).

[2] Sabatier, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 58.

with methanol vapor at the same temperature.[1] In Expt. 1 copper hydroxide was precipitated with ammonia at 100° and the gel was not further washed, only the supernatant liquor being drawn off. A sample of this same gel was dialyzed for two weeks at about 60° and used in Expt. 2. Expts. 3 and 4 are duplicates of the first two except that sodium hydroxide was used for precipitation instead of ammonia.

Table I

Results of Experiments

Experiment	1	2	3	4
Precipitating agent	NH_4OH	NH_4OH[a]	NaOH	NaOH[a]
Wt. of catalyst, g.	0.2297	0.2373	0.2007	0.2917
Temp. of experiment, °C.	385	385	356	356
Life of catalyst, % of time	100	100	23.6	...
CH_3OH decomposed, %	8.0	8.7	44.0	0.0
CH_3OH dec. occur. as CO_2, %	5.3	1.4	4.5	...
CH_3OH dec. occur. as CO, %	5.9	2.1	66.5	...
CH_3OH dec. occur. as $HCOOCH_3$, %	61.2	77.5	17.9	...
CH_3OH dec. occur. as CH_2O, %	27.2	19.2	11.3	...

[a] Dialyzed.

From these data it follows that the catalyst prepared by precipitation with sodium hydroxide without washing possesses a much higher activity than the corresponding catalyst resulting from precipitation with ammonia. This is brought out by the figures for percentage of methanol decomposed, 44.0 and 8.0%, respectively, in spite of the fact that the sodium hydroxide precipitated catalyst is operated about 30° lower than the other. While the ammonia precipitated catalyst is practically unchanged after two weeks' dialysis, the one prepared with sodium hydroxide loses its activity completely at the somewhat lower temperature of 356°. These results point very strongly to promoter action of the sodium salts occluded in the hydroxide.[3]

From Table I it will be seen that the sodium hydroxide precipitated catalyst remained active for only about twenty minutes, at which time the activity proceeded to fall off rapidly until the catalyst became completely dead. The ammonia precipitated catalyst, however, showed constant activity throughout the entire one and one-half-hour period of the run. This temperature effect on the sodium hydroxide precipitated catalyst was studied in a subsequent series of experiments illustrated in Fig. 1. As before, the catalysts were prepared by precipitation with sodium hydroxide with no further washing than drawing off the supernatant liquor on the suction filter. It is seen that by operating at 313°, or below, the activity does not change appreciably with time, but that

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[3] It will be noticed that the temperature differed for the two types of catalysts. The reason for this was that the activity of the ammonia precipitated catalyst would be too low for reliable measurements at the lower temperature, whereas the sodium hydroxide precipitated copper would lose its activity too rapidly at the higher temperature, as will be apparent from the discussions to follow.

the higher the temperature of operation above this temperature, the shorter is the time the catalyst remains active. At about 380° the catalyst is "dead" before the run can be started. It will also be noted that these curves break very definitely, and for the higher temperatures sharply, indicating the occurrence of some sudden change in the state of the catalyst.

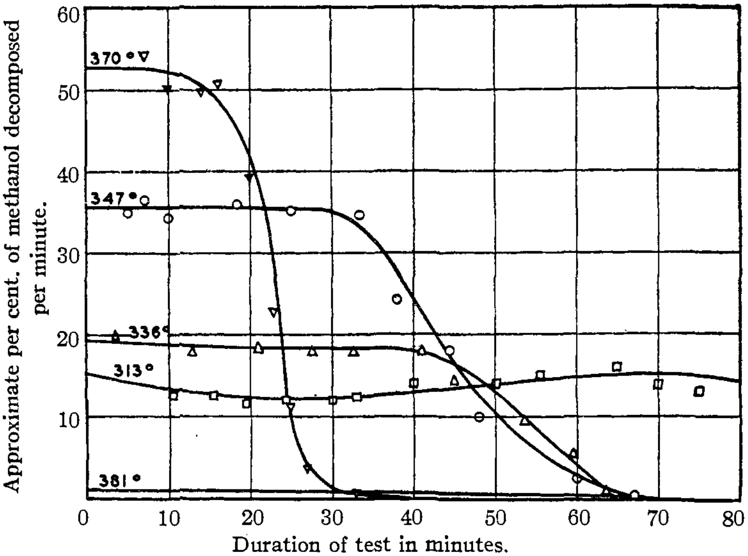

Fig. 1.—Effect of temperature on life of unwashed sodium hydroxide precipitated copper catalysts.

In order to investigate more thoroughly the effect of sodium salts on the catalytic activity of pure copper, a copper hydroxide gel was prepared by precipitation with ammonia and, after careful washing, divided into several portions, to which were added various amounts of sodium nitrate. The following percentages of sodium nitrate, calculated on the basis of copper oxide present, were incorporated in the gel: 0.01, 0.1, 1.0 and 5.0%. From these mixtures catalysts were prepared by the regular procedure of drying and reduction and then run at 300° with the results shown in Table II. The data prove beyond doubt that the sodium nitrate, presumably changed into sodium hydroxide during the preparation of the catalyst, is responsible for the higher activity of the sodium hydroxide precipitated catalyst.

Table II

Results of Runs

Sodium nitrate added, %	0.0	0.01	0.1	1.0	5.0
Methanol decomposed, %	0.0	0.5	3.6	36.6	37.0

Apparently, the dying-out effect observed with the sodium hydroxide precipitated catalysts, as illustrated by Fig. 1, is due to the fusion of the occluded salts, the melting points of sodium nitrate and sodium hydroxide being 316 and 318°, respectively. Since the sodium salt has a marked promoter effect on the copper, it must be in very close proximity to the activated copper atoms or nuclei, and when it melts it apparently covers or blots out these active patches of the catalyst. This explanation is substantiated by the fact that the activity curve breaks only when the temperature is above 313°, as shown by Fig. 1. A pure copper catalyst, such as is prepared by precipitation with ammonia, does not lose its activity within the temperature range studied.

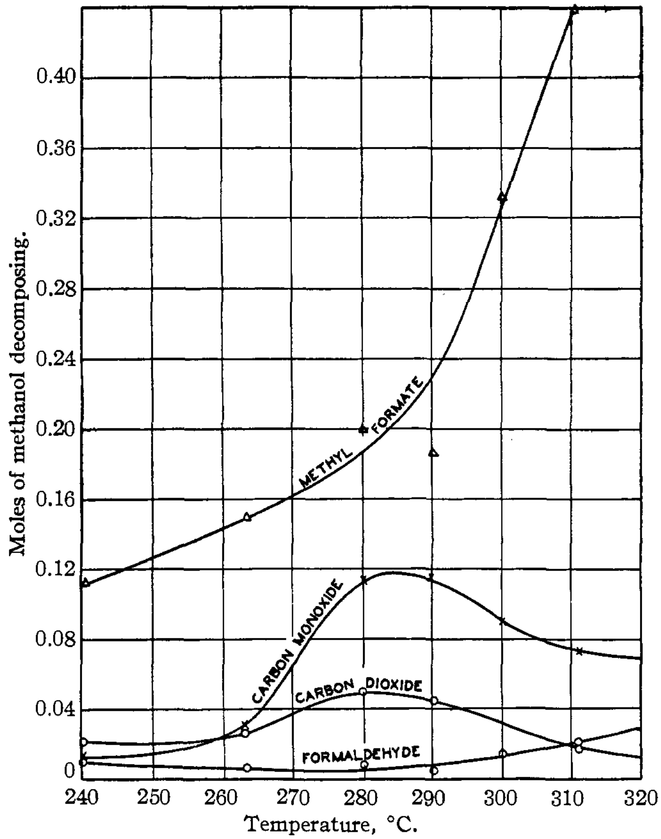

Fig. 2.—Moles of methanol decomposed into the various products as a function of temperature with unwashed sodium hydroxide precipitated copper catalysts. Basis: one mole of entering methanol.

It is to be noted that the decomposition of methanol is an endothermic reaction. Thus when methyl formate is the product, 9000 cal. are absorbed per mole of methanol decomposed, while with carbon monoxide as the product, the corresponding amount of heat is 24,000 cal. Since the reaction is assumed to occur on the surface, it is apparent that the catalyst must be at a somewhat lower temperature than the surrounding space. This may explain why the catalyst is active for a short time even though the temperature is well above the critical value of 315–320°. It also follows that the higher the temperature, the shorter will be the time required for the catalyst to retain this critical temperature, as is brought out by the data in Fig. 1.

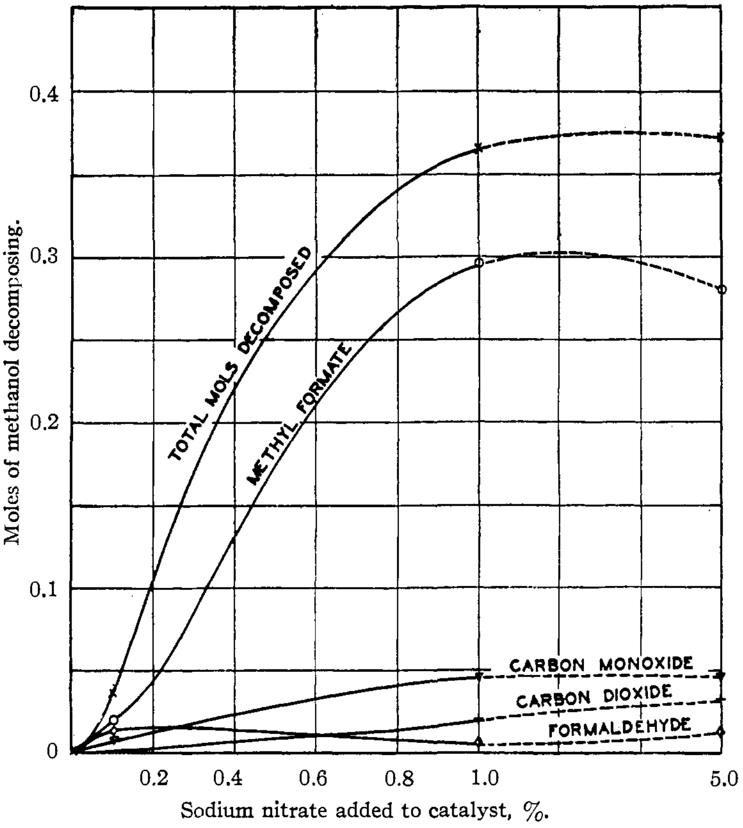

Fig. 3.—Effect of sodium nitrate on the activity of copper and on the mechanism of the decomposition.

In order to incorporate into and promote the copper with other sodium salts of higher melting points, the hydroxide was prepared from copper chloride and copper sulfate by precipitation with sodium hydroxide. The results are shown in Table III, from which it will be seen that the

TABLE III

RESULTS OF EXPERIMENTS

Catalyst	Temp., °C.	Methanol decomposed, %
$CuCl_2$ precip. with NaOH at b. p., unwashed	336–392	0.0
Same but washed with large amt. of water	387–400	2.2
$CuSO_4$ precip. with NaOH at b. p., unwashed	385	0.0
Same but washed with large amt. of water	385	0.0
Calcination of copper nitrate	336–400	4.0
Calcination of copper acetate	336–400	0.0

traces of sulfate and chloride which are retained even on washing are sufficient to poison the catalysts practically completely.

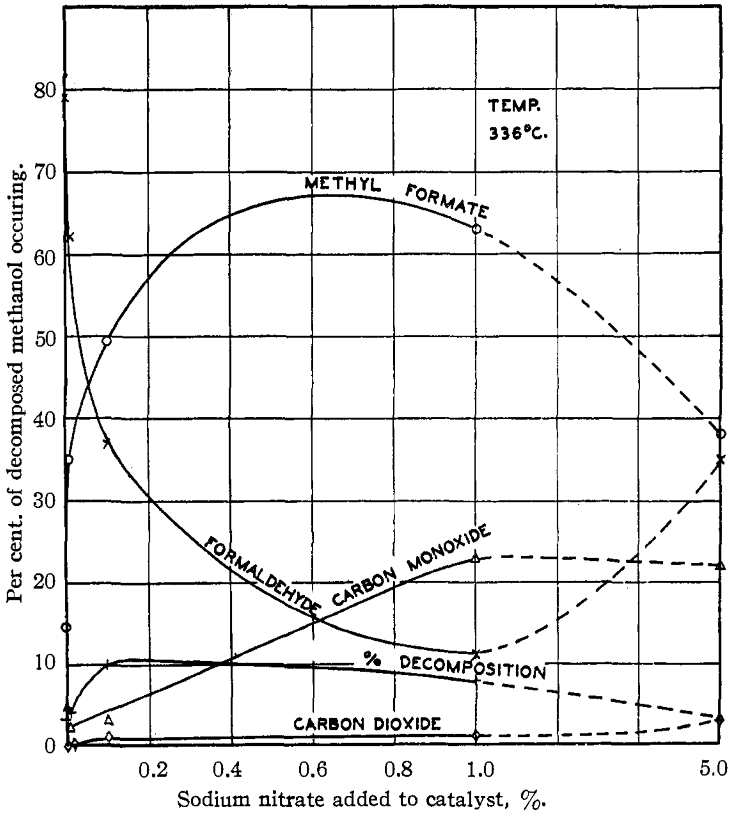

Fig. 4.—Effect of sodium nitrate on the activity of copper and on the mechanism of the decomposition.

Referring again to the sodium hydroxide precipitated catalysts, Fig. 2 shows the effect of temperature on the amounts of the various products of decomposition. The plot shows that the yield of methyl formate increases more rapidly than that of any other constituent, as the temperature increases.

Figs. 3 and 4 give the products of decomposition as a function of the amount of sodium nitrate added to the ammonia precipitated gel. Here it is seen again that the more active catalyst favors the production of methyl formate, as was pointed out in the first paper of this series and in a previous publication on copper catalysts promoted with zinc oxide.[4] Thus, in going from a pure to a promoted copper catalyst, the predominating constituent in the decomposition products changes from formaldehyde to methyl formate.

Conclusions

From the results presented above, it is apparent that copper catalysts prepared by precipitation with sodium hydroxide owe their high activity to the sodium salts thereby incorporated. It is not possible, however, to foretell what effect sodium hydroxide precipitation has on other types of catalysts as, for instance, on those composed of metallic oxides and used in the high pressure synthesis from water gas. In the absence of similar data for such catalysts, it is nevertheless advisable to precipitate with ammonia in order to avoid any disturbing influence of sodium salts, particularly when quantitative information is sought on the effect of promoters purposely added to a catalyst. In the past precipitation with ammonia and with sodium hydroxide has been used interchangeably, and this undoubtedly accounts for the divergent results reported by different experimenters. Thus Patart[5] states that copper gave very poor results when used as a catalyst for the high pressure synthesis of methanol, while Audibert[6] obtained good yields with alkali precipitated copper. Experiments made in the past in this Laboratory with ammonium hydroxide as the precipitating agent check Patart's observations in so far as lack of activity of the pure copper is concerned.[7]

Summary

Copper catalysts prepared by precipitation with sodium hydroxide are more active than those resulting from precipitation with ammonia, the difference being due to promoter action of occluded sodium salts.

These sodium hydroxide precipitated catalysts resemble other promoted copper catalysts in that they favor methyl formate rather than formaldehyde production by decomposition of methanol vapor.

It is suggested that failure to realize the significance of the promoter action of occluded alkali salts may account for the divergent results reported by workers in the field of high pressure synthesis from water gas.

CAMBRIDGE, MASSACHUSETTS

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

[5] Lormand, *Ind. Eng. Chem.*, **17**, 430 (1925).

[6] Audibert and Raineau, *ibid.*, **20**, 1105 (1928).

[7] Frolich and co-workers, *ibid.*, **20**, 1327 (1928).