magnesium hydroxide with the copper hydroxide–magnesium hydroxide mixture precipitated at first. If this rearrangement were complete, each catalyst of this series should have the same activity as one of the homogeneous catalysts of the same composition. This is not the case, for all of the catalysts of this series except catalyst 6 fall well below the curve for the homogeneous catalysts.

Applications.—In conclusion, it may be desirable to suggest possible applications of the ideas presented here. As already pointed out, they should be considered in any attempt to prepare highly efficient promoted catalysts, and in any research dealing with the effect of promoter concentration on activity. They may have a bearing on X-ray studies of the degree of dispersion of one component in the other. Finally, they may be important in helping to explain the effect upon activity of alternative methods of preparation.

Summary

1. Successive portions of a copper hydroxide–magnesium hydroxide catalyst have been prepared by fractional coprecipitation.

2. Five pairs of copper hydroxide–magnesium hydroxide catalysts of varying composition have been prepared, each pair consisting of one catalyst prepared by ordinary and one by reverse coprecipitation from solutions of the same composition.

3. Physical and analytical observations prove that catalysts of these components prepared by ordinary coprecipitation are inhomogeneous.

4. Rate experiments on the decomposition of hydrogen peroxide on these catalysts show that the inhomogeneity has a marked effect on the activity.

5. The bearing of these results on research in the field of promoter action has been discussed.

SALT LAKE CITY, UTAH RECEIVED AUGUST 6, 1941

[CONTRIBUTION NO. 64 FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF UTAH]

The Effect of Method of Preparation upon the Activity of Coprecipitated Copper Hydroxide–Magnesium Hydroxide Catalysts

BY JOHN W. HOLMES AND ELLISON H. TAYLOR[1]

It was suggested in the previous paper[2] that part of the effect of preparational variables upon the activity of multi-component catalysts might be explained by the inhomogeneity there shown to exist in such catalysts. A change in the rate of precipitation, for example, could change both the original amount of inhomogeneity in each portion of material, and the time available for homogenization during precipitation. Thus, although the over-all composition was identical with that of a previous preparation, the composition of the active surface might be significantly different.

It is the purpose of this paper to show that, in the case of a particular two-component catalyst, the details of the method of preparation affect importantly the activity, and that the results can be explained with the aid of the ideas previously advanced.[2] Data are presented which show the effect upon catalyst activity of systematic variations in the rate of precipitation and the number of washings. Two different ratios of components were used, and catalysts were prepared both by ordinary and by reverse coprecipitation. As in the previous paper,[2] the catalysts studied were of copper and magnesium hydroxides, and the reaction used to assess the activity was the decomposition of dilute hydrogen peroxide. Table I classifies the catalysts according to the preparational variables.

TABLE I

Series	Molar ratio Cu:Mg	Direction of pptn.	No. catalysts	Variable	Range of variable
A	1:3	Forward	13	Time of pptn.	0–8 hr.
B	1:1	Forward	9	Time of pptn.	0–8 hr.
C	1:1	Reverse	7	Time of pptn.	0–6 hr.
D	1:1	Forward	4	No. of washes	0–3 washes
E	1:1	Reverse	4	No. of washes	0–3 washes
F	1:3	Forward	5	Special[a]	....
G	...	Reverse	10	Composition	$Mg(OH)_2$–$Cu(OH)_2$

[a] Rate of precipitation different at different stages of precipitation.

Experimental

Preparation of Catalysts.—The catalysts fall into two classes with respect to the details of preparation. Those of series F and G were prepared by adding 180 ml. of sodium hydroxide from a buret to 140 ml. of the vigorously stirred nitrates (vice versa for series G). The solution of

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[2] E. H. Taylor, THIS JOURNAL, 63, 2906 (1941).

TABLE II

EFFECT OF RATE OF PRECIPITATION

				25°			35°			
Catalyst	Molar Cu:Mg	Direction of pptn.	Time of pptn.	Runs	Av. $k \times 10^2$	Av. dev., %	Runs	Av. $k \times 10^2$	Av. dev., %	Wt. % Cu
A-1	3:1	Forward	0.001	3	2.19	2	3	3.94	2	21.3
2	3:1	Forward	.233	3	1.57	5				21.8
3	3:1	Forward	.467	6	2.33	2				21.4
4	3:1	Forward	.961	3	3.72	0				20.8
5	3:1	Forward	1.483	3	3.06	3				19.7
6	3:1	Forward	1.967	3	3.62	2	3	6.19	3	21.4
7	3:1	Forward	2.467	3	3.41	4	3	5.65	2	21.0
8	3:1	Forward	3.056	5	4.03	3	3	6.68	1	20.9
9	3:1	Forward	3.587	6	4.42	4	3	7.15	2	21.4
10	3:1	Forward	4.039	3	5.21	3	3	7.28	3	21.6
11	3:1	Forward	4.992	3	3.70	1	3	5.94	3	20.7
12	3:1	Forward	5.879	5	3.85	8	3	6.30	3	21.9
13	3:1	Forward	8.025	3	3.95	1	3	9.37	1	22.1
B-1	1:1	Forward	0.001	3	2.49	2	3	4.50	2	39.3
2	1:1	Forward	.222	3	2.46	2				38.7
3	1:1	Forward	.458	3	3.03	2	3	4.28	1	40.1
4	1:1	Forward	.961	3	3.39	3				40.1
5	1:1	Forward	1.996	3	3.85	2	3	5.86	2	39.4
6	1:1	Forward	2.989	6	3.12	7				39.2
7	1:1	Forward	4.013	3	3.61	4	3	4.90	0	40.2
8	1:1	Forward	6.061	3	4.05	0				40.8
9	1:1	Forward	8.046	3	6.33	2	3	11.2	1	40.0
C-1	1:1	Reverse	0.001	3	2.94	3	3	4.51	2	38.7
2	1:1	Reverse	0.491	3	3.46	1				41.5
3	1:1	Reverse	1.029	3	3.50	1	3	5.18	1	41.7
4	1:1	Reverse	1.971	3	3.35	2	3	5.02	1	40.4
5	1:1	Reverse	3.066	3	3.54	2				40.1
6	1:1	Reverse	4.129	3	3.75	1				39.7
7	1:1	Reverse	5.797	3	3.90	3	3	6.00	1	39.2

TABLE III

EFFECT OF WASHING

Molar Cu:Mg = 1:1

Catalyst	Direction of pptn.	Time of pptn.	Washes	Runs	Av. $k \times 10^2$ at 25°	Av. dev., %	Wt. % Cu
D-1	Forward	0.962	0	3	3.17	2	34.4
2	Forward	.972	1	6	3.75	3	38.9
3	Forward	.917	3	4	2.41	9	38.8
E-1	Reverse	1.023	0	3	2.79	6	30.9
2	Reverse	1.005	1	3	3.37	1	39.1
3	Reverse	1.033	3	3	3.72	1	44.9

nitrates for series F was 0.0669 *M* in copper and 0.15 *M* in magnesium, and the sodium hydroxide was 0.407 *M*. For series G, the sodium hydroxide was 1.078 *M* and the mixed nitrates had a total molarity of 0.6, ranging from pure copper nitrate to pure magnesium nitrate. In series G, the time of precipitation was 2.0 hours. The catalysts of both series were centrifuged immediately after precipitation, and were washed twice with 300-ml. portions of water using centrifugal separation. They remained moist for one to four days, and were then dried in an oven at about 110° for twenty hours. They were ground in an agate mortar to a nearly uniform fineness (judged by the reproducibility obtained in unpublished work from different preparations of the same catalyst).

The catalysts of series A through E were prepared similarly, but with certain modifications designed to give closer control over important variables. All the water used for stock solutions and for washing was redistilled from alkaline permanganate through a block tin condenser, using ample precautions against entrainment. One stock solution of sodium hydroxide (0.9971 *M*) was used for all catalysts. Two stock solutions of nitrates were used, one prepared from equal volumes of 0.1999 *M* copper nitrate and 0.2004 *M* magnesium nitrate, and the other from one volume of the former and three volumes of the latter (205.0 ml. of the sodium hydroxide and 200.0 ml. of the appropriate nitrate solution were used for each catalyst). All the chemicals were of reagent grade.

The rate of precipitation was more carefully controlled by equipping the constant rate addition vessel used previously[2] with a micrometer stopcock to govern the rate of efflux. This was a 1-mm. bore stopcock with an 8-inch extension on one arm of the handle of the plug. The free end of the extension rested on a small machine screw. By adjusting the stopcock at the start to give the necessary drop-frequency and checking the frequency at five-minute intervals it was possible to obtain times of precipitation ranging from fifteen minutes to eight hours with an accuracy (and uniformity) ordinarily better than 5%.

Each catalyst was centrifuged immediately after the end of precipitation. It was then washed twice with 300-ml. portions of water, each washing followed by centrifuging. The time of stirring with each wash water was 5.0 minutes.

To minimize possible changes in the catalysts caused by high-temperature (above 100°) drying of wet material, each catalyst, after washing and centrifuging, was dried for four days at room temperature in a desiccator. It was then dried for five hours in an oven at 60°, and finally transferred to a very long-necked Erlenmeyer flask which was immersed for five hours in a toluene vapor bath (about 105° under the prevailing pressure). This ensured a very nearly constant temperature for final drying of all catalysts.

Each catalyst was then ground and sieved.[3] Only the portion passing 100-mesh and retained by 200-mesh was used for the standard rate runs.

The authors wish to thank Ruth Y. Taylor for assistance in the preparation of these catalysts.

Determination of Activity.—The activities toward hydrogen peroxide decomposition of the catalysts of series F and G were determined exactly as previously described.[2] For the catalysts of series A to E the method was similar except that the water used was redistilled.

Experimental Results

The results are presented in the tables below. The times of precipitation are in hours and the rate constants, k, are in sec.$^{-1}$ (g. catalyst)$^{-1}$. The columns headed "Av. dev." give the average deviations (in %) of the individual runs from the appropriate means.

TABLE IV

SPECIAL

Direction of pptn., forward. Cu:Mg = 1:3. No. of runs, 2

Catalyst	Method	Av. $k \times 10^2$ at 25°	Av. dev.	Wt. % Cu
F-1	All pptd. in 10.5 min.	1.19	0	21.4
2	All pptd. in 1 min., then stirred 2.0 hr.	4.22	2	22.5
3	All pptd. in 2.0 hr.	6.67	3	21.9
4	Cu pptd. in 1 min. Mg pptd. in 93 min.	7.18	3	22.6
5	Cu pptd. in 26 min. Mg pptd. in 1 min.[a]	4.23	1	22.0

[a] These times are only approximate. In the standard two-hour catalyst, F-3, twenty-six minutes is about the time in which the sodium hydroxide equivalent to the copper was being added, and ninety-three minutes is the corresponding time for the magnesium.

TABLE V

EFFECT OF COMPOSITION[a]

Direction of pptn., reverse. No. of runs, 2

Catalyst	Wt. % Cu	Av. $k \times 10^2$ at 25°	Av. dev.
G-1	76.1	0.19	1
2	74.3	.27	1
3	63.6	3.47	2
4	60.4	6.05	1
5	49.5	8.33	2
6	38.1	4.50	0
7	31.4	3.53	2
8	23.3	1.64	14
9	11.8	1.68	4
10	0.0	1.00	6

[a] These data show but one maximum, at about 50% Cu. The results of the previous paper[2] pointed to such a maximum, although the composition range did not extend far enough to define it. The maximum at about 19% Cu, found previously, may have been missed here because of too large intervals of composition, or because of error in one or two points.

Discussion

The most obvious conclusion to be drawn from these results (shown in Fig. 1) is that the preparational variables studied have a marked effect upon the activities of the catalysts prepared by ordinary coprecipitation. The curve for series A at 25° shows that a greater than three-fold change in activity accompanied the changes in time of precipitation, and that in the region around the greatest activity a change of 25% in time gave a change of 20 to 25% in activity. The curves for series A at 35° and for B at 25 and 35° are similar. The data for activity as a function of number of washings show variations of 25 to 35% over the range covered. These effects are more significant when compared with the results for activity as a function of composition, which show that changes of 25% in composition near the maximum change the activity by 40 to 45%. It is apparent that the rate of precipitation and the extent of washing exert effects upon the activity which are comparable to those caused by rather large changes in composition, and that adequate control must be maintained over such variables if correlations of activity with composition are to have meaning.

Almost as obvious as the wide variability of catalysts of series A and B (prepared by ordinary coprecipitation) is the contrast which they show with those of series C (prepared by reverse coprecipitation). The curves for series C are almost straight and horizontal, but are crossed and recrossed by those for series A and B. In its whole length, also, the curve for series C at 25°

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(3) This procedure makes direct comparison of these catalysts with those of the preceding paper[2] impossible. The latter contained a good deal of material finer than 200-mesh, and experiment showed that, as expected, material passing 200-mesh was considerably more active than the standard sieved samples.

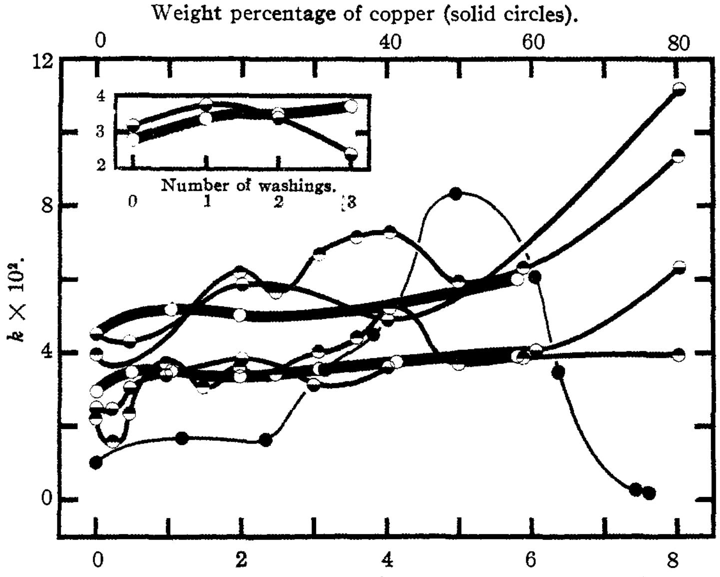

Fig. 1.—Catalyst activity as a function of rate of precipitation, number of washings, and composition.

Curve	Series	Variable
	Large Figure	
Thin	G	Composition, reverse
Medium	A(●), B(◒)	Rate of pptn., forward
Heavy	C	Rate of pptn., reverse
	Insert	
Medium	D	Washing, forward
Heavy	E	Washing, reverse

Upper curves for A, B and C at 35°; all others at 25°.

rises but 33% of its initial value, while the corresponding ones for A and B show variations of 170 and 160%. The curves for series D and E (effect of washing upon activity) show a similar contrast between the ones prepared by ordinary (D) and the ones prepared by reverse (E) coprecipitation.

This will be discussed in more detail later. It is clear that reverse coprecipitation is more suitable than ordinary coprecipitation for these catalysts (and presumably for others to which it is applicable), because the resulting catalyst has an activity more nearly independent of the conditions obtaining during its precipitation.

Although a quantitative treatment of the results is impossible at present, a qualitative explanation may be found in the hypothesis previously advanced[2] as to the effect of inhomogeneity upon activity. At the start of the precipitation of each catalyst, material rich in copper hydroxide will be precipitated until the copper is exhausted. Then the bulk of the magnesium will come down as the hydroxide. Depending on the rate of precipitation, there will be a variable time for the inter-diffusion of these portions of material, so that the resulting catalyst will consist of a continuum of material of varying composition, the distribution in composition depending on the time available for diffusion. The activity of each differential portion will be that of a homogeneous catalyst of the same composition, and the total activity will be a summation over all such portions; hence the total activity will depend both upon the time of precipitation and upon the shape of the activity–true composition curve. Since this curve for these catalysts exhibits maxima, the activity–time of precipitation curve must also, and for certain ranges of composition relative to the maxima the latter could show more maxima than the former. This seems to be the case here. One would also expect that initial mixtures of different compositions would show different behavior, and this is confirmed by the curves for series A and B. Those for series B have fewer and flatter maxima than those for series A.

The essential correctness of this picture is indicated also by the results for the catalysts of series F. Rapid addition of all of the sodium hydroxide (ten and a half minutes) gave a catalyst of poor activity, $k = 1.2$. Rapid addition of all (one minute) followed by stirring for 119 minutes gave a catalyst of definitely higher activity, $k = 4.2$. This activity was not, however, so great as that of a catalyst prepared by slow addition of the sodium hydroxide (in two hours), for which $k = 6.7$. These results are what one would expect from the proposed hypothesis, because the extra time available for rearrangement in the two latter catalysts should lead to higher activities (note the general upward trend from zero to four hours of the curve for series A at 25°). It is reasonable that the rearrangement would proceed farther in the last catalyst than in the second, because each portion had more time to rearrange by exchange through the open solution. In the second catalyst, with all the precipitate thrown down at once, any rearrangement must have taken place principally by diffusion through occluded solution, a process necessarily slow compared with diffusion through an open, stirred solution. That the important variable is the time during which both components are present and able to exchange is shown by catalysts F-4 and F-5. In the former, the copper (and, unavoidably, some of the magnesium) was precipitated rapidly (one minute) and the magnesium at the rate for a two-hour catalyst (ninety-three minutes). Thus there was approximately the same opportunity for exchange of the components as in the standard two-hour catalyst, and the activity ($k = 7.2$) was nearly the same as that of the two-hour catalyst ($k = 6.7$). The difference between these is probably within the experimental error for this series. In marked contrast to this activity is that for catalyst F-5 ($k = 4.2$). Here the copper was precipitated at the two-hour rate (twenty-six minutes) and the magnesium in one minute, allowing only one minute for the bulk of the magnesium to exchange with the copper–magnesium mixture precipitated at first.

The results for variation of activity with washing may be explained as follows. The initial rises in both curves probably result either from removal of adsorbed material, giving access to more active portions of the surfaces, or to decrease in particle size from incipient peptization. The further slow increase in activity of the catalysts prepared by reverse coprecipitation is perhaps caused by continuation of either of these effects, or by an actual change in surface composition through differential solubility. The rather rapid fall in activity with further washing of the catalysts prepared by ordinary coprecipitation may have one of two explanations. Either it results from actual change in composition of the surface through differential solubility, or, as seems more likely when the results of the analyses are considered, some of the more active material is lost in the wash water through peptization (which began to be marked from the second washing on). The composition change with washing is erratic for this series, as would be expected for peptization, while that for the reverse series is uniform and in the direction demanded by the solubilities.

Summary

1. The activities for hydrogen peroxide decomposition of copper hydroxide–magnesium hydroxide catalysts prepared by ordinary coprecipitation are affected by changes in the rate of precipitation and the extent of washing. These changes in activity are comparable to those caused by wide variations in composition.

2. Similar catalysts prepared by reverse coprecipitation (addition of metal nitrates to base) are affected only slightly by these variables.

3. The results can be interpreted in terms of the inhomogeneity previously shown to exist in catalysts prepared by ordinary coprecipitation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Anhydrous Sodium Soaps. Heats of Transition and Classification of the Phases*

BY ROBERT D. VOLD†

It has already been established[1] that instead of melting directly from crystal to liquid, sodium salts of long-chain fatty acids pass through a remarkable series of forms, each constituting a definite stable phase existing over a definite range of temperature. A calorimetric investigation has now been made of sodium laurate, myristate, palmitate, stearate and oleate to aid in interpretation of the phenomena occurring at transitions between these phases. This study has given values for the heats of transition and provides an independent determination of the transition temperatures. Further confirmation has been obtained of the reality of some of the transitions which had previously been found only with the microscope or with the dilatometer, but not with both.

An important initial problem in connection with the multiplicity of soap phases is that of classification. To what extent can phases occupying the same numerical position in the sequence, beginning with isotropic liquid, be regarded as similar? A beginning[1,2] had already been made

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(1) M. J. Vold, M. Macomber and R. D. Vold, THIS JOURNAL, 63, 168 (1941).

(2) M. J. Vold, *ibid.*, 63, 160 (1941).