Application of thermal energy may induce further redistribution of the "holes" in such a manner that at high temperatures the lattice becomes pseudo face-centered. It is also possible that at the higher temperatures a further loss of oxygen occurs, giving rise to a minor modification in the ionic arrangement but leaving the main features of the structures intact.

Summary

Over one hundred preparations were made by heating mixtures of barium carbonate and ferric oxide whose composition ranged from ten to ninety-nine per cent. barium carbonate. The temperate range was from 500 to 1000°. The composition of the products was determined by means of X-ray analysis.

1. Evidence is found for the formation of a compound having a perowskite-like structure from all mixtures containing fifty to ninety-five per cent. barium carbonate. The composition of this compound is probably represented by $Ba_8Fe_8O_{21}$, the lattice being deficient in oxygen. A unit cell (a = 8.05 Å) containing eight perowskite units best explains the diffraction pattern of this substance.
2. Barium oxide is formed from mixtures with a wide range of composition and is produced in maximum concentrations above 800° for compositions between forty and fifty per cent. barium carbonate.
3. $BaO \cdot 2Fe_2O_3$ is formed above 550° from mixtures containing between ten and fifty per cent. barium carbonate. Maximum formation occurs at forty per cent. barium carbonate and 800°. The interplanar spacings and intensities of the reflections are recorded for the first time.
4. $BaO \cdot 6Fe_2O_3$ is formed above 750° from all mixtures having barium carbonate content between five and forty per cent. The diffraction pattern was checked with literature values for a compound prepared at 1100°.
5. X-Ray evidence indicates that an unstable or poorly crystallized phase is present in mixtures containing ten to twenty per cent. barium carbonate which have been heated at temperatures below 750°.
6. Contour diagrams have been shown to be useful in correlating data involving changes of concentration of compounds with composition of mixture and temperature of preparation.

BROOKLYN, N. Y. RECEIVED MARCH 18, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Catalytic Properties of the Products of the Solid Phase Reaction between Barium Carbonate and Ferric Oxide[1]

BY MICHAEL ERCHAK, JR., AND ROLAND WARD

Substances which have been prepared by the interaction of solids in absence of a flux are usually in a very finely divided state provided the temperature of preparation is well below the melting points of any of the reactants or products or their mixtures. Such materials are in very suitable physical condition to act as catalysts and this property has been the subject of many investigations. Hüttig[2] and his students have published many papers on so called "active oxides," which are prepared by solid phase reaction. The results of investigations of this kind on zinc and cadmium ferrites have been taken to indicate that products obtained under conditions in which there is incipient formation of compounds have superior catalytic activity. It was further observed that the more extensive the formation of cadmium ferrite the poorer was the catalytic activity.

An investigation of the products of interaction of barium carbonate and ferric oxide has been reported.[3] This paper describes an investigation in which some correlation is sought between the catalytic activities of these products and their composition as revealed by X-ray analysis.

Experimental

The procedure followed was similar to that of Lamb, Bray and Frazer[4] in which the catalysis of the oxidation of carbon monoxide by oxygen was used as a criterion of relative catalytic activity. One gram of the catalyst was placed in an 8-mm. Pyrex tube and was held in contact with a thermometer bulb by means of glass wool plugs. The tube was placed in a furnace in such a way that the gas which passed over the catalyst was pre-heated. The furnace was adjusted to 325° and dry oxygen was first passed through the catalyst bed to cause activation. A dry mixture of carbon monoxide with excess oxygen (free from carbon dioxide and hydrogen) was then passed over the catalyst at a constant rate. The carbon dioxide formed in the catalyst chamber was absorbed in ascarite and weighed. The remaining carbon monoxide was oxidized by passing the residual gas mixture through a tube filled with Hopcalite maintained at 150°, absorbed in ascarite and weighed. The percentage conversion of carbon monoxide to carbon dioxide by the catalyst could thus be determined.

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(1) Abstracted from a thesis submitted by Michael Erchak, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate School of the Polytechnic Institute of Brooklyn, 1945.

(2) G. F. Hüttig, J. Funke and H. Kittel, *Z. Elektrochem.*, **40**, 306 (1936); G. F. Hüttig, *et al.*, *Acta Physicochim.*, **2**, 129 (1935).

(3) M. J. Erchak, I. Fankuchen and R. Ward, THIS JOURNAL, **68**, 2085 (1946).

(4) A. B. Lamb, W. C. Bray and J. C. W. Frazer, *J. Ind. Eng. Chem.*, **12**, 217 (1920).

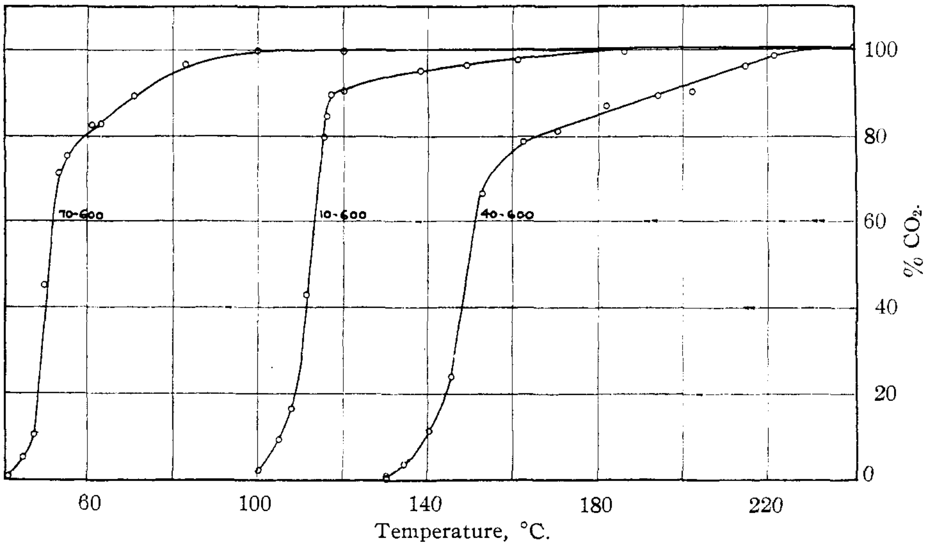

Fig. 1.—Catalytic activity of several catalysts as a function of temperature in the reaction $CO + {}^1/_2O_2 \rightarrow CO_2$.

The temperature of the catalyst sample was lowered stepwise until the rate of conversion became negligible. To reach this temperature with the more active catalysts, it was necessary to remove the catalyst chamber from the furnace and immerse it in ice or Dry Ice–alcohol mixtures. The percentage conversion–time curves could be duplicated for any one sample within a few per cent. Some typical curves are shown in Fig. 1. The identifying numbers, 70–600, 10–600, refer to the composition and temperature of preparations of the catalyst.[3] The temperature at which a catalyst gave 10% conversion of carbon monoxide to carbon dioxide was chosen for comparison since the slope of the conversion–time curves (Fig. 1) was favorable at this point. For the least active samples, this temperature was about 240°. Numbers from 1 to 15 were assigned to cover the range from 240 to −40° at 20-degree intervals. The more active the catalyst, the higher the number.

Results

To correlate the catalytic properties of the samples with their temperature of preparation and the mixtures from which they were prepared and also with the results of X-ray analysis, it was found convenient to construct a contour diagram (Fig. 2), in which the abscissas represent the composition of the original mixture of barium carbonate and ferric oxide and the ordinates indicate the temperatures to which they were heated. The numbers representing the catalytic activity of the samples were placed at the appropriate points and smooth curves drawn through equivalent points in such a manner that no lines intersected.

Inspection of Fig. 2 reveals that there are certain regions of maximum activity. These are, in order of decreasing activity, 70–850, 70–700, 90–700, 50–750, 35–850, 10–700, 30–400. There are also regions in which the catalytic activity falls to a minimum, for example 30–650, 45–600, 70–500. Maxima and minima are related to the nature or the catalysts as revealed by X-ray analysis.[3]

In the region 10–400 to 50–400 the catalysts are much more active than pure ferric oxide. All of them contain unchanged ferric oxide and barium carbonate and the 10–400 to 20–400 products show evidence for the presence of a poorly crystallized substance. One may assume that the enhanced catalytic properties are due either to the dissemination of the ferric oxide through the barium carbonate or the presence of the poorly crystallized ferrite.

It is convenient for the purpose of discussion to consider separately the catalytic activity of catalysts prepared from mixtures containing 10, 30, 50, 70 and 90% barium carbonate. The temperature cited in the following section is the temperature at which the catalyst was prepared. Reference should be made to the preceding article Figs. 3 to 8 for the composition of the catalysts.

Catalysts Prepared from 10% Mixtures.—These products increase slowly in activity as the temperature is raised to 700°, just below the temperature at which the compound $BaO \cdot 6Fe_2O_3$ becomes detectable. Further increase in temperature at this composition results in a rapid decrease in activity which is concurrent with the increase in formation of $BaO \cdot 6Fe_2O_3$.

Catalysts Prepared from the 30% Mixtures.—A steady decrease in activity with increasing temperature is observed from 400 to about 600°. This is followed by a rapid increase in activity as the temperature rises from 700 to about 750°.

The decrease in activity is accompanied by an increase in the amount of barium oxide and $BaO \cdot 2Fe_2O_3$ in the catalysts, while the rapid increase is observed with the products which first show the presence of $BaO \cdot 6Fe_2O_3$. The decrease in activity observed from 20–900 may be associated with the increase in concentration of $BaO \cdot 6Fe_2O_3$ in the catalysts.

The catalysts prepared from 20% mixtures are intermediate in their properties between those

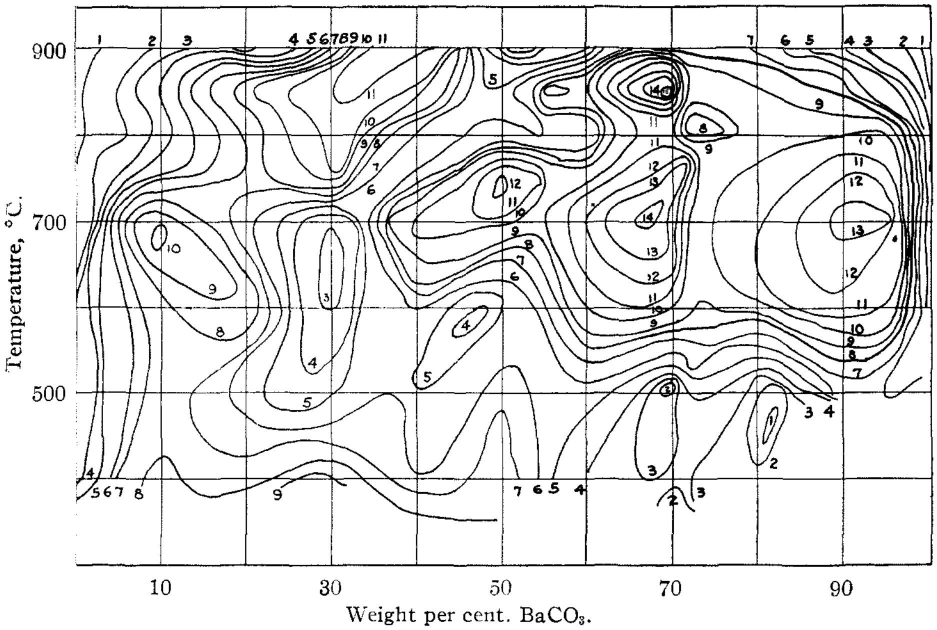

Fig. 2.—Catalytic activity contour diagram showing the dependence of activity upon composition of mixture and temperature of preparation.

prepared from 10 and 30% mixtures. The decrease in activity of the 30% mixture counterbalances the increase in activity of the 10% mixtures so that no great variation in activity is found with increasing temperature of preparation.

Catalysts Prepared from 50% Mixtures.—The initial decrease in activity as the temperature is increased from 400 to 600° may be due to the disappearance of the low temperature active phase. The mixture 50–600, which exhibits lowest activity in this series lies outside the regions in which $BaO{\cdot}2Fe_2O_3$ and $Ba_8Fe_8O_{21}$ are detectable.

The increase in efficiency as the temperature of preparation is increased from 600 to 750° and the decrease with further increase in temperature seems to be related to the appearance and disappearance of $Ba_8Fe_8O_{21}$ which is detectable in those samples prepared in the temperature range 700 to 800°.

The 40% mixtures are of some interest since it is at 40–800 that we find the maximum formation of $BaO{\cdot}2Fe_2O_3$. Increasing concentrations of this substance in the 30% mixtures was accompanied by decreasing catalytic activity. This sequence appears to be modified in the 40% mixtures by the influence of the maximum at 50–750 which extends toward 35–650 beyond the region in which $Ba_8Fe_8O_{21}$ is detectable by X-rays.

The variations in catalytic properties observed up to this point seem to be in reasonable agreement with the hypothesis of Hüttig. The maximum of 10-700 may well be due to incipient formation of $BaO{\cdot}6Fe_2O_3$ which may be so dispersed or so poorly crystallized that no detection with X-rays is possible in samples prepared at this temperature. The decrease in activity at 20-900 and 40-800 could be attributed to the increasing concentrations of $BaO{\cdot}6Fe_2O_3$ and $BaO{\cdot}2Fe_2O_3$, respectively, or to the formation of more perfect crystals of these substances.

Catalysts Prepared from 70% Mixtures.—The rapid rise in efficiency of these catalysts to 14 between 500 and 700° is followed by a decrease to 11 at 800° and a further increase to 15 at 850° and subsequent decrease to 8 at 900°. All the preparations made above 600° are very good catalysts.

These catalysts were prepared from mixtures which give the maximum formation of $Ba_8Fe_8O_{21}$. No evidence for the existence of this compound was found in mixtures prepared below 650°. One could assume, therefore, that the observed activity is due to $Ba_8Fe_8O_{21}$ in a poorly crystallized state or to its presence in small quantities. With increasing crystallinity or increasing concentration of this compound between 650 and 800°, however, we find a substantial increase in activity instead of a decrease. The catalytic properties of the perowskite-like substance differ in this respect from those of $BaO{\cdot}6Fe_2O_3$ and $BaO{\cdot}2Fe_2O_3$.

Catalysts Prepared from 90% Mixtures.—The activity of these materials increases uniformly from 500 to 700° and then decreases up to 900°. There is a very close correlation between this behavior and the variation in concentration of $Ba_8Fe_8O_{21}$, which increases from 650 to 700° and diminishes from 700 to 800°. There are no complications introduced by the presence of other compounds. It is also interesting to note that poor diffraction patterns were obtained from mixtures of this composition fired at temperatures above 800°. In these mixtures, some iron compound must be formed which is neither well crystallized nor a good catalyst. It should be observed that over the entire region bounded by the points 55-900, 45-700, 70-650, 95-700, 80-900 there is a high concentration of $Ba_8Fe_8O_{21}$ and that all of the catalysts within these limits are reasonably active. In this range there is little or no ferric oxide and widely varying amounts of barium oxide and barium carbonate. Some of the fluctuations in catalytic efficiency may be attributable to the presence of these substances or to variations in their promoter action on the perowskite-like substance.

A rather simple hypothesis may be advanced to explain the unusual catalytic efficiency of this substance. The compound corresponds approximately to the formula $Ba_8Fe_8O_{21}$ although the structure calls for the formula $BaFeO_3$ so that only one-fourth of the iron ions are in the oxidation state 4. Such a crystal could readily accommodate more oxygen ions without any fundamental change occurring in the lattice. Some of the tervalent iron merely has to be oxidized to the quadrivalent state.

Thus the reaction

$$Ba_8Fe_8O_{21} + O_2 \longrightarrow Ba_8Fe_8O_{23}$$

would cause three-fourths of the iron ions to be in the quadrivalent state. The upper limit of this reaction would be $BaFeO_3$ but all degrees of oxidation up to 4 are possible. The oxidation of the carbon monoxide at the surface of the oxidized crystal could readily occur.

$$Ba_8Fe_8O_{23} + 2CO \longrightarrow Ba_8Fe_8O_{21} + 2CO_2$$

The oxygen ions removed in this way would not necessarily be derived from the oxygen molecule. Such a mechanism would not require the presence of active centers since any part of the crystal surface would be available for the exchange.

Summary

The relative catalytic activity of the products of the solid phase reaction between barium carbonate and ferric oxide have been determined using the oxidation of carbon monoxide as a means of comparison. Good correlation between the catalytic properties and the composition of the catalysts as revealed by X-ray analysis has been obtained.

For the compounds $BaO{\cdot}6Fe_2O_3$ and $BaO{\cdot}2Fe_2O_3$ the maximum activity is obtained with mixtures in which it can be assumed that incipient formation of the compounds is occurring and that with increasing crystallinity or increasing concentration of these compounds, the catalytic properties of the mixtures decrease. This is in accord with the results of Hüttig. With mixtures containing the compound $Ba_8Fe_8O_{21}$, however, the catalytic activity increases as the concentration or crystallinity of the compound increases. An explanation of this phenomenon based upon the deficient lattice of the substance and the variable valence of the iron is advanced. A contour diagram correlating catalytic efficiency with temperature of preparation and composition of the original mixtures is shown to be useful in problems of this kind.

Brooklyn, N. Y. Received March 18, 1946

[Contribution from the Research Laboratories of Merck & Co., Inc.]

Streptomyces Antibiotics. X. The Degradation of Streptomycin and Dihydrostreptomycin with Ethyl Mercaptan

By Frederick A. Kuehl, Jr., Edwin H. Flynn, Norman G. Brink and Karl Folkers

The cleavage of streptomycin hydrochloride, I, by the action of methanolic hydrogen chloride to give streptidine[1] and the amorphous methyl streptobiosaminide dimethyl acetal hydrochloride, II, which upon acetylation was obtained as the crystalline tetraacetyl derivative, III, has been described.[2] The methyl streptobiosaminide dimethyl acetal hydrochloride was degraded further to a new hexosamine, N-methyl-*l*-glucosamine,[3] which was isolated as the pentaacetyl derivative, IV. These reactions and products may now be formulated according to the following graphic scheme. The pyranose ring structure for the N-methyl-*l*-glucosamine derivatives is written at present by analogy with the work of Neuberger relating to the ring structure of N-acetyl-α-methylglucosaminide.[4]

Streptomycin has now been cleaved with ethyl mercaptan and hydrogen chloride to streptidine and a new derivative of the disaccharide, ethyl thiostreptobiosaminide diethyl mercaptal hydrochloride, V. This degradation of streptomycin is accomplished by shaking overnight at 25° a suspension of streptomycin hydrochloride in ethyl mercaptan saturated with hydrogen chloride. After removing the excess ethyl mercaptan, the residue is dissolved in a small amount of water from which the mercaptal hydrochloride crystallizes, leaving the streptidine in solution.

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[2] Brink, Kuehl and Folkers, *ibid.*, **102**, 506 (1945).

[3] Kuehl, Flynn, Holly, Mozingo and Folkers, This Journal, **68**, 536 (1946).

[4] Neuberger, *J. Chem. Soc.*, 47 (1941).