an agreeable flavor. The addition of materials, such as gelatin and egg albumin, to a viscous medium obtained by the use of sucrose, corn sirup, and water serves to reduce surface tension, and when the mixture is violently agitated a large proportion of air is incorporated in the mass. This incorporated air produces both lightness of texture and whiteness of color. The problems of marshmallow manufacture are primarily those of texture and stability. Both depend to a great extent upon suitable water content, which, in turn, is influenced by the other constituents. There are many colloid problems in the candy industry, and the facts and principles of colloid chemistry find ever-increasing application.

Use of Chocolate

Chocolate, which is one of the most important ingredients in many candies, presents a large number of problems. Although chocolate is relished by most persons for its agreeable consistency and flavor, its extensive use in the candy industry has resulted from other considerations as well, the most important of which is the fact that it serves as an excellent protective coating, which, on account of its high fat content serves to retard evaporation of moisture from the coated center. This protective feature is so important that, if a suitable substitute for chocolate were ever provided, the use of chocolate would in all probability decrease. The candy industry uses most of its chocolate in the form of coating, and, aside from considerations of flavor and color, the candy manufacturer is principally concerned with the fluidity of the chocolate coating. The fluidity should be sufficiently high and sufficiently uniform, particularly in coatings to be applied mechanically by means of enrobing machines. Although the fluidity is determined to a great extent by the quantity of cocoa fat present, the fineness of milling and the extent to which the individual cacao particles in the mass are enveloped by fat undoubtedly play an important part. The fluidity of chocolate coating is a subject which has not been investigated adequately.

New Types of Candy

In some fields of manufacture, industry is best served by the mass production of standard articles. In others, there is danger of too much standardization, and the continued production of novelties and new types is vital to success. Old favorites will doubtless continue to play an important part in the stability of the candy industry, but there is also an urgent need for the production of new types of confections.

The problem of producing new confections, so far as it involves combining and blending basic raw materials, flavors, and colors from the standpoint of their gustatory and esthetic appeal to the consumer, belongs more to the creative chef or candy maker than to the chemist. The appropriateness of texture and consistency, the constancy with which the desired consistency can be obtained, and the stability with which it may be retained, however, are essential and vital features in any confection, new or old, and it is here that the chemist has an indispensable function in the creation of new confections. An excellent illustration of this is in the production of a new type[4] of candy containing dextrose instead of sucrose in the solid phase, the liquid phase containing levulose and being saturated with respect to dextrose. This is a distinct novelty, in that in all the usual types of candy containing both liquid and solid phases the solid phase consists of sucrose. On account of the difference in physical characteristics of dextrose and sucrose crystals, a confection of this type has a consistency quite different from that of candies containing sucrose as the solid phase.

Conclusion

Chemistry as so far employed in the candy industry has been used primarily for the purpose of analysis and control, and even then it has been restricted to certain phases of manufacture, especially to the control of dyes to obtain the desired shades. The field of application of chemistry in a constructive and creative way, to devise new types of confections, to obtain suitable consistency and texture, to retard aging, and to design appropriate types of packages has hardly been touched. Herein lies a definite opportunity. The situation demands active coöperation between the chemist and the candy maker. As in other industries, the "practical man" often depreciates the value of the chemist or other technical man, and the chemist frequently views so-called "practical" knowledge with some disdain. It is undoubtedly by close coöperation between the two that the greatest and most rapid progress can be made.

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[4] Schneller, U. S. Patent 1,551,175 (1925).

Catalysts for the Formation of Alcohols from Carbon Monoxide and Hydrogen

II—Synthesis of Methanol with Catalysts Composed of Copper and Zinc[1]

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THE recently developed processes for the high-pressure synthesis of alcohols and other organic products from water gas owe their success primarily to the development of a new type of catalysts composed of mixtures of metallic oxides at various stages of reduction. The lack of detailed knowledge concerning the reactions involved in this promising field of industrial chemistry warrants a careful study of the fundamental nature of the metallic oxide catalysts employed. In initiating an investigation along this line, data were obtained on the decomposition of methanol in the presence of catalysts prepared from the oxides of copper and zinc in various proportions, ranging from 0 to 100 mol per cent of each constituent. The results of this work, published as the first paper of the present series,[2] showed that there was a profound change in mechanism of the decomposition reaction in going from 0 to 100 mol per cent zinc oxide. Thus, while pure copper gave predominately formaldehyde, the addition of a small percentage of zinc oxide to the catalyst resulted in methyl formate production with a maximum yield at about 88 mol per cent copper and 12 mol

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[1] Received July 24, 1928. Presented before the Division of Industrial and Engineering Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Frolich, Fenske, and Quiggle, IND. ENG. CHEM., 20, 694 (1928).

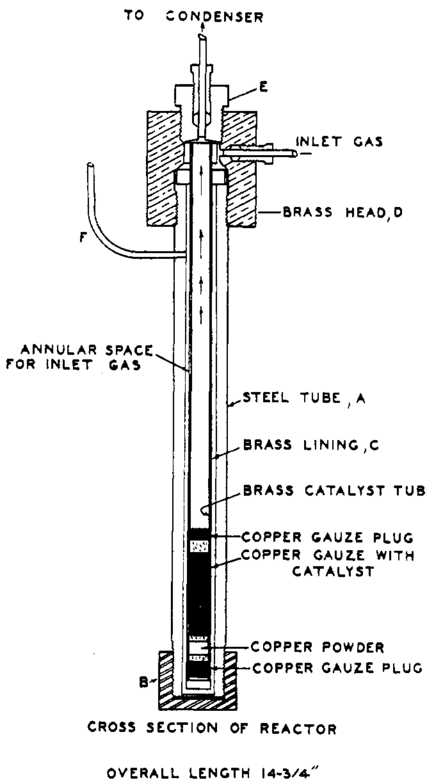
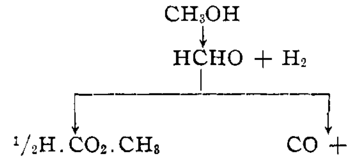


Figure 1—Reactor Used for Catalyst-Testing at High Pressure

per cent zinc oxide, when approximately 80 per cent of the decomposed methanol occurred as this ester. Further additions of zinc oxide, however, decreased the methyl formate yield with a simultaneous increase in carbon monoxide production. With catalysts containing an excess of zinc oxide, carbon monoxide predominated in the products. It was suggested that the decomposition occurred according to the following scheme:



$$CH_3OH \rightarrow HCHO + H_2 \rightarrow \begin{cases} {}^1/_2H.CO_2.CH_3 \\ CO + H_3 \end{cases}$$

Attention was also called to the fact that the relatively rapid change to carbon monoxide production coincided, roughly, with the 50 mol per cent point of the catalyst mixture and this result was compared with statements frequently made in the patent literature to the effect that such binary systems must contain an excess of the more basic constituent in order to be active catalysts for the high-pressure syntheses of methanol. It was therefore suggested that those catalysts which yielded carbon monoxide in the decomposition experiments would also catalyze the synthesis of the alcohol from carbon monoxide and hydrogen at high pressure, while the methyl formate-producing catalysts would be inefficient for the synthesis. To test this supposition, the decomposition data have been correlated with experiments on methanol synthesis using identically the same catalysts.

Apparatus and Experimental Procedure

Considerable difficulty was experienced in perfecting a suitable apparatus for careful testing of the catalysts under parallel conditions, the reason being that the copper-zinc oxide mixtures seemed to be particularly sensitive to poisoning by carbonyl. It was therefore necessary to line all steel surfaces with some other metal, brass and copper being preferable. Under these conditions it was difficult to avoid clumsy construction if direct temperature measurements were to be made by introduction of a pyrometer well into the reactor itself. Since it was also desirable to cut down the size of the reactor and the volume of the catalyst to a minimum in order to reduce the amount of heat liberated per unit time, the pyrometer well was eliminated.

For these reasons the reactor was submerged in a lead bath and the temperature of the bath measured by means of a pyrometer. In addition, to avoid local overheating in the contact mass the catalyst was suspended in a roll of fine copper gauze.

Since the methanol reaction is quite exothermic, the temperature of the bath may be somewhat lower than that of the catalyst, but not more than 10° C. lower owing to the large area for heat dissipation compared to the volume of gas used. As a matter of fact, this does not seriously affect the relation between catalyst composition and activity.

The final reactor construction arrived at is shown in Figure 1. Its compactness, simple construction, and ease of operation make it particularly useful for small-scale work of this type. The reactor consists of an outer steel tube, *A*, fitted with a steel cap, *B*, at one end. Inside this tube fits a brass lining, *C*, turned from a solid rod to avoid the difficulty of sealing one end. The open end of the brass lining is expanded into a ring whose upper and lower edges form line seats with the chamfered surfaces of the brass head, *D*, and steel tube, respectively. The catalyst chamber is a thin-walled brass tube which fits rather loosely into the brass lining. This tube is flanged at the top and seated in the head by a brass cap screw, *E*. The carbon monoxide-hydrogen mixture enters through the brass head, passes down between the brass tube and the brass lining, thereby being brought up to reaction temperature before it comes in contact with the catalyst, which is held in the lower end of the brass tube. The catalyst is ground to 60 mesh and supported on a copper screen spiral, 3-cc. samples of the powdered catalyst mixture being used for each experiment. To prevent the building up of gas pressure between the steel tube and the brass lining,

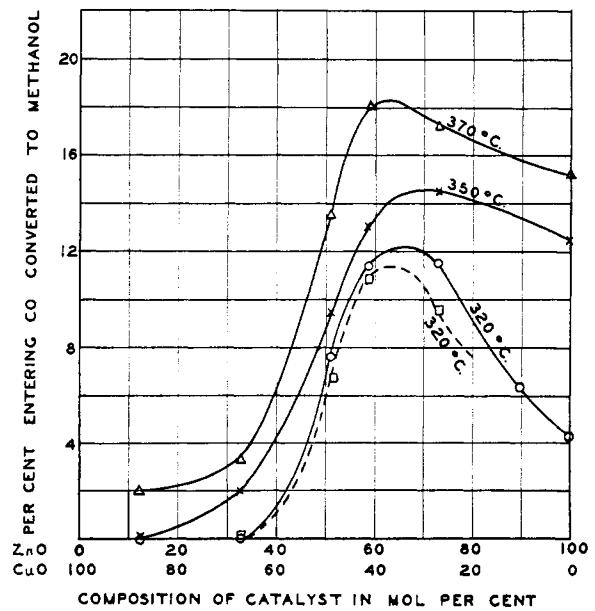


Figure 2—Conversion of Carbon Monoxide to Methanol at 3000 Pounds (204 Atmospheres) Pressure and Various Temperatures, as a Function of Catalyst Composition

The dotted line represents conversion at 320° C. after the catalyst has been exposed to the higher temperatures.

and to permit detection of any leakage of gas through the lining, a small hole is drilled in the steel tube and fitted with a short pipe, *F*, leading to a water trap.

The gas mixture used in these experiments analyzed 70.8 per cent hydrogen, 26.5 per cent carbon monoxide, 0.6 per cent oxygen, and 2.1 per cent nitrogen. The gas was passed at a constant pressure of 3000 pounds per square inch (204 atmospheres) from the supply cylinder through a purifier into the reactor. In going into the purifier the gas passed through successive layers of soda lime, calcium chloride, and activated charcoal. After entering the purifier the gas mixture did not come in contact with anything but copper and brass surfaces. The products from the reactor passed through a condenser to a combined separator and receiver, where the liquid product was separated from the unconverted gas under full pressure. The liquid product was withdrawn into a graduated glass container, which was cooled by a mixture of solid carbon dioxide and ether to eliminate evaporation losses in releasing the pressure. The exit gas passed through a wet meter to a holder. From the volumes and analyses of the liquid and gas collected the percentage of entering carbon monoxide converted into methanol was calculated.

To simplify the control the experiments were made at constant rate of flow of the exit gas, corresponding to 28 liters of gas collected per hour per 3 cc. of catalyst. Thus, the rate of entering gas flow varied with the methanol production so as to give a somewhat shorter time of contact for the more active catalysts. Obviously, this tends to reduce the percentage of carbon monoxide converted with the active catalyst, but the effect can be neglected for any practical purpose.

Discussion of Results

After reduction with methanol vapor at atmospheric pressure and 220° C., the catalysts were immediately transferred to the high-pressure reactor. While a slow stream of gas was passed through the apparatus, the temperature of the lead-antimony bath was permitted to build up to 320° C., at which temperature the first run was made, the pressure being held constant at 3000 pounds (204 atmospheres). As soon as complete data had been obtained, usually after 2 hours' running, the temperature was raised to 350° C. for a second series of readings. This was followed by an experiment at 370° C., after which the temperature was again brought back to 320° C. for a final determination of methanol yield. By comparing the results of the first and the last runs it was possible to ascertain whether the catalyst had suffered any appreciable loss in activity during the complete test. This same procedure was followed for all catalysts, and the results obtained[3] are plotted in Figure 2 as percentage of entering carbon monoxide converted to methanol at the various temperatures as function of the catalyst composition.

From the curves in Figure 2 it is apparent that the mixtures consisting essentially of copper are exceedingly poor catalysts for the synthesis of methanol. It should be emphasized that these catalysts were prepared from the corresponding hydroxides, precipitated from the nitrate solutions with ammonium hydroxide. Thus they contain no foreign constituent other than the traces of impurities which might have been present in the C. P. copper and zinc nitrates from which they were prepared.

With increasing percentages of zinc oxide the activity of the catalysts for methanol synthesis increases, at first slowly, then in the neighborhood of the 50 mol per cent point very rapidly, reaching a maximum between 60 and 70 mol per cent, and finally falling off somewhat toward the point corresponding to pure zinc oxide. The resemblance of the synthesis curves to the carbon monoxide curves obtained in the decomposition work is remarkable, as is brought out very clearly by Figure 3, which gives both curves plotted with the same abscissa and with the ordinates so adjusted as to permit ready comparison. It is apparent that, within the experimental error, the two curves coincide in the neighborhood of the 50 mol per cent point, where the break occurs. It may be added that the decomposition curve is somewhat uncertain for the pure zinc oxide catalysts, making the final values for carbon monoxide formation between 97 and 100 mol per cent zinc rather uncertain. Except for this upper region, the two curves show no divergency in their general shape.

In analyzing these results it is necessary to bear in mind that the decomposition curve represents percentage of carbon monoxide formed on the basis of methanol actually decomposed. While this carbon monoxide yield reaches 60 to 70 per cent, the methanol decomposed represents less than 50 per cent of the total amount passed over the catalyst. Since the equilibrium concentration of methanol with respect to carbon monoxide and hydrogen is less than 1 per cent at the conditions of operation, 360° C. and atmospheric pressure, it follows, therefore, that the decomposition data were obtained sufficiently far from equilibrium to make the results representative of the activity of the catalysts used. While the equilibrium data available for methanol synthesis under high pressure are somewhat unreliable, it seems safe to conclude that the synthesis curves also represent conditions remote from equilibrium, as may be seen from a comparison with data previously published by this laboratory.[4]

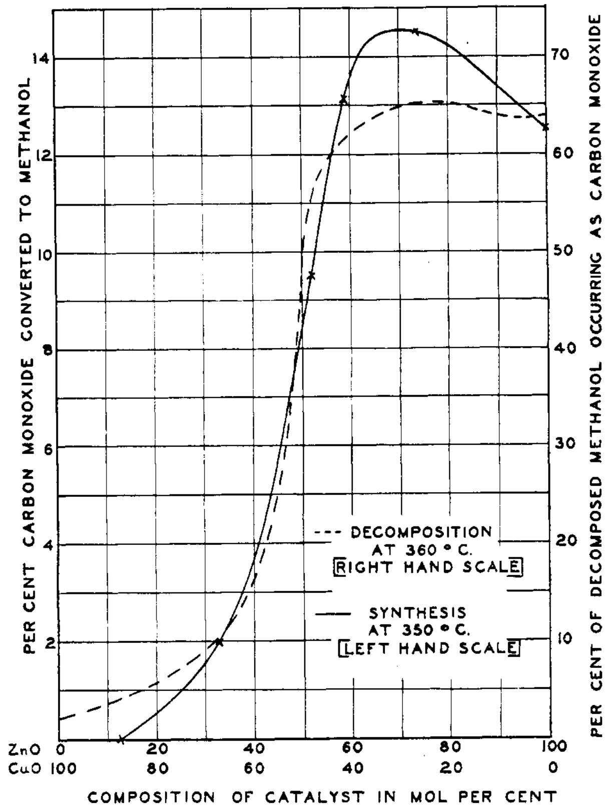


Figure 3—Comparison of Methanol Decomposition at 360° C. and Atmospheric Pressure with Synthesis at 350° C. and 3000 Pounds (204 Atmospheres) Using the Same Catalysts

From the two curves for 320° C. in Figure 2 it follows that there is a slight but measurable decrease in activity of these copper–zinc oxide catalysts during the cycle, involving operation for a total period of about 8 hours between temperatures

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[3] Taylor and Southwick, Thesis (1928), M. I. T. Library.

[4] Lewis and Frolich, IND. ENG. CHEM., **20**, 285 (1928).

of 320° and 370° C. The dotted line represents the conversions at the end of the run—i. e., after the catalysts have been operated at the higher temperature levels.

Conclusions

In the absence of similar data on other catalyst mixtures it seems justifiable to conclude that the decomposition method of testing is eminently fitted for studies of the activity of catalysts for the methanol synthesis from water gas at high pressure. While such a result had been hoped for in light of the data recorded for other catalytic reactions, the good agreement between the independent methods of testing is nevertheless surprising in view of the rather complicated nature of the methanol decomposition reactions discussed in the first paper of this series.[2] It is particularly interesting to note that formation of methyl formate, by polymerization of the supposedly intermediately formed formaldehyde, does not occur in the high-pressure synthesis of methanol with these catalysts.

In addition to the fact that the decomposition at atmospheric pressure is a much simpler method of catalyst-testing than the direct synthesis of the alcohol at high pressure, it also follows from these researches that the decomposition method is greatly illuminating as a means of disclosing the mechanism of the underlying reactions. The decomposition method of catalyst study therefore promises to be a valuable tool in researches on the synthesis of higher alcohols and more complicated organic compounds. Work along this line is now in progress.

Acknowledgment

The writers are indebted to E. J. Tauch for design of the high-pressure reactor used in the catalyst test, and to Miss D. Quiggle for preparation of the catalysts.

New Catalytic Processes for the Utilization of Coal-Tar Crudes[1]

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THE purpose of this discussion is to focus attention on some extremely interesting possibilities for the chemical industry arising from the development of new and very effective processes for purifying various crude aromatic hydrocarbons, such as light-oil fractions, crude naphthalene, and, particularly, crude anthracene by selective catalytic oxidation. This is accomplished by the use of new classes of contact masses which, by selective action, remove part or all of the impurities.

Difficulties of Anthracene Purification

To illustrate the usefulness of such new catalytic processes may be cited the difficulties involved in the recovery of anthracene of high purity from coal tar, as hitherto practiced. This has long been one of the most baffling problems in the coal-tar distillation industry. Even yet the most important source for the technical recovery of anthracene is anthracene oil or green oil. This is the last fraction coming over in the distillation of coal tar and is collected in the range of temperature of 270–400° C. From this fraction 6 to 10 per cent is recoverable as crude anthracene of 15 to 30 per cent anthracene content. The recovery of the crude anthracene from the green oil fraction is made by filtration, centrifuging, and cold and hot pressing. By washing as well as possible with solvent naphtha or creosote oil, the adhering oil and other impurities are to some extent removed and an enriched product is obtained, which, however, still contains only 30 to 50 per cent anthracene.

Many difficulties are encountered in the commercial purification of such grades of crude anthracene to such an extent that the product is sufficiently pure for the production of anthraquinone, which is the most important intermediate in the dye-making industry for alizarins and vat colors.

The impurities which must be removed in this purification are many and various. Phenanthrene, acenaphthene, fluorene, carbazole, methylanthracene, acridine, etc., are all present as well as, in many cases, high-boiling paraffins such as ecosane, decosane, and the like. Other impurities are sometimes present in small amounts and the relative proportions of the different impurities will vary considerably with the nature of the coal tar from which the crude anthracene is produced. The impurities present in largest quantities, however, are carbazole and phenanthrene. Although carbazole is not the most troublesome contaminant, its removal is a critical problem. The paraffins and the alkyl derivatives of anthracene, however, are not only more troublesome to remove but are also more harmful to the quality of the product.

Many processes have been worked out for the further purification of the various grades of crude anthracene. As examples may be mentioned the removal of contaminants by washing or by recrystallization. Since carbazole behaves much like anthracene in solubility in most solvents and in vapor pressure special treatments have been devised for its removal, such as conversion to potassium salt by treatment with potassium hydroxide, conversion to nitroso compounds, formaldehyde derivatives, and so on. One solvent has been found which is somewhat specific for the removal of carbazole, and that is pyridine.

All of these processes are expensive and slow. Many require several repetitions in the principal operations and on that account are high in labor cost. They entail relatively high health hazards, since the crude anthracene contains many compounds which are very irritating to the skin and may even initiate cancerous growths. The processes are also very wasteful, since only certain grades of crude anthracene can be used. For example, certain coke-oven tars produce a crude having less than 24 per cent and sometimes as low as 14 to 16 per cent anthracene content. Such crudes cannot be economically worked up by the processes hitherto used. Moreover, cannel coal or other highly paraffinoid coals, when cracked, result in tar fractions containing relatively large amounts of paraffins. These contaminants cannot be satisfactorily removed by any of the methods of purification hitherto known, so that the raw materials from such tars have been quite useless for making intermediates for dyes.

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[1] Paper presented before the Second International Conference on Bituminous Coal, Pittsburgh, Pa., November 19 to 24, 1928.

[2] Technical director, The Selden Company.