

The average yearly operation of the producer plant calls for the continuous operation of three generators and the additional operation of a fourth generator for 12 hours per day during 6 months of the year. Thus, three generators are in use three-fourths of the time and four generators, one-fourth of the time. When three generators are running, the average evaporation per day in the boilers is 30,000 cubic feet from feed water at 170° F. to steam at 90 pounds pressure. When four generators are running, the amount of lampblack produced increases proportionately, but the steam production only increases to 32,500 cubic feet. Since all the lampblack and tar are fired, some of the fuel must go to waste under these conditions. Table III shows the average operating data calculated from the test data and from the information given above, and the boiler efficiencies calculated from these data.

Table III—Calculation of Boiler Efficiencies with Lampblack and Tar as Fuel

	3 GENERATORS	4 GENERATORS	AVERAGE
Average gas production for plant, cu. ft. per day	13,410,000	17,900,000	14,530,000
Weight of lampblack burned, lbs. per hr.	7,580	10,106	8,211
Weight of tar burned, lbs. per hr.	1,460	1,957	1,584
Heat from lampblack, B. t. u. per hr.	113,000,000	150,700,000	122,400,000
Heat from tar, B. t. u. per hr.	20,200,000	26,900,000	21,900,000
Total heat from fuel, B. t. u. per hr.	133,200,000	177,600,000	144,300,000
Evaporation, cu. ft. per day from water at 170° F. to steam at 90 lbs. pressure	30,000	32,500	30,600
Heat content of steam above water at 170° F., B. t. u. per hr.	81,600,000	88,400,000	83,300,000
Boiler efficiency, per cent	61.2	49.8	57.7

A boiler efficiency of 80 per cent may safely be assumed for oil-firing. On this basis there would be required $\frac{83,300,000 \times 24}{18,554 \times 0.80} = 134,950$ pounds of oil per day. With oil at \$1.18 per barrel of 333 pounds, the daily cost of oil for fuel would be $\frac{134,950}{333 \times 1.18} = \478 .

The comparative cost of firing lampblack and tar as against firing oil is calculated and shown in Table IV, which gives the resultant equivalent value of lampblack and tar as fuel.

Table IV—Equivalent Cost per Day of Lampblack and Tar as Fuel Compared with Oil

	LAMPBLACK	OIL
Fuel oil		\$478.00
Firing expenses:		
32 firemen at \$6.00 per day	\$192.00	
3 firemen at \$6.25 per day		18.75
3 water tenders at \$6.25 per day	18.75	18.75
3 boiler cleaners at \$5.25 per day	15.75	15.75
Equivalent value of lampblack and tar	304.75	
	\$531.25	\$531.25

From the value of \$304.75 found in Table IV for the equivalent value of lampblack and tar per day as fuel, it follows that the value of the heat content of these materials per million B. t. u. when used as fuel is $\frac{304.75}{144.3 \times 24} = \0.088 .

The value of one million B. t. u. in manufactured gas, however, with gas worth \$0.30 per 1000 cubic feet at the generator, is $\frac{0.30}{0.579} = \$0.518$. The economic efficiency of the gas-producing process can therefore be materially increased, if it is possible to eliminate the production of lampblack and tar in the generator and put the heat now represented by their removal back into the manufactured gas, with the corresponding change to oil as fuel for the boiler plant of the producers. While it is possible to increase the economic return from the lampblack by briquetting it for sale, the value of the heat units in the lampblack will invariably be lower than the value of the same number of units in the gas, and the highest economic efficiency will result from complete gasification.

The senior author has developed a modification of the Jones process² in which lampblack is eliminated or greatly reduced by passing the gas from the primary through an intermediate shell before enriching it. In this intermediate shell sufficient heat is stored in the checker brick, and sufficient time is allowed for all the lampblack to react with the steam.

Acknowledgment

Acknowledgment is due Willis S. Yard, vice president in charge of the gas department of the Pacific Gas and Electric Company, for advice relative to the practical aspects of gas-making.

² Pike, U. S. Patent 1,644,146.

Catalysts for the Formation of Alcohols from Carbon Monoxide and Hydrogen¹

III—X-Ray Examination of Methanol Catalysts Composed of Copper and Zinc

Per K. Frolich, R. L. Davidson, and M. R. Fenske

DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

IN THE experiments on the decomposition and synthesis of methanol previously reported,^{2,3} the catalysts composed of copper and zinc were prepared by precipitating the mixed hydrates from the corresponding nitrate solutions, dehydrating the gel, and subsequently reducing the oxides with methanol vapor at the lowest temperature at which reduction would possibly take place—i. e., about 200° to 220° C. Although zinc oxide is usually considered non-reducible at this temperature, it was, nevertheless, found to be partly reduced by the above treatment when present in mixture with copper oxide. Such reduction of zinc oxide has been reported

in the patent literature⁴ as well as in a recent publication by Rogers.⁵ The reduction manifested itself in the present catalyst mixtures by a somewhat greater loss in weight than that corresponding to reduction of the copper oxide alone. In a previous publication² attention was called to the fact that the free-energy change in the reduction process varies somewhat depending upon the type of products formed from the methanol used for reduction. It was pointed out that the carbon dioxide concentration of the reducing gas mixture might build up to as high a value as 7 per cent according to the equilibrium:

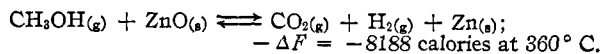
¹ Received August 10, 1928.

² Frolich, Fenske, and Quiggle, *IND. ENG. CHEM.*, **20**, 294 (1928).

³ Frolich, Fenske, Taylor, and Southwick, *Ibid.*, **20**, 1327 (1928).

⁴ British Patent 273,030 (July 23, 1925).

⁵ *J. Am. Chem. Soc.*, **49**, 1432 (1927).



Clearly, the reduction does not proceed according to this one simple reaction, but such considerations show in a qualitative way that zinc oxide may be reduced partly by methanol vapor even when it is present alone. Furthermore, the reduction of copper oxide by methanol is exothermic and could furnish the necessary energy for the zinc oxide to be reduced when these two compounds are present in an intimate mixture.

While the loss in weight on reduction of the catalyst shows that the zinc oxide gives up some of its oxygen, the results thus obtained are not absolutely quantitative since there is always a possibility of the oxide mixtures not being completely dehydrated when the reduction is started. Furthermore, the loss in weight does not tell whether the zinc is reduced to the free metal or merely to a lower stage of oxidation. To obtain further information along this line, the spent catalysts were therefore examined by x-rays.

Experimental Work

The source of x-rays used in determining the lattice dimensions was a molybdenum target Coolidge tube. By employing a zirconium oxide filter, the beam was made essentially monochromatic, corresponding to wave lengths of 0.708 Å. ($K\alpha_1$) and 0.712 Å. ($K\alpha_2$). The diffraction pattern was recorded on a photographic film in regular way by passing the x-ray beam through a capillary glass tube holding the finely divided catalyst (60 mesh). Since the details of the experimental procedure and calculations involved will be discussed elsewhere by R. H. Aborn, who cooperated with the authors in carrying out the x-ray phases of this research, the present paper will be limited to a correlation of the x-ray results with the data previously obtained on the activity of the catalysts.

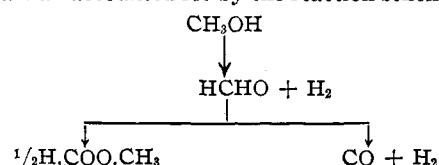
Discussion of Results

The study of the complete series of copper-zinc oxide mixtures demonstrates that at every composition the catalyst is decidedly crystalline, possessing the characteristic crystal structure of the two components. The copper has the same structure as that of the metal in bulk, and the zinc oxide has the same structure as when prepared by any other method. However, the unit-cell sizes of both are markedly influenced by the presence of the other constituent. Thus, it will be seen from Figure 1 that the side of the unit cell of the copper lattice expands with increasing additions of zinc oxide, passes through a maximum between 50 and 60 mol per cent zinc oxide, decreases somewhat, and then rises again. The maximum elongation recorded is 1.3 per cent, corresponding to 90 mol per cent zinc oxide, which is the highest concentration studied.

The unit cell of the zinc oxide suffers a similar elongation on addition of copper, with the exception that the curve first passes through a minimum value for 10 to 20 mol per cent copper. The dimensions of the zinc oxide lattice have been determined along both the vertical and horizontal axes, but

since the axial ratio remains practically constant it is apparent that the two curves have the same general form, and only the curve representing the changes in the vertical axis is reproduced in Figure 1.

It is interesting to compare these results with the activity measurements previously made with the same catalysts. Figure 2 is a reproduction of data showing how the products of decomposition of methanol (at atmospheric pressure and 360° C.) vary with the composition of the binary catalyst mixture. From these curves it follows that formaldehyde is the principal product of decomposition with pure copper, but that small amounts of zinc oxide greatly favor production of methyl formate, presumably due to polymerization of initially formed formaldehyde. As the composition of the catalyst changes to an excess of zinc oxide, the mechanism of the decomposition reaction is altered rather suddenly so as to yield predominantly carbon monoxide. These various products are all accounted for by the reaction scheme:



In continuing the study of the fundamental nature of the metallic oxide catalysts employed in high pressure synthesis of alcohols and other organic products from water gas, an x-ray investigation has been made of the copper-zinc oxide catalysts previously studied. The results point to a definite relation between the specific catalytic effect and the distance between the atoms of the two components, as is brought out by comparison of data obtained for various ratios of copper to zinc oxide. Zinc oxide, ordinarily considered a non-reducible compound, is undoubtedly partly reduced in the presence of copper oxide. It is not possible to decide, however, whether this reduction proceeds down to elementary zinc, although the indications are that this is the case. Over the whole range the structure of the catalyst mixtures is decidedly crystalline.

From a consideration of the decomposition data in Figure 2, it seems, then, that formaldehyde and particularly methyl formate production is characteristic of the copper end of the diagram, while carbon monoxide formation is closely associated with the zinc oxide. To compare this catalytic behavior with the x-ray data, Figures 3 and 4 have been drawn. Figure 3 gives methyl formate production and expansion of the copper lattice both plotted as function of the catalyst composition—i. e., of the ratio of copper to zinc oxide.

Similarly, Figure 4 shows the curves for carbon monoxide formation and expansion of the zinc oxide lattice with the catalyst composition as abscissa. It will be noticed that the two solid curves representing the lattice dimensions have been plotted upside down, making a fall in the curve corresponding to an elongation of the unit cell. This is, of course, entirely justifiable in an attempt to bring out any possible relation between the two sets of data.

The similarity in the shape of the curves in Figures 3 and 4 cannot be coincidental. The general character of the two diagrams is convincing evidence of a relation between the selective catalytic activity and the atomic spacing of the copper-zinc oxide mixtures. It is particularly interesting to note that a break in the activity curves invariably corresponds to a point of discontinuity in the lattice dimensions. In the copper curves in Figure 3 this relation shows up even for the small percentages of zinc oxide which cause the peak in the methyl formate curve with a corresponding reduction in formaldehyde production (Figure 2). Furthermore, the sudden changes in both activity curves are accompanied by marked dimensional changes in the two space lattices, the only difference being that the atomic disarrangement occurs within a somewhat wider range of catalyst composition than does the change in preferential catalytic activity.

It has already been mentioned that some of the zinc oxide is reduced in the presence of copper, as shown by chemical analysis. On the assumption that this reduction results in the formation of elementary zinc, it is probable that the zinc goes into solid solution in the copper as alpha brass.

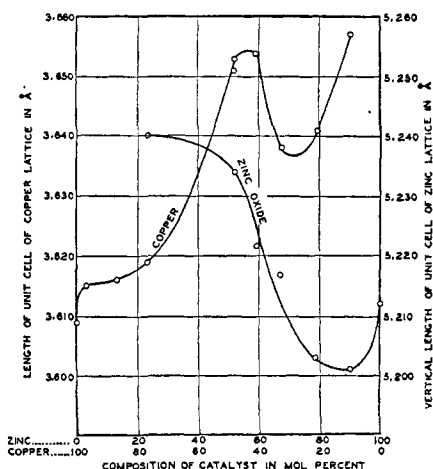


Figure 1—Distance between Atoms in Copper-Zinc Oxide Catalysts as Function of Catalyst Composition

Although there is room for other interpretations of the x-ray data,⁶ it is significant that the amount of zinc required for the observed elongation of the copper lattice on the basis of alpha brass⁷ is always less than that present according to the loss in weight on reduction of the catalysts. However, even in the absence of copper the zinc oxide suffers some change during the treatment with methanol vapor at 200–220° C., as evidenced by the fact that the pure zinc oxide thus treated has a somewhat smaller unit cell than usually, 5.213 Å. vs. 5.226 Å. It seems, therefore, that the reduction of the zinc oxide is not very well defined, and may perhaps involve the formation of both metallic zinc and a compound corresponding to a lower stage of oxidation.

Although the mechanism by which methanol decomposes in the presence of these catalysts is profoundly influenced by their composition, as shown by Figure 2, it was pointed out in the first paper of this series² that the percentage methanol decomposed varied only slightly after a small percentage of zinc oxide had been added to the relatively inactive pure copper.

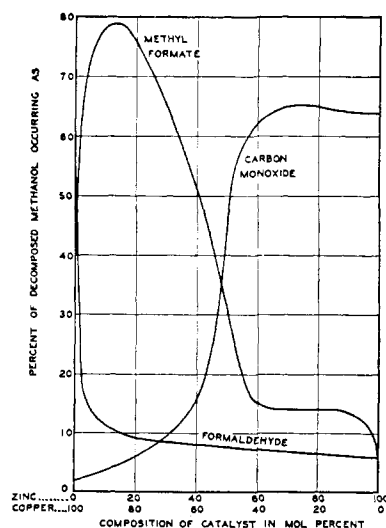


Figure 2—Products of Methanol Decomposition as Function of Catalyst Composition

copper. Thus, the essential feature of these catalysts is their selective nature with respect to the mechanism by which the decomposition occurs. While it is possible that there exists a simple relation between this selective catalytic activity and the distance between the atoms of the two constituents, it is not justifiable to draw any final conclusions or make generalizations in the absence of data on other catalysts.

⁶ Davidson, Thesis, 1928, M. I. T. Library.

⁷ Owen and Preston, *Proc. Phys. Soc. London*, **36**, 49 (1923).

Conclusions

The foregoing results point to an important relation between selective catalytic activity and distance between the atoms in mixed catalysts. It is particularly noteworthy that catalysis, which apparently is a surface effect, seems to be closely associated with the internal structure of the crystalline catalytic material as disclosed by x-ray analysis.

It seems very likely that one of the governing factors in determining the specific nature of a catalyst is the relation between the size of the molecules of the possible reaction products and the distance between the atoms on the surface of the catalyst. This effect may be purely geometrical, or it may be the result of a change in the distribution of the residual forces or valences on the surface of the catalyst with changing interatomic distances.

Rather than attempt a specific explanation of the remarkable relationship between the curves for selective catalytic activity and space lattice dimensions shown above, it will probably serve the purpose better to present these data simply as evidence of the future possibilities in this field of research.

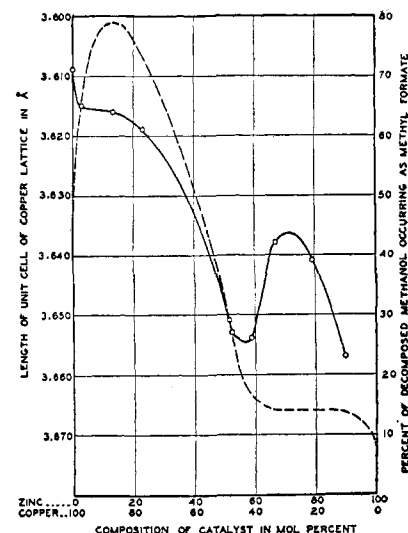


Figure 3—Expansion of Copper Lattice Compared with Methyl Formate Production (dotted line), Both as Function of Catalyst Composition

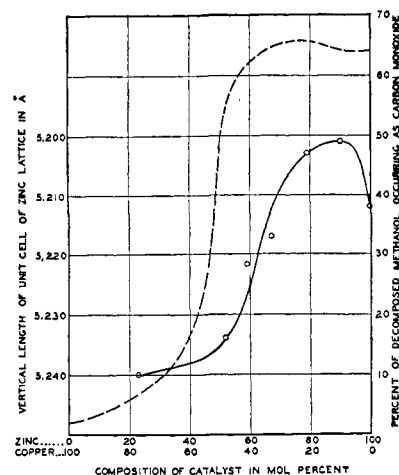


Figure 4—Change in Zinc Oxide Lattice Compared with Carbon Monoxide Formation (dotted line), Both as Function of Catalyst Composition

Acknowledgment

The writers are indebted to R. H. Aborn for his coöperation in the x-ray work and to Miss D. Quiggle for preparation of the catalysts.

Chemical Exemptions from British Key Industry Duties Extended

Exemption from the key industry duty of 33.33 per cent which has been in effect on nearly fifty chemicals has been extended by the Board of Trade to December 31, 1929. Exemption has not been extended on reagent acetone, acetone (fermentation), acetone (synthetic), ethylene glycol, and radium compounds. The following chemicals have been added to the list exempted from import duty: cerium oxide, quinosol, dicyanodiamide, dysprosium oxide, erbium oxide, europium oxide, gadolinium oxide, holmium oxide, lutecium oxide, samarium oxide, terbium oxide, thulium oxide, ytterbium oxide.