THE ACTIVITY OF VARIOUS METALS AND METAL OXIDE CATALYSTS IN PROMOTING THE OXIDATION OF METHANE BY AIR[1]

By W. P. Yant[2] and C. O. Hawk[3]

Received March 23, 1927 Published June 7, 1927

In a search for a catalytic material for use in methane indicators or detectors to be used for inspecting mine atmospheres, the United States Bureau of Mines[4] has investigated the range of temperatures at which oxidation of 3 to 5% of methane in air takes place in the presence of certain metals and metallic oxides. Although the research did not disclose a material ideally suitable for the specific purpose, it did give information regarding the oxidation of methane-air mixtures which may serve as an aid in future work on the same or analogous problems.

Description of Apparatus

The apparatus consisted of a large storage bottle for preparing the gas-air mixtures; a purifying train for removing carbon dioxide, and drying or humidifying; a flowmeter for measuring the rate of flow; a Pyrex tube 1.33 sq. cm. cross section by 10 cm. length for containing the catalyst; and a device for sampling the effluent gas. The catalyst tube was held vertically in a drilled, brass-core electric furnace equipped with a thermoregulator, thermometer and thermocouple.

Procedure and Test Conditions

To promote uniformity of surface conditions for the various materials, which differed among themselves in physical properties, a carrying medium of 8- to 14-mesh quartz granules was used. Quartz was selected because it is non-porous, and was found to cause no appreciable catalytic oxidation of methane at the temperatures used.

Table I gives the results of recirculating 300 cc. of a 3% methane-air mixture at the rate of 30 cc. a minute through the Pyrex catalyst tube filled to a depth of 10 cm. with 8- to 14-mesh quartz granules.

In the regular test procedure, the catalyst was ground in an agate mortar to pass a 200-mesh sieve. One g. was deposited on the quartz granules by mixing the dry catalyst with the granules, moistening with water and

---

[1] Published by permission of the Director of the U. S. Bureau of Mines, Carnegie Institute of Technology, and Mining Advisory Board.

[2] Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[3] Research Fellow, 1925–1926, Carnegie Institute of Technology.

[4] This work was conducted under the student fellowship coöperative agreement existing between the Bureau of Mines and Carnegie Institute of Technology, and was submitted in greater detail by the junior author as a thesis requirement for a Master's Degree in Chemistry. The fellowship was sponsored and financed by the Mine Safety Appliances Company of Pittsburgh.

TABLE I

OXIDATION OF 3% METHANE-AIR MIXTURE AFTER RECIRCULATION IN A PYREX TUBE FILLED WITH QUARTZ GRANULES

Temp., °C.	Period of recirculation, min.	Original CH_4 oxidized, %
150	120	Not detectable[a]
200	60	Not detectable[a]
360	30	3.7
400	30	4.7

[a] Less than 0.5%.

drying at 100°. The catalyst tube was filled to a depth of 10 cm. The methane-air mixture was passed through the tube at a constant rate of 25 cc. a minute for all experiments.

The furnace was heated in steps of 25°, and the temperature was maintained at any given step long enough to allow the catalyst tube and furnace to come to thermal equilibrium, and the catalyst tube and effluent connections to become purged of gases from the previous trial. The average temperature of the furnace at the time the samples were collected was taken as that of the catalyst.

The gas-air mixtures which usually contained 3.75 to 4.10% of methane were prepared from natural gas of the percentage composition: CH_4, 97.46; C_2H_6, 1.40; C_3H_8, 0.07; C_4H_{10}, 0.07; N_2, 1.00. A measured amount of the gas was admitted to the storage bottle which contained a known amount of air. The mixture was then shaken with the displacing liquid and allowed to stand for an hour or more before using.

Method of Analyses

Analyses of the entering and the effluent gas were made on the Haldane apparatus,[5] which has an accuracy of ± 0.02.

Analyses of effluent gas included the determination of both the carbon dioxide formed during the reaction and the residual methane. On the assumption of complete combustion, the composition of the entering gas was recalculated from these data and compared to the composition of the entering gas as found by analysis. In all cases these were in close agreement, indicating the reaction $CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$.

Selection of Catalytic Materials

The selection of catalysts was primarily made on the basis of known catalytic properties of certain materials or their chemical and physical similarity to compounds showing such activity. Metals forming two or more oxides were given special consideration, since in this case the possibility of alternate oxidation and reduction might favor the desired reaction.

---

[5] Burrell and Seibert, *U. S. Bur. Mines Bull.*, No. **42** (1913); revised in 1926 by Jones as No. **197**, 108 pp.

Catalysts Studied and Their Preparation

Uranium Oxide.—The uranium oxide was prepared by heating reprecipitated ammonium uranate for four hours at 325° in an electric-tube furnace to drive off the ammonia.

Thorium Oxide.—Thorium oxide was prepared from thorium nitrate by decomposition with heat.

Cerium Oxide.—Cerium oxide was prepared by igniting reprecipitated cerium oxalate at a dull red heat in a quartz dish.

Platinum Black.—Acid-washed, dry asbestos pellets were impregnated with 30% platinum tetrachloride solution (2 cc. per gram of asbestos) and the platinum was reduced by heating in a quartz crucible at a dull red heat. In placing this material in the catalyst tube of the apparatus, the pellets were disintegrated and loosely packed until the depth of the mass was 10 cm. This was the only deviation from the use of quartz granules as a catalyst carrier.

Nickel.—Nickelous hydroxide was prepared by slowly adding cold 3% sodium hydroxide solution to a cold 20% solution of nickel sulfate (mechanically stirred), filtered, dried at 100°, pulverized, and ignited at red heat. This material was ground in an agate mortar to pass a 200-mesh sieve, placed in a quartz tube, heated to a red heat, and reduced with pure, dry hydrogen. Metallic nickel produced in this manner is a finely divided, light gray powder, not noticeably pyrophoric.

Platinum-Nickel.—Platinum was displaced from platinum tetrachloride by adding an excess of nickel, as prepared in the above manner. The nickel chloride was washed out with water and the residual product dried at 100°. The mixture used contained 90% of nickel and 10% of platinum by calculation.

Copper-Cobalt.—Freshly precipitated oxalates of copper and cobalt were separately dried at 125°, thoroughly ground together in the desired proportions and reduced at a red heat by pure, dry hydrogen.

Manganese Dioxide.—Manganese dioxide was prepared according to the procedure described by Merrill and Scalione[6] for the preparation of Hopcalite, except that the individual oxide was not pressed and was dried separately.

Cobaltic Oxide.—In the preparation of cobaltic oxide, Merrill and Scalione's procedure was also followed in general. Three separate preparations were made, one according to their procedure and two others by allowing the material to stand for several hours in a distinctly acid solution (hydrochloric acid and sulfuric acid, respectively), after precipitation with sodium hypochlorite and washing by decantation. The variation of the method of preparation appeared to have a remarkable effect on the activity of the resultant material (Table II), which shows efficiencies for the three products.

[6] Merrill and Scalione, THIS JOURNAL, **43**, 1982 (1921).

TABLE II

CHANGE IN EFFICIENCY OF Co_2O_3 THROUGH VARIATION IN METHOD OF PREPARATION

Prepared from	Temp., °C. 150	200	250	300
Sulfuric acid soln.	0.8	6.2	34.8	97.2
Hydrochloric acid soln.	2.0	7.3	31.9	81.8
Alkaline soln.	1.3	3.9	19.1	68.8

Except as noted, all of these preparations were treated in the same manner.

The apparent increase of activity in the case of the acidified oxide may be due to the removal of the small quantity of cobaltous hydroxide left unaltered by the treatment with sodium hypochlorite. This removal is effected by the addition of acid, which readily dissolves cobaltous hydroxide, but reacts only very slowly with cobaltic oxide. The work of Howell[7] suggests that the lesser activity of the preparation carried out in the presence of hydrochloric acid as compared to sulfuric acid may be due to a partial reduction of the peroxidized product in the presence of hydrochloric acid.

Nickelic Oxide.—Nickel sulfate and potassium chlorate in the proportion of 1:2 were mixed together and fused in a quartz dish. After the evolution of chlorine had ceased, the black residue was removed, thoroughly washed with hot water, filtered, and dried at 125°.

25:75 and 75:25% Ferric Oxide-Cobaltic Oxide.—The hydroxides were precipitated from mixtures of 10% ferric chloride and cobalt sulfate solutions (in proportions which would yield the oxides in the above proportions on ignition), and the cobaltous compound was oxidized by sodium hypochlorite, according to Merrill and Scalione's procedure. The precipitate was washed by decantation, filtered by suction, dried for four hours at 90° under reduced pressure, and finally heated to 200° at atmospheric pressure for about 30 minutes, to drive out residual moisture.

20% Nickel—80% Manganese Dioxide; 20% Nickel—80% Cobaltic Oxide; and 20% Nickel—80% Nickelic Oxide.—These mixtures were made up by weight from stock catalyst materials prepared by methods already described, and thoroughly mixed (dry) by vigorous shaking in a small stoppered bottle for five minutes; 1 g. was used for each experiment. This was then moistened with water, mixed with the quartz granules and dried.

80:20, 60:40 and 10:90% Cobaltic Oxide—Manganese Dioxide.—These mixtures were made up in the same manner as those of the preceding group.

90:10, 40:60 and 20:85% Chromic Anhydride—Cobaltic Oxide.—A weighed amount of chromic anhydride was dissolved in a beaker containing the quartz granules and a known quantity of dry cobaltic oxide added. The mass was thoroughly mixed and dried at 125°.

[7] Howell, *J. Chem. Soc.*, **123**, 669 (1923).

Hopcalite.—The Hopcalite was the commercial material as used in carbon-monoxide gas masks.

Results of Investigation

As the methane content of over 80% of the gas-air mixtures used was between 3.75 and 4.10%, and the remaining mixtures 3.16, 3.22, 3.55 and 3.46% for Hopcalite, platinum black, 20% manganese dioxide, 80% cobaltic oxide and nickelic oxide, respectively, the results have been calculated to an efficiency basis for the purpose of comparison.

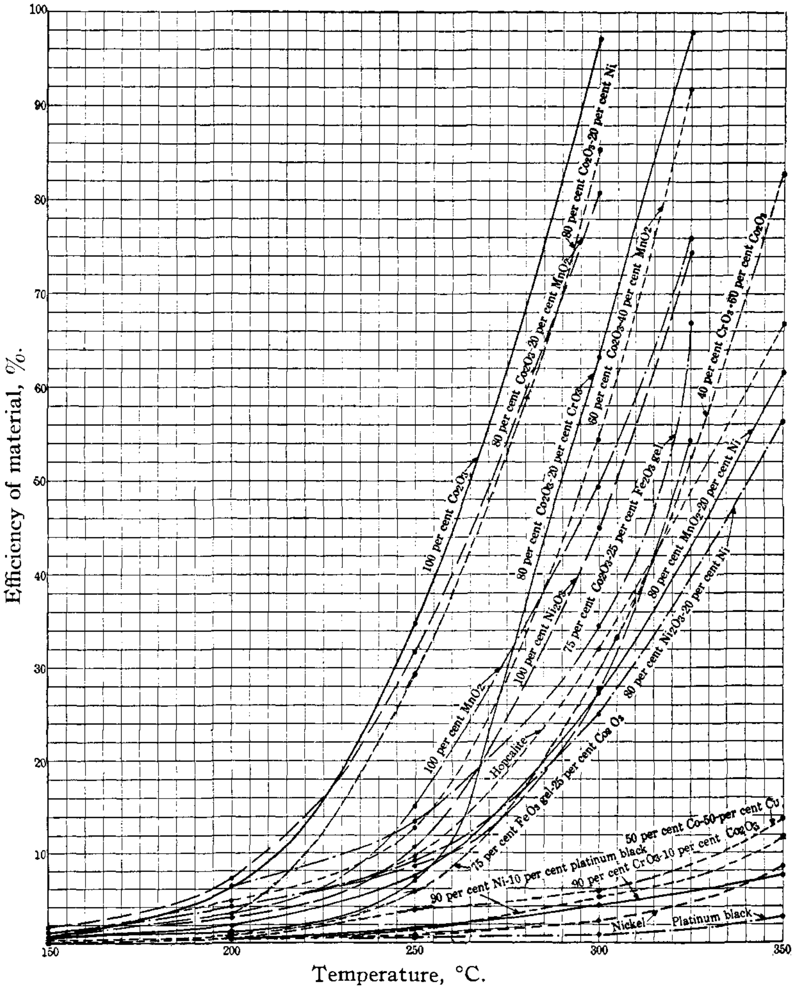

Fig. 1.—Efficiency of compounds and mixtures tested.

Fig. 1 shows these efficiencies. Although the data are given for temperature intervals of 50°, in actual experimental work determinations were made at 25° intervals in order to detect any sharp break that might occur in the reaction. No breaks of that type were noted, hence the presentation in 50° intervals is sufficient to describe the reaction over the temperature range.

Efficiency of the Catalysts Tested

In addition to the materials included in Fig. 1, the oxides of thorium (ThO_2), cerium (CeO_2) and uranium (UO_3) were examined. Their efficiencies at 350° were 3.7, 5.2 and 10.7%, respectively, about the same order as shown for platinum black and nickel.

It will be noted from Fig. 1 that cobaltic oxide was the most efficient material studied. The next most efficient single materials, in order, are manganese dioxide and nickelic oxide. Mixtures of these oxides as well as mixtures of these with other compounds such as iron oxide gel, chromic oxide and nickel gave results corresponding in a general way to the proportionate activity of each compound in the mixture. This also appears to be true for Hopcalite.

The addition of 10% platinum black to metallic nickel appears to act as a promoter, as the efficiency of the mixture is slightly greater than either of the metals alone.

In addition to the reaction tests, three experiments were made in connection with deterioration of the most efficient materials, namely, oxides of cobalt, manganese and nickel. By using the same test apparatus and a temperature at which the efficiency was 80% or more for the first two and 40% for the latter, the gas-air mixture was passed through the catalyst tube continuously for seven to nine hours and the efficiency determined at hourly intervals.

In the case of cobaltic oxide and nickelic oxide a slow and comparatively small decrease in efficiency was noted, although in the latter the activity appeared to become constant after approximately four hours. Mixtures of cobaltic oxide with either manganese dioxide or chromic oxide in the proportion of 60:40 or 80:20, respectively, showed no distinct decrease of activity over a period of eight or nine hours. In fact, in the case of chromic oxide, there appeared to be a slight increase in the efficiency during the first two hours.

Summary

The catalytic oxidation of approximately 4.0% of methane in air by the aid of uranium oxide, thorium oxide, cerium oxide, platinum (black), nickel, platinum and nickel copper and cobalt, cobaltic oxide, nickel oxide, and mixtures of cobaltic oxide, and nickelic oxide with manganese dioxide, ferric oxide, chromic oxide including Hopcalite, was studied over the temperature range of 150 to 350°. Cobaltic oxide was found

to be the most efficient, with manganese dioxide and nickelic oxide next in order. In general, mixtures of the oxides gave results corresponding to the proportion of each active material in the mixture. These data are presented in the form of a graph.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE CHAIN-REACTION THEORY OF NEGATIVE CATALYSIS[1]

BY HANS L. J. BÄCKSTRÖM[2]

RECEIVED MARCH 25, 1927 PUBLISHED JUNE 7, 1927

In the fall of 1923 the author, at the suggestion of Professor Hugh S. Taylor, began an investigation of negative catalysis as exhibited in the reaction between benzaldehyde and oxygen. In the course of preliminary experiments, the reaction was soon found to be highly light-sensitive, and it was also discovered that a substance which had been found by Dr. Taylor to be an excellent inhibitor for the dark reaction, namely, the well-known anti-knock compound, lead tetra-ethyl, had marked retarding effect on the photochemical reaction, the addition of one drop of this liquid to 4 cc. of benzaldehyde lowering the reaction rate in the light of a mercury arc from 6.2cc./min. to 0.1cc./min. Thus, also, the photochemical reaction showed negative catalysis, a property often exhibited by those reactions that deviate from the Einstein photochemical equivalence law by giving abnormally high quantum yields, in other words, by photochemical chain reactions. At this stage of the investigation, our attention was called to a theory of negative catalysis, advanced by Christiansen,[3] which is based on the assumption that those thermal reactions which exhibit this phenomenon are *thermal chain reactions*. It was then apparent that a test of this hypothesis might be obtained by finding out, with quantum-efficiency measurements, whether, in the case under investigation, the photochemical reaction was actually a chain reaction, and whether the similarity between the thermal and the photochemical reactions in their behavior towards inhibitors, which was indicated by the experiments with lead tetra-ethyl, was sufficiently general to support the theory that the reaction mechanism is analogous in the two cases.

This has been done for the auto-oxidation of benzaldehyde, enanth-

---

[1] A preliminary report of this investigation was presented before the April, 1924, meeting of the American Chemical Society at Washington, D. C., and abstracted in *Science*, **59,** 489 (1924).

[2] Charlotte Elizabeth Procter Fellow of Princeton University, 1923–1924.

[3] (a) Christiansen, *Dissertation*, Copenhagen, **1921.** (b) Christiansen and Kramers, *Z. physik. Chem.*, **104,** 451 (1923). (c) Christiansen, *J. Phys. Chem.*, **28,** 145 (1924).