

On the Catalytic Decomposition of Carbon Monoxide by Iron.

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Introduction. It is known that carbon monoxide is decomposed catalytically by iron or the other transition metals, and free carbon is formed. Studies on this phenomenon were carried out on the standpoint of chemical kinetics by some investigators⁽¹⁾. It was also pointed out by U. Hofmann⁽²⁾ and T. Watanabe⁽³⁾ that the free carbon formed by the decomposition of carbon monoxide on iron surface has graphitelike properties. Commonly, carbons are amorphous, as soot or carbon black, when they are formed by thermal decomposition of carbon compounds. In order to graphitize them, it is necessary to heat them again over the temperature of 2500°C at least. If carbon which is formed by the catalytic decomposition of carbon monoxide at comparatively low temperature such as 500°C, is already graphitized, there must be some special reason for this graphitization.

To find the mechanism of this reaction, we investigated the changes of the structure of iron surface (catalyser) at some intermediate stages of the reaction by the method of electron diffraction.

Experimental and Results. The experimental procedure was not much different from those which had been used by former investigators. Carbon monoxide, produced by the reaction with formic acid and concentrated

(1) H. A. Bahr, *Ber.*, **61** (1928), 2177; **63** (1930), 2226; H. A. Bahr and V. Jessen, *Ber.*, **66** (1933), 1238; U. Hofmann, *Ber.*, **61** (1928), 1180; U. Hofmann and E. Groll, *Z. anorg. allgem. Chem.*, **191** (1939), 414; U. Hofmann and D. W. Münster, *Z. Elektrochem.*, **42** (1936), 504; H. Tsuchiya, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **8** (1929), 206, 609; **10** (1931), 556, 951; S. Horiba and Taikei Ri, *Rev. Phys. Chem. (Japan)*, **2** (1928), 11; **4** (1930), 73; **5** (1931), 41; F. Olmer, *J. Phys. Chem.*, **46** (1942), 405.

(2) U. Hofmann, *Ber.*, **61** (1928), 1180.

(3) T. Watanabe, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **7** (1928), 1077; **8** (1929), 288.

sulphuric acid, was flowed into the reaction tube from the reservoir after passing through a dryer such as concentrated sulphuric acid and phosphoric anhydride. For the reason which will be described in the latter section, attention was paid to remove the trace of oxygen in the reaction gas. For this purpose, the gas was passed through the basic solution of potassium pyrogallate and then the heated copper gauze.

The reaction tube was a quartz tube, a part of which could be heated by an electric furnace. The furnace was a small type one, of which length was about 20 cm., and could be slid along the reaction tube. To take out the catalyser from the reaction tube at a certain stage of the reaction, the electric furnace was slid off and the tube could be quickly cooled.

A piece of iron, Kahlbaum's electrolytic iron, was used as catalyser. For the investigation by the electron diffraction method, the surface of the catalyser was polished to flatness by emery paper. To set the catalyser in the reaction tube, a porcelain boat was used.

The gas flowing out from the reaction tube was exhausted after passing through the baryta solution. This solution will be turbid with carbon dioxide when the reaction proceeds as $2\text{CO} \rightarrow \text{C} + \text{CO}_2$.

It took commonly 5~10 hours till the decomposition began to proceed, under the condition in which the reaction temperature was 500°C , and the flowing velocity of carbon monoxide was 400 c.c. per hour. Once the reaction began to proceed, however, the decomposition took place smoothly and free carbon would be formed gradually on the surface of the catalyser.

The electron diffraction patterns of the surface of the catalyser were taken at two intermediate stages of the reaction. The first was when the decomposition had just begun to proceed, that was after a short time when the turbidness of the baryta solution by CO_2 had begun to take place. At this stage, free carbon was not yet found on the catalyser, while the iron surface had lost metallic lustre and become opaque. The observed values of the electron diffraction pattern are shown in Table 1. It is quite different from the pattern of pure iron. It was proved that this pattern belongs to that of cementite. In Table 1, the x-ray diffraction data of cementite⁽⁴⁾ are also shown. Both spacings observed by x-ray and electron diffraction coincide satisfactorily with each other. From this result, it was found that at the first stage of the reaction cementite had been formed on the surface of iron catalyser.

The second electron diffraction pattern was taken when further decomposition had proceeded (after 15 hours from the beginning). At this stage, the surface of the catalyser was changed to black or blacky

(4) The X-ray data of cementite are taken from the values observed by A. Ōsawa and S. Takeda, *Kinzoku no Kenkyū*, 8 (1931), 181.

Table 1.

The electron diffraction pattern of the surface of the iron catalyst at the first stage of the reaction. (Cementite).

Values of Spacings observed by Electron Diffraction			Corresponding x-ray Data for Cementite.	
2.10 Å	w.	2.10 Å	m.	(210)
2.025	m.	2.01	v.s.	(211), (103)
1.86	m.	1.855	v.s.	(122), (113)
1.685	w.	1.675	m.	(023)
1.59	w.	1.58	m.	(123), (014)
1.51	w.	1.50	m.	(301)
1.36	v.w.	1.36	m.	(302), (320)
1.21	v.w.	1.21	v.s.	(141)
1.155	w.	1.155	v.s.	(142), (400)
1.125	m. diffuse.	1.121	v.v.s.	(240)
0.912	w.			
0.795	m.			

grey color in parts, but carbon had not yet been separated in powder form. The spacings observed from this pattern are shown in Table 2. It consists of the carbon pattern principally, but some spacings belonging to cementite are also found. The latter were weak. By using the shorter wave of the cathod-ray, however, the reflected rings belonging to cementite could be made strong to a certain degree. It was known from this fact that the ground substance was also cementite underlying the carbon layer.

Table 2.

The electron diffraction pattern of the surface of the catalyst at the second stage of the reaction.

Values of Spacings observed by Electron Diffraction			Corresponding Indices of Graphite or Cementite.		
3.40 Å	v.s.	(002)	3.39 Å		
2.12	s.	(100)	2.12		
2.03	m.	(101)	2.02		
1.85	w.			(122), (113)	1.855 Å
1.69	m.	(004)	1.69		
1.228	s.	(110)	1.228		
1.17	m. diffuse.	(112)	1.150		
1.125	m. diffuse.	(006)	1.120	(240)	1.121
1.056	w.	(201)	1.049	(225)	1.050
0.981	w.	(106)	0.991	(413) (422) (340)	0.99

When the decomposition proceeded further, the surface of the cata-

lyser was covered all over by a carbon layer which took the powder form. The electron diffraction pattern was also attributed to carbon alone, and the cementite pattern could not be found already because of the existence of a thick layer of carbon.

On the Structure of Carbon produced by this Reaction. It has been pointed out that the crystal structure of so-called amorphous carbon is somewhat different from that of graphite⁽⁵⁾. In graphite, the three-dimensional atomic lattice is completed by a definite arrangement of atoms along every crystal axis. On the other hand, in amorphous carbon, the complete three-dimensional atomic lattice is not produced. It is made of pseudo-crystals, or it would be better to say, a kind of layer lattice consisting of hexagon planes of carbon atoms. The hexagon planes of carbon atoms are arranged in such a way that although they are parallel to each other along the *c*-axis, still along the *a*- or *b*-axis they are not arranged in any definite manner. For this reason, x-ray or electron diffraction patterns from amorphous carbons lack the spacings corresponding to the general indices (*hkl*) excepting (*hk0*) and (*00l*). As well known, the pattern of amorphous carbon consists of small numbers of diffused rings corresponding to (*002*), (*100*) and (*110*), and lacks other spacings such as (*101*) and (*112*) which are comparatively strong rings in the case of graphite. Thus, it may prove to be graphite, when the spacings corresponding to (*101*) and (*112*) be found in the pattern of carbon.

The observed pattern, as shown in Table 2, consists of many sharp rings. They can correspond to carbon and cementite respectively. There are also same spacings which can not be made distinct whether they are attributed to carbon or cementite, for the same values may be found in both substances. However, the spacings corresponding to the values of 2.03 Å can be attributed to graphite at least, for they are moderately strong in comparison with the ring of 1.85 Å, this latter being the typical ring of cementite. From this fact and the sharpness of reflected rings, the whole appearance of the pattern closely resembles the graphite pattern. It will be possible to conclude reasonably that the carbon formed at the early stage of the decomposition is not amorphous but is graphitized.

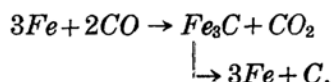
On the Poisoning Action by Oxygen. It has been known already that in this reaction the catalyser is poisoned by some substances such as sulphur or arsenic compounds⁽⁵⁾. We found that the reaction is also hindered by the existence of oxygen. When the pulverized iron was used as catalyser, the poisoning effect by the trace of oxygen was not so

(5) H. Akamatu, *J. Chem. Soc. Japan*, **64** (1943), 1251; H. Akamatu and K. Nagamatsu, *J. Colloid Science*, **2** (1947), 593.

remarkable as to be noticed. However, when an iron plate was used as catalyser, the decomposition did not proceed when a trace of oxygen existed in the carbon monoxide. In the latter case, we found that the oxide layer had been formed on the surface of the catalyser. By the electron diffraction, it was proved that the layer was made of Fe_3O_4 or sometimes of Fe_2O_3 .

Summary and Conclusion. It was found that carbon produced by catalytic decomposition of carbon monoxide by iron is not amorphous carbon as ordinary soot, but seems to be graphite, at least at the early stage of the decomposition. It was found by the electron diffraction that at the first stage of this reaction, cementite is formed on the surface of iron. It was also found that the catalytic decomposition of carbon monoxide never takes place if iron is oxidized before cementite is formed.

From these results, it will be concluded that carbon is produced by the decomposition of cementite, in other words, cementite is one of the intermediate compounds, at least, which is formed before free carbon is separated. This conclusion suggests that the reaction takes place following the schema as:



This conclusion is not far from that assumed by some of the former investigators. Some investigators have assumed that Fe_2C also is the other intermediate compound, but we have not yet found it by our experiments carried out at 500°C .

It is interesting also that carbon has the structure of graphite when it is separated from cementite.

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