Studies on Reactions Between Gas and Solid. VIII. The Mechanism of Nitrogenation of Calcium Carbide.

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(Received February 24, 1941.)

Introduction. The chemical process of the nitrogenation of calcium carbide to calcium cyanamide, $CaC_2+N_2=CaCN_2+C$, is very much interesting not only for its technical importance but also for its complicity of chemical change itself. For the explanation of the mechanism of cyanamide formation and the action of its catalysts, many hypothetical theories have been proposed and discussed. The author intends here to review those theories and discuss this problem from his experimental results and reaction-dynamical considerations.

Reaction Velocity. It was found by the author,(1),(2),(3),(4),(5) and also by H. H. Franck and his co-workers(6) that, when calcium carbide was heated in vacuo at high temperature and nitrogen was suddenly introduced, the fixation of nitrogen by the carbide starts with very small velocity, which increases with the proceeding of the reaction to a maximum point. (See Fig. 1). This means that, for this reaction something like an initial activation is necessary either in side of carbide or in side of nitrogen.

The fact that the velocity increases with the proceeding of the reaction was explained by the author formerly(3) as the results of (1) liberation of heat of reaction, (2) liberation of nascent carbon, which activates the reaction, (3) formation of new crystal germs of $CaCN_2$, the boundary between which and CaC_2 will also favors the reaction.

It was also found by the author(2) that the velocity of nitrogenation is not directly proportional to the pressure of nitrogen, but follows the equation $-(dP/dt)=P/(aP+b)$. The temperature relations and the effect of size of grain of carbide and additional substances on the velocity were also determined experimentally and computed kinetically.(3) (4) (5)

Activation of Nitrogen. In 1933 J. Gelhaar(7) investigated that this reaction proceeded in nickel tubes twice as fast as in quartz tubes. It was said to be shown that the reaction velocity is directly proportional to the degree of ionization of the nitrogen, the values obtained being in close agreement with mathematical computations that are outlined. Because

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(1) T. Aono, This Bulletin, **7** (1932), 143.
(2) T. Aono, *ibid.*, 247.
(3) T. Aono, *ibid.*, 274.
(4) T. Aono, *ibid.*, 287.
(5) T. Aono, *ibid.*, **16** (1941),
(6) Frank, Hochwald, Hoffman, *Z. physik. Chem. Bodénstein-Festband*, (1931), 895.
(7) J. Gelhaar, *Teknisk Tidskrift Uppl. C. Kemi*, **63** (1933), 25, 37, 41, *Chem.-Ztg.*, **57** (1933) 242; *ibid.*, **57** (1933) 506; *C. A.* **27** (1933) 811, 4751.

of lack of the original paper of Gelhaar, the author cannot discuss his work, but these conclusions were said by Birger⁽⁸⁾ to be based on misinterpreted observations, and the ionization theory invalid. According to Birger the true degree of ionization at 1000° C is normally about 10^{-32}, and in a Ni-tube it is even less, 10^{-54}. The increase in the reaction velocity with nickel tube is to be attributed to the ability of this metal to remove CO from the reaction chamber either by direct absorption or formation of $Ni(CO)_4$.

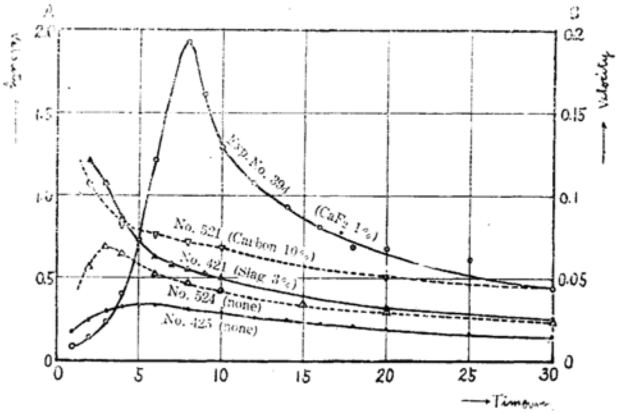

Fig. 1. Effect of catalysts on the velocity of nitrogenation.
Use scale A for full lines (at 1000°C)
and scale B for dotted lines (at 870°C).

The action of CO on calcium carbide at elevated temperatures was experimentally discussed by the author.⁽⁹⁾ And the action of nickel on the nitrogen, containing CO as impurities, was also studied by the author,⁽¹⁰⁾ the conclusion of which did not agree with that of Birger. Indeed carbon monoxide reacts with nickel at high temperature, but the nickel carbonyl, then formed, can not exist as such at these high temperatures; it breaks up instantly into Ni and CO again.

Nickel and iron have the action of decomposing acetylene, which is liberated from carbide and calcium hydroxide into its elements, C and H, at high temperatures.⁽⁹⁾ This nature will play some rôle on the nitrogenation process.

Activation by Adsorption. Now we come to the second problem "adsorption theory" of the author. At the beginning of nitrogenation, it was found that the reaction velocity is commonly very small. This can be attributed to lack of reacting or adsorptive position on the side of carbide. Such state of carbide can be called "inactive". The assumption of the author that the formation of cyanamide and separation of fresh carbon will favor the reaction, and if an active carbon is previously added to the carbide, the reaction will begin with a greater velocity, have all been proved to be true by the author with the experiments.⁽²⁾⁽³⁾⁽⁴⁾ (See Fig. 1.). Bredig's experiments⁽¹¹⁾⁽¹²⁾ that sugar charcoal accelerates the

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(8) Birger W, *Nordlander Tek. Tid. Uppl. C. Kemi*, **64** (1934), 9.
(9) T. Aono, *J. Electrochem. Assoc. Japan*, **9** (1941), 81, 83.
(10) T. Aono, Unpublished.
(11) G. Bredig, *Z. Elektrochem.* **13** (1907), 69.
(12) G. Bredig, W. Fraenkel, E. Wilke, *ibid*, **13** (1907), 605.

reaction, while powder of cokes has no effect, will also support this hypothesis, because the adsorptive power and activity of cokes is commonly very small compared with sugar charcoal.

The famous experiment of Moissan,(13) that pure CaC_2 does not react with nitrogen, can be attributed to lack of the initial adsorptive positions, which is necessary to introduce the reaction. Technical carbide contains always about 2% of free carbon, and beside this, the $Ca(OH)_2$, which is always found in varying quantities by absorption of atmospheric moisture by the carbide, reacts with carbide at elevated temperatures, separating carbon as a very fine powder on the surface of carbide.(9) $Ca(OH)_2=CaO+H_2O$, $CaC_2+H_2O(vap.)=CaO+C_2H_2$, $C_2H_2=2C+H_2$. Le Blanc and Eschmann(14) attributed this decomposition of carbide by heating to the catalytic action of nickel used in their experiments as the container of carbide. Their conclusion is not true, because the decomposition always occurs even in the absence of nickel. This unnecessity of nickel was also pointed out by P. Dolch,(15) V. Ehrlich(16) and also by Ruff and Förster.(17)

These carbon must always be acting an important rôle in starting the reaction.

An analogous example is the formation of nitride of alkali-earth metals from their elements, in case of which argon in the nitrogen forms a layer on the metals, and retards the reaction velocity remarkably.(18)

Another example, which support this adsorption hypothesis is that which was already reported and discussed in the former papers.(1),(5) The adsorption of nitrogen on carbon and carbide at these high temperatures will chiefly be of chemical nature or activated adsorption. This nitrogen will form an intermediate compound with carbide, say $CaC_2\cdot N_2$, which, being very unstable, will rapidly liberate off nitrogen again or change to the second compound $Ca(CN)_2$. This $Ca(CN)_2$ is also unstable at the nitrogenation temperature and changes to $CaCN_2$ and C, which will again act as catalysts.

Formation of Cyanide. The formation of calcium cyanide as an intermediate product was verified by the author with the following experiment.

5.0372 g. of carbide (CaC_2=80.0%, without any catalyst), contained in a nickel tube was subjected to nitrogenation at 1000° C for 55 minutes by the method previously reported. It was then suddenly taken out and rapidly cooled in cold water. The results of analyses were: increase in weight=0.4236g=8.40%, residual CaC_2 in the product=55.5%, total N=7.40%, cyanamide N=5.96%, cyanide N=0.74%, insoluble N=0.23%.

The presence of cyanide in the cyanamide in small quantities had already been reported by Bredig.(11) H. Franck and his co-workers discussed the equilibrium $Ca(CN)_2 \rightleftarrows CaCN_2+C$ with their close experiments.(19) According to them $Ca(CN)_2$ is stable, when it is side by side with $CaCN_2$, only at above the melting temperature of the system (ordinarily about 1150°C in case of technical cyanamide), or under 400°C. At the intermediate temperatures $Ca(CN)_2$ soon decomposes into $CaCN_2$

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(13) Moissan, *C. r.*, **118** (1894), 501.

(14) M. Le Blanc and M. Eschmann, *Z. Elektrochem.* **17** (1911), 20.

(15) P. Dolch, *Z. Elektrochem*, **26** (1920), 455.

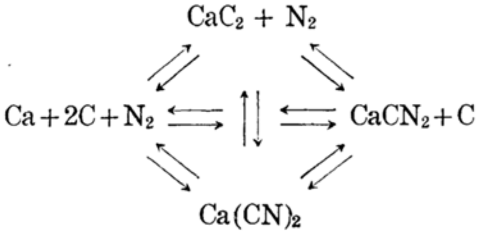
(16) V. Ehrlich, *Z. Elektrochem*, **28** (1922), 529.

(17) O. Ruff and E. Förster, *Z. anorg. allgem. Chem.*, **131** (1923), 321, 332.

(18) A. v. Antropoff, *Z. angew. Chem.* **44** (1931), 921; *Chem. Ztg.* **56** (1932), 424.

(19) H. H. Franck, W. Makkus and F. Janke, „Der Kalkstickstoff in Wissenschaft, Technik und Wirtschaft," Stuttgart (1931).

and C. Many other works have been reported on this problem(20)(21)(22)(23)(24)(25), and H. H. Frank and Kendler(26) proposed the following scheme for the nitrogenation equilibrium:



The formation of $Ca(CN)_2$ as the intermediate compound is thus a matter of no question.

Action of Catalysts. In 1909 G. Bredig(11) and his co-workers(12) studied the action of various substances on this nitrogenation, and objected to many explanatory hypotheses which had been offered by many persons at their time, such as "Oxydbildungstheorie", "Initialzündungstheorie", "auflockerunde Wirkungstheorie" and "Abdissoziationstheorie". They left however "Verflüssigungstheorie" as a plausible one. Ehrlich(16) reported that the system ($CaCN_2 = 75\%$, $CaO = 10\%$, $CaCl_2 = 15\%$) began to melt at about 820–900°C, while calcium cyanamide, prepared without any additions, sintered slightly at about 1100°C and became viscous fluid at 1200–1250°C. He concluded from his research that the catalytic action of $CaCl_2$ is to be attributed to the lowering of the melting point and depression of the vapour pressure and decomposition pressure of $CaCN_2$. H. Franck and Heimann(27) also measured the melting points of $CaCN_2$ with additional substances. According to them the melting point of $CaCN_2$ is 1180°C, the lowest eutectic point of $CaCN_2$-CaC_2-CaO system is 1146°C, and when CaF_2 is added to this system, the melting point lowers down to 953°C with 20% CaF_2, while the lowest melting point of CaC_2-CaO-CaF_2 system is 1070°C. They also came to the same conclusion with Ehrlich. J. Gelhaar,(7) on the contrary, reported that the melting point lowering of the mixtures due to additions has no relation to the reaction velocity.

The author has also perceived the lowering action of these salts, although CaF_2 has smaller effect on this point. Indeed their catalytic action can be attributed greately to those lowering actions, but as those lowering powers are not parallel to their catalytic powers, there must be something more left to consider.

Chemical explanations have also been given. Polzeniuss(28) tried

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(20) O. Kühling and O. Berkold, *Z. angew. Chem.*, **22** (1909), 193.
(21) H. Ewan and T. Napier, *J. Soc. Chem. Ind.*, **32** (1913), 467.
(22) P. Askenasy and F. Grude, *Z. Elektrochem.*, **28** (1922), 131.
(23) H. H. Franck and C. Bodea, *Z. angew. Chem.*, **44** (1931), 379.
(24) H. H. Franck and R. Neubner, *Z. Elektrochem.*, **40** (1934), 693.
(25) G. Petersen and H. H. Franck, *Z. anorg. allgem. Chem.*, **237** (1938), 1.
(26) H. H. Franck and W. Kendlery, *Z. Elektrochem.*, **45** (1939), 541.
(27) H. H. Franck and Heimann, *Z. Elektrochem.* **33** (1927), 469.
(28) Polzeniuss, *Chem. Ztg.* **31** (1907), 958.

to explain the action of salts, such as $CaCl_2$ and NaF, with their low melting points and high ionization constants, which favor the formation of his so-called intermediate compound Ca_3N_2. The formation of calcium nitride by this reaction was also supported by Krase and Yee,(29) who thought that CaC_2 dissociates to Ca and C, and this dissociated Ca combines with nitrogen to Ca_3N_2, which quickly changes to $CaCN_2$ by the action of C and N_2. The dissociation of CaC_2 into Ca and 2C had already been reported by Briner and Kühne,(30) while Erlwein and his co-workers(31) said that CaC_2 dissociates to their so-called "subcarbides" and carbon. Ehrlich(16) supported this and said that their subcarbide will be CaC, being the primary dissociation product of CaC_2 and $CaCN_2$. This "subcarbide theory" was denied by Ruff and Förster.(17) The existence of $(CaC)x$ is thus a matter yet undetermined.

The fact that the catalysts for nitrogenation of carbide have an action of decomposing CaC_2 and make it easy to combine with nitrogen was perceived by Erlwein and his co-workers.(31) Although their conclusion was objected by Ruff and Förster,(17) but Ehrlich and also Krase and Yee reported that $CaCl_2$ greatly accelerate the decomposition of CaC_2 by heating. The author(32) recognized the decomposition of CaC_2 when a piece of carbide was thrown into molten $CaCl_2$ or NaCl. One of the decomposition products was determined as carbon, while others are left yet as a matter of interesting problem to study. Of course it is difficult to say that this decomposition might not have been due to presence of traces of water remaining in the molten salts, though it was heated for a longer time.

It is known that calcium tends to monovalent at elevated temperatures. The action of CaF_2 and $CaCl_2$ on CaC_2 at their melting temperatures might be considered conveniently as follows:

$$\begin{aligned} & 3CaC_2 + CaCl_2 \rightleftarrows CaC \vdots CCa + 4C^* + Ca_2Cl_2^* \,, \\ \text{or} \quad & 3CaC_2 + CaF_2 \rightleftarrows CaC \vdots CCa + 4C^* + Ca_2F_2^* \,, \\ \text{and} \quad & CaC \vdots CCa + 2N_2 \rightleftarrows 2CaCN_2 + 2C^* \,. \end{aligned}$$

Of course this is only an hypothetical explanation of the author and has no experimental proof. But we are able to say surely that the action of $CaCl_2$ or CaF_2 is not equal to that of active carbon and phosphorus slag, because the latter affect the reaction at the starting point, while the former accelerate the reaction only after it has begun. (Compare the curves in Fig. 1.)

This postulation has another support.

The reduction of metals from their oxides with calcium carbide was experimentally studied by the author. For example, magnesia was reduced with carbide by heating the mixture at 1000~1300° C in vacuum. Mg metal was distilled off, and carbon was set free.

$$MgO + CaC_2 = CaO + Mg + 2C.$$

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(29) H. J. Krase and J. Y. Yee: *J. Am. Chem. Soc.*, **46** (1924), 1358.

(30) Briner and Kühne, *J. du four Electr.* **1913**, 137, *C. r.* **156** (1913), 620.

(31) Erlwein, Warth and Beutner, *Z. Elektrochem.* **17** (1911), 177.

(32) T. Aono, Reported before the meeting of Chemical Society of Japan in Feb. (1932).

For this reaction, which occurs between the two solids, addition of CaF_2 in 10–30% shows favorite action.(32) Matsuno, Uchino and Tsuda also obtained the same results.(33) They tested many other additions such as $AlF_3 \cdot 3NaF$, CoS, CuS, Fe_2S_3, $Ca(BO_2)_2$, but CaF_2 was recognized to be the only favorite catalyst in this reaction, all the others having negative effect. The effect of CaF_2 in this case must be attributed to its physical, such as melting point lowering, rather than chemical action upon the CaC_2–MgO system; it facilitates the reaction just like the nitrogenation of carbide.

Heat of Activation and Catalytic Power. From the velocity constants and their thermal relations, the apparent heat of activation for the reaction,

$$CaC_2+N_2=CaCN_2+C,$$

was determined by the author to be 58.6 Cal./mol. at 1000–1060°C. Above 1080°C, where the reaction proceeds very rapidly, the heat of activation decreases to 33 Cal./mol. in case of powdered carbide containing CaF_2 in 1%.(2) These values coincide with those which were determined recently by H. Franck and Endler(34) fairly well. They found the heat (at 950–1000°C) to be about 54 Cal./mol. for pure carbide (crystal structure I, II, III), 54 Cal./mol. for carbide containing sulphur, 40 Cal./mol. for carbide containing cyanamide nitrogen (melted together with $CaCN_2$) and 33 Cal./mol. for carbide containing CaF_2.

From the above figures we can recognize certainly the fact that the effective catalysts depress the heat of activation at temperatures where the catalysts play their rôle effectively.

Action of Carbon. In the earlier section of this paper, it was stated that the nascent carbon, liberated by the reaction, may act as a catalyser. It was found that addition of active carbon not only affects the reaction velocity, but also changes the character of the velocity curves of nitrogenation. (See Fig. 1.)

It was also pointed out by the author(4) that the slag of phosphorus furnace, having the composition $P_2O_5=1.29$, $SiO_2=18.3$, $Fe_2O_3=1.75$, $Al_2O_3=16.55$, total $CaO=49.40\%$, had also catalytic action. It is very interesting that the slag has the same character as the active carbon (See Fig. I.). This can be explained by the fact that the slag, being oxides of metals, decomposes carbide as follows:

$$CaC_2+MO=CaO+2C^*+M,$$

Some kind of metals thus liberated, also with the nascent C*, may accelerate the reaction.

At temperatures of the nitrogenation CaC_2 and C will not react with each other, therefore the influence of C on the activity of CaC_2 must be of physical nature, such as adsorbing property due to the boundary surface action. The freshly separated carbon will not only sorbs nitrogen on its own surface, but also will give CaC_2 an active boundary, and thus the nitrogen will be activated to form $Ca(CN)_2$ with these surrounding carbide.

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(32) G. Harada, T. Aono, I. Kobayashi, Report in the Denki-Kagaku-Kogyo- K. K. (1938).

(33) Matsuno, Uchino and Tsuda, *J. Soc. Chem. Ind. Japan*, **42** (1939), 597.

(2) T. Aono, *loc. cit.* see also Landolt-Börnstein's Physikalische-Chemische-Tabellen, Eg. III C. (1936), 2892.

(34) H. H. Franck and H. Endler, *Z. physik. Chem.* **184** (1939), 127.

It is known that in case of "case-hardening" of steel, presence of nitrogen is effective for the carburization of iron with charcoal. Comparing this with the effectiveness of CN-compounds as carbonizers, it can be thought that nitrogen will be adsorbed by the carbon chemically and acts as a CN-compound to the surface of adjascent iron, giving carbon to it and setting nitrogen free again.

Analogous mechanism could be given in our case. Some of the nitrogen, which is adsorbed by carbon at these high temperatures, may react with CaC_2 (or its dissociated product, if there is any of such) to form $Ca(CN)_2$ or $CaCN_2$ and C.

Mathematical considerations. With the reaction scheme proposed by the author:

$$\begin{array}{ccccccc} \text{Inactive} & & \text{Active} & & \text{Adsorption} & & \\ N_2+CaC_2 & \xrightarrow{k} & N_2+CaC_2 & \underset{k_2}{\overset{k_1}{\rightleftarrows}} & (CaC_2\cdot N_2) & \underset{k_4}{\overset{k_3}{\rightleftarrows}} & Ca(CN)_2 \underset{k_6}{\overset{k_5}{\rightleftarrows}} CaCN_2+C^* , \\ (N)\quad(S_i) & & (P)\quad(S) & & (\sigma) & & (\rho) \qquad\qquad (\delta) \end{array}$$

the following equations were deduced previously,(5)

$$S=\frac{S_{i0}}{k_1P-k}\cdot e^{-kt}-\left(\frac{S_{i0}}{k_1P-k}-S_0\right)\cdot e^{-k_1Pt} \qquad \text{and}$$

$$-\frac{dN}{dt}=\frac{k_1(k_3-k)PS_0'}{K-k}\cdot e^{-kt}-\frac{k_1P(k_3-k_1P)(S_0'-S_0)}{k_2+k_3}\cdot e^{-k_1Pt}$$

$$-(k_1P+k_2)\left\{\sigma_0-k_1P\left(\frac{S_0'}{K-k}-\frac{S_0'-S_0}{k_2+k_3}\right)\right\}e^{-Kt}$$

Comparing the curves represented by these equations and those of experimentally found, we can find that the physical meanings of these equations give us fair agreement with the above considerations.

For example, the active carbon and phosphorus slag give considerably large values for S_0, which means that they are initial activators, and in presence of them the reaction begins with a larger velocity at once, while calcium fluoride gives no influence upon S_0. In the latter case S_0 is nearly equal to zero, and the reaction starts with nearly zero velocity.

On the contrary, calcium fluoride increases the velocity constants k_3 and k_5 and also the stability of $CaCN_2$,which means that it makes k_4 small and shifts the equilibrium to the right hand. Calcium chloride and sodium chloride increase k_3, k_5, k_6 simultaneously. These halogenides are not mere catalysts in this reaction.

As it was stated, the above equations represent mainly the earlier stage of the nitrogenation of powdered carbide at comparatively lower temperatures. For granular carbide, in case of which the reaction velocity is chiefly determined by penetration of nitrogen into the inner part from the surface, as was formerly studied by the author(3), the action of carbon is negligible, while $CaCl_2$ and CaF_2 play an important rôle, depressing the melting points and reducing the chemical resistance of the reaction.

Classification of the Catalysts. Conclusively the author considers the action of catalysts to be quite different with each other. Active carbon and phosphorus slag favor the first stage of the nitrogenation, i. e. adsorption and activation of nitrogen, and makes the start of the reaction easy, (Class I.), while calcium fluoride favors chiefly the third stage, diminishing the resistance in the $CaCN_2$ formation, both chemically and physically, and also it keeps the cyanamide stable. (Class IV.).

The second stage, i.e. the formation of $Ca(CN)_2$ is favored by adding alkali- and alkali-earth-chlorides such as NaCl and $CaCl_2$. (Class II.). Of course these additions are not welcomed in industry, because they increase the contents of cyanide in the cyanamide, which is dangerous to our health.

$Ca(CN)_2$ and $CaCN_2$ formed by the reaction or co-melted previously with carbide, facilitate the cyanamide formation by activating the carbide (Class III), while CaS hinders the reaction by inactivation.

Some of the catalysts, mentioned above, have combined actions, affecting on two or three stages simultaneously, and cannot be confined to a definite class.

Summary.

In this paper the theories of nitrogenation of calcium carbide were summarized and discussed, and the mechanism of these catalytic action was explained.

1. The mechanism of nitrogenation was ascertained as follows:
   - I. activated adsorption of nitrogen on active positions of carbide, (at comparatively lower temperatures);
   - II. formation of an intermediate compound, $Ca(CN)_2$, temporarily,
   - III. breaking up of $Ca(CN)_2$ into $CaCN_2$ and C,
   - IV. further propagation of the $CaCN_2$—formation.
2. The action of catalysts can be classified also in four kinds:
   - I. catalysts which affect the adsorption of nitrogen on the carbide surface and make the start of the reaction easy, (active carbon or nascent carbon and carbon separating material such as phosphate-slag,)
   - II. catalysts which favor the cyanide formation as well as the procession of cyanamide formation, (alkali and alkali-earth chlorides), they also affect the equilibrium $Ca(CN)_2 \rightleftarrows CaCN_2+C$,
   - III. catalysts which activate the carbide and facilitate the cyanamide formation, ($Ca(CN)_2$ and $CaCN_2$ formed by the reaction or co-melted previously with the carbide; CaS being a negative catalyst in this class,)
   - IV. catalysts which accelerate the propagation of the reaction diminishing chemical resistance physically as well as chemically, (CaF_2, $CaCl_2$ etc.)

Of course some of these catalysts have combined actions affecting on two or three stages simultaneously.

3. The depression of melting points, heat of activation, dissociation pressure of the cyanamide and the CaC_2–$CaCN_2$ system by these catalysts were also discussed.
4. Some chemical interpretations for the action of some catalysts were also proposed, (hypothetically).

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