Brief Overview of the Synthesis of Hydrogen Cyanide from Methane

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Abstract

Hydrogen cyanide (HCN) is an important precursor for the synthesis of a variety of chemicals, such as acrylonitrile and adiponitrile, which are used in the production of synthetic fibers, plastics, and resins. It is also used in the mining industry for the extraction of gold and silver from ores, as well as in the production of various pharmaceuticals, pesticides, and other chemicals. Despite its importance, HCN is a highly toxic gas that must be handled and stored with great care to ensure safety. The synthesis of HCN from methane is a challenging process that has gained significant attention due to the importance of HCN in various industrial applications. Today, the majority of HCN is produced industrially through the Andrussow process, which involves the reaction of methane, ammonia, and oxygen over a platinum or rhodium catalyst at high temperatures and pressures. This process is highly efficient and produces high yields of HCN, making it the preferred method for industrial production. However, the catalytic conversion of methane to HCN remains a challenging process, as methane is a very stable molecule and requires high activation energy to break its strong C-H bonds. Therefore, the ongoing research is focused on developing more efficient and cost-effective catalytic systems for the conversion of methane to HCN, as well as on improving safety measures for its handling and storage.

Keywords: Methane, hydrogen cyanide, Andrussow process, BMA process.

Introduction

Hydrogen cyanide (HCN) is an important precursor for the synthesis of a wide range of chemicals including acrylonitrile and adiponitrile. It is also used in the synthesis of polymers such as nylon and in the synthesis of fibers, pesticides, medicines, metallurgy, fuels, and potassium and sodium cyanide which are used in silver and gold mining [1, 2]. HCN was first isolated from a pigment called Prussian Blue [3]. Due to its demand in mining, in 1892 George Beilby invented a method to synthesize it by passing ammonia over glowing coal [4]. Later in

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1894, Hamilton Castner developed another method which involved the synthesis of sodium cyanide from coal and ammonia. The produced sodium cyanide then reacts with an acid to form gaseous HCN [4].

In recent years, the production of hydrogen cyanide has increased by 500% since 1956 due to the rapid population growth [5, 6]. The production of HCN is currently met through two industrial processes, the Andrussow process and the Blausäure Methan Ammoniak (BMA) or Degussa process [7]. The Andrussow process involves the reaction of methane with ammonia in an oxygen-deficient environment over a Pt/Rh gauze catalyst at high temperatures of around 1100°C, with very short contact times (0.1 ms). It was first developed in 1930 at IG Farben, Germany [8]. The BMA process, developed by Degussa-Huls in the 1950s, involves the reaction of ammonia with methane in the absence of oxygen, using supported platinum as a catalyst at temperatures reaching approximately 1400°C [9]. Other processes uncommonly used for HCN production include the Shawinigan process in which hydrocarbons such as propane, are reacted with ammonia. This is a noncatalytic process that has been first industrially used in New York, America in 1961 [10].

The main challenge of the most commonly used processes for HCN production (Andrussow and BMA) is the requirement of very high reaction temperatures[11]. Due to the high energy input required for these processes, several studies on enhancing the production process were performed. The studies involved the enhancement of platinum catalyst performance by the addition of promoters and testing other metals as alternatives to the expensive platinum catalyst [12]. Other studies involved the utilization of low thermal plasma to induce the formation of reactive radicals on the catalyst surface, therefore, reducing the temperature required for the reaction [5, 6]. Studies done on the production of HCN from the conversion of methane using NO as an oxidant were also performed [13].
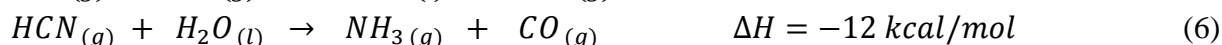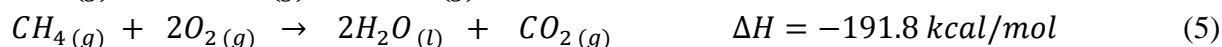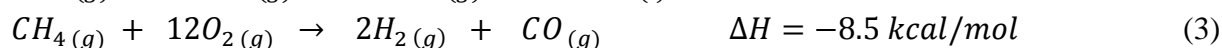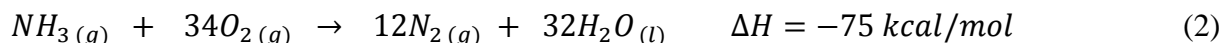
Methane being the main component of natural gas (70-90%) and a main constituent of biogas, has gained great attention in its activation and utilization as a chemical feedstock [14]. The catalytic conversion of methane has been long used for the synthesis of hydrogen cyanide [15]. Industrially as until now mainly Andrussow and BMA processes utilizing supported Pt and Pt-Rh catalysts are used. In both Andrussow and BMA processes, multiple side reactions can take place such as methane and ammonia decomposition which reduces the yield of HCN [16]. This study represents a critical review on the conversion of methane to hydrogen cyanide. The current industrial processes are discussed in detail including the mechanism of methane conversion. Factors affecting the production of HCN and studies involving catalyst improvement or alternatives are also discussed.

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Andrussow process

Andrussow process involves the exothermic reaction of methane and ammonia in an oxygen-deficient environment to produce HCN and water [17, 18]. The process takes place at high temperatures (~1100°C), atmospheric pressure, and at very short contact times (~0.1 ms). 90%Pt-10%Rh gauze is the catalyst used in this process. The desired reaction Eq. (1) occurring in this process is [1, 19, 20]:

$$CH_{4\,(g)} + NH_{3\,(g)} + {}^3\!/_2\,O_{2\,(g)} \rightarrow HCN_{(g)} + 3H_2O_{(l)} \quad \Delta H = -115\,kcal/mol \qquad (1)$$
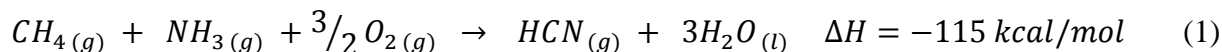
Multiple side reactions can take place including the decomposition of ammonia and methane and the combustion of both. In addition, steam reforming of methane producing hydrogen and carbon monoxide gases can also occur. The side reactions Eq. (2-6) are illustrated below [21].

$$NH_{3\,(g)} + 34O_{2\,(g)} \rightarrow 12N_{2\,(g)} + 32H_2O_{(l)} \qquad \Delta H = -75\,kcal/mol \qquad (2)$$
$$CH_{4\,(g)} + 12O_{2\,(g)} \rightarrow 2H_{2\,(g)} + CO_{(g)} \qquad \Delta H = -8.5\,kcal/mol \qquad (3)$$
$$NH_{3\,(g)} \rightarrow 12N_{2\,(g)} + 32H_{2\,(g)} \qquad \Delta H = 11\,kcal/mol \qquad (4)$$
$$CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow 2H_2O_{(l)} + CO_{2\,(g)} \qquad \Delta H = -191.8\,kcal/mol \qquad (5)$$
$$HCN_{(g)} + H_2O_{(l)} \rightarrow NH_{3\,(g)} + CO_{(g)} \qquad \Delta H = -12\,kcal/mol \qquad (6)$$

The addition of oxygen provides the energy required for the catalyst through the combustion of ammonia and methane. Oxygen is added in low concentrations to provide sufficient heat without reducing the selectivity towards HCN. A tubular reactor containing 20 to 50 layers of gauze catalyst is operated adiabatically [11]. Oxygen is consumed within the first few layers and HCN is formed within milliseconds [22]. The gases are immediately cooled down in a heat exchanger after the reaction is complete to prevent side reactions from taking over and to minimize the formation of HCN polymers.

Kondratenko et al. studied the mechanism of the Andrussow process using temporal analysis of the products reactor with sub-millisecond-time resolution using isotopic traces [1, 22]. The complex reaction mechanism is illustrated in Figure 1. The mechanism of the Andrussow process involves Eley-Rideal and Langmuir Hinshelwood mechanisms. The mechanism starts with dissociative chemisorption of oxygen on the surface. The adsorbed oxygen induces the dehydrogenation of methane and ammonia. Adsorbed oxygen and hydroxyl then react with dehydrogenated free or adsorbed methane and ammonia (CH_y and NH_x, y=0-3, x=0-2). In the case of high adsorption of oxygen, NO will form, and depending on the number of adsorbed NH_x and CH_y, N_2 or HCN are formed. It is interpreted from this proposed mechanism that the ratio of adsorbed oxygen to adsorbed CH_y and NH_x should be optimized and well maintained as any

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imbalance may lead to reducing the selectivity towards HCN or lead to the decomposition or combustion of HCN to N_2 or CO and CO_2 [22].
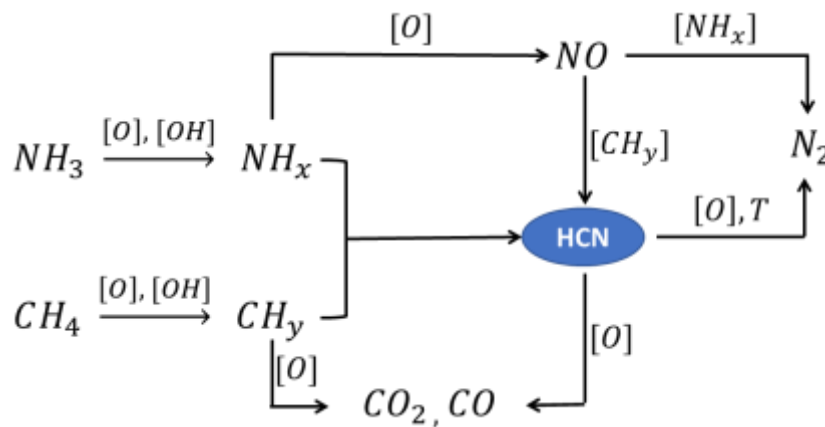
Figure 1. Schematic representation of the reaction mechanism of the Andrussow process proposed by Kondratenko et al [22].

BMA process

The BMA process developed by Degussa involves an endothermic reaction of methane with ammonia in the absence of oxygen producing HCN and hydrogen gas using supported platinum as a catalyst Eq. (7) [23, 24].

$$CH_{4\,(g)} + NH_{3\,(g)} \rightarrow HCN_{(g)} + 3H_{2\,(g)} \qquad \Delta H = 251\ kJ/mol \qquad (7)$$
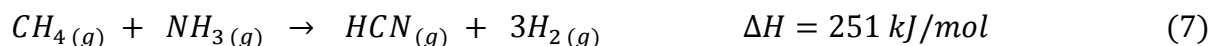
The heat required for this reaction is provided externally. Tubes coated with platinum can be made of Al_3N_4, BN_3, TiN_3, and Si_3N_4. Aluminum oxide Al_2O_3 is predominantly used [25]. The heat required for this reaction is provided externally by heating the tubes to 1200–1400 °C [26]. The side reactions that can take place are the decomposition of methane and ammonia into N_2 and H_2. The decomposition of ammonia is more thermodynamically favoured at a temperature lower than 650 °C. A temperature above 1200 °C should be maintained to ensure the highest HCN selectivity [27]. The BMA process has the advantage of producing higher HCN yields over the Andrussow process. (90% HCN yield as opposed to 60-70% by Andrussow oxidation). However, the endothermicity of the reaction in the BMA process makes it more energy intensive [10].

Schwarz et al. studied the reaction mechanism of the BMA process through experiments in a Fourier Transform Ion Cyclotron Resonance mass spectrometer and B3LYP calculations. Two reaction pathways were proposed [28]. The proposed mechanism is shown in Figure 2. The first step in HCN production was proposed to be the dehydrogenation of methane and the adsorption

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of the dehydrogenated CH_x species. Later ammonia in the gas phase reacts with the adsorbed dehydrogenated methane forming a NH_3CH_2 complex on the catalyst surface. The complex can then undergo one of two reaction pathways. It can either undergo further dehydrogenation forming CNH complex which then desorbs as HCN or it may desorb from the surface as methyleneimine. Methyleneimine can undergo further dehydrogenation in the gas phase forming HCN and hydrogen gas as shown in Eq. (8). The reaction pathways represent an Eley-Rideal mechanism.

$$H_2C = NH_{(g)} \rightarrow HCN_{(g)} + H_{2(g)} \tag{8}$$

Horn et al. studied the reaction mechanism of the BMA process by quenching the gases in the middle of the reaction and analyzing the quenched intermediates by molecular beam mass spectrometry [29]. The finding of this study confirmed the formation of methyleneimine in the gas phase which agreed with the second reaction pathway of the mechanism proposed by Schwarz et al.
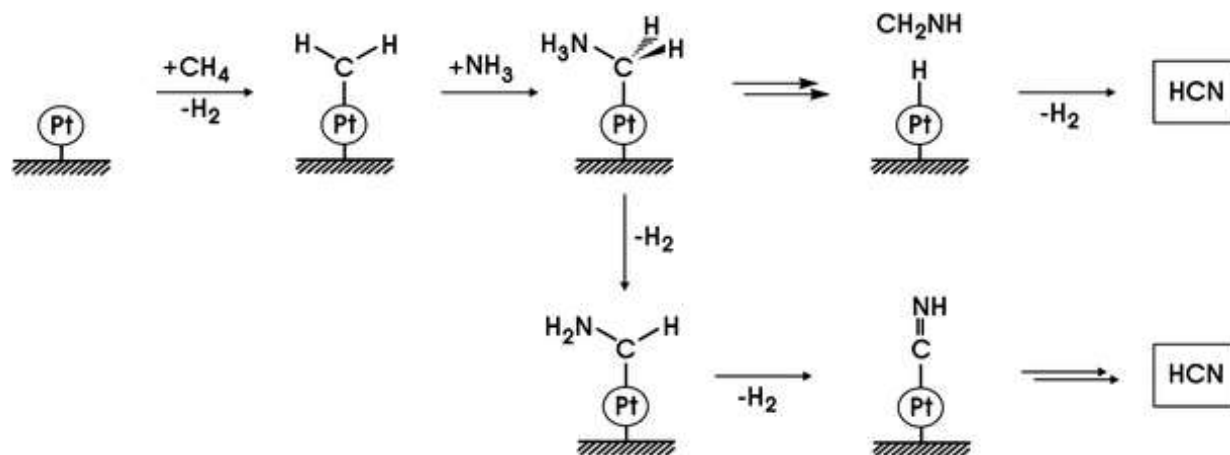
Figure 2. Schematic representation of the reaction mechanism of the BMA process proposed by Schwarz et al. [28]

Alternative catalysts and processes for CH$_4$ conversion to HCN

Very few alternatives for platinum and platinum-rhodium as catalysts for BMA and Andrussow processes were studied over the years. Most failed in outperforming platinum and none has made it to the industry. Table 1 shows the performance of some of the investigated catalysts along with the traditional platinum and Pt-Rh catalysts.

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Table 1. Investigated catalysts for the catalytic conversion of methane to HCN.

Catalyst	Process	Results	Reference
Platinum	BMA process	74% HCN yield at 1300 °C, 1013 mbar	[29]
90%Pt-10%Rh gauze	Andrussow process	60% HCN yield	[9]
Polycrystalline Rh	BMA process.	HCN selectivity of 90% at high temperatures and a total pressure of 1 Torr.	[30]
Copper supported on titanosilicate zeolite	BMA process. Non-thermal plasma of CH_4/NH_3 mixture utilized to reduce required temperature	30% methane conversion and 79% HCN selectivity at 673 K	[5]
Platinum supported on titanosilicate zeolite	BMA process. Non-thermal plasma of CH_4/NH_3 mixture utilized to reduce required temperature	25.9 % CH_4 conversion and 80.9 % HCN selectivity at 673 k	[6]

To make Andrussow and BMA processes more economically feasible, some studies investigated the utilization of CH_4/NH_3 non-thermal plasma to reduce the high temperature required in these processes [31]. For instance, Guo et al. used CH_4-NH_3 non-thermal plasma to allow the reaction to be carried out at lower temperatures [6]. Platinum supported on titanium silicate zeolite Pt/TS-1 was used as the catalyst. 25.9 % CH_4 conversion and 80.9 % HCN selectivity were achieved at a temperature of 400 $^{\circ}$C. The production of the non-thermal plasma is done by applying an electric field to a mixture of methane and ammonia causing the activation of these gas molecules into reactive species, including radicals, excited atoms, molecules, and ions. This enables the reactions to occur on the catalyst surface at much lower temperatures. The reactive radical species formed in the non-thermal plasma were determined by optical emission spectrum and were found to be NH_3*, •NH_2, •NH, •CN, and •CH. The catalyst contributes to the formation of HCN by promoting a C-N coupling reaction on the catalysts' surface. A mechanism very similar to that of the BMA process proposed by Schwarz et al. was also proposed by the authors of this study. Figure 3 shows the proposed mechanism.

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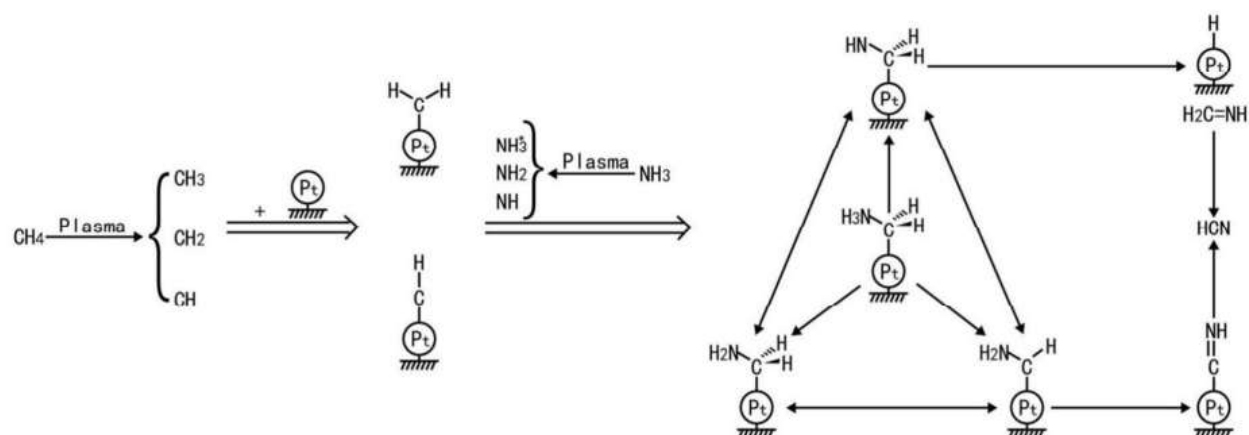
Figure 3. Schematic representation of reaction mechanism for HCN production from CH_4/NH_3 non-thermal plasma [6].

In another study, Yi et al. studied the utilization of the same plasma however using copper supported on titanium silicate as a catalyst Cu/silicalite-1 [5]. Higher methane conversion of 30% and slightly lower selectivity of 79% HCN were achieved. The copper catalyst can significantly reduce the cost of the industrial process as it costs less than 5% of the commercial platinum catalyst.

Other studies offered an alternative route for the production of HCN at lower temperatures by the conversion of methane using nitric oxide NO instead of NH_3 as an oxidant. For instance, Yamasaki et al. studied the conversion of methane activation using nitric oxide and platinum supported on alumina (Pt/Al_2O_3) as a catalyst [13]. Using this process, at 425 °C, 3.2% HCN yield, and 49% selectivity were achieved. Increasing the temperature showed a positive effect on the yield of HCN.

Later Yamasaki and his co-workers studied the effect of platinum nanoparticles' size on HCN yield [2]. The different Pt particle sizes were obtained by changing the platinum loading from wt2.5% to wt10%. It was shown that the particle size had a significant effect on the selectivity of HCN and NO conversion. Larger platinum particles showed higher HCN selectivity and NO conversion. It is suggested that the reaction of HCN to CO_2 and NH_3 is catalyzed at the metal-support interface. Hence, larger particles offering smaller metal-support interface decreased the yield of CO_2 and increased the yield of HCN. An HCN selectivity of 53.5 % was achieved using 10 wt% Pt/Al_2O_3 at 400 °C.

Some studies involved the addition of promoters to enhance the performance of platinum. For instance, Moehmel et al. investigated the effects of the support and the addition of metal promoters such as Ir, Au, Ni, Mo, Zn, and Re on the HCN yield using high throughput

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experimentation along with genetic algorithm, analysis of variance, and regression trees [12]. The results showed that the best catalytic performance is achieved using Si_3N_4, SiC, and AlN as support materials along with the metal additives Ir and Au. In the study, the utilization of Ir and Re along with platinum increased the yield of HCN from 64.8% to 78.5%. Figure 4 shows the regression tree that represents the obtained HCN yield from the utilization of different supports with different Pt loadings.
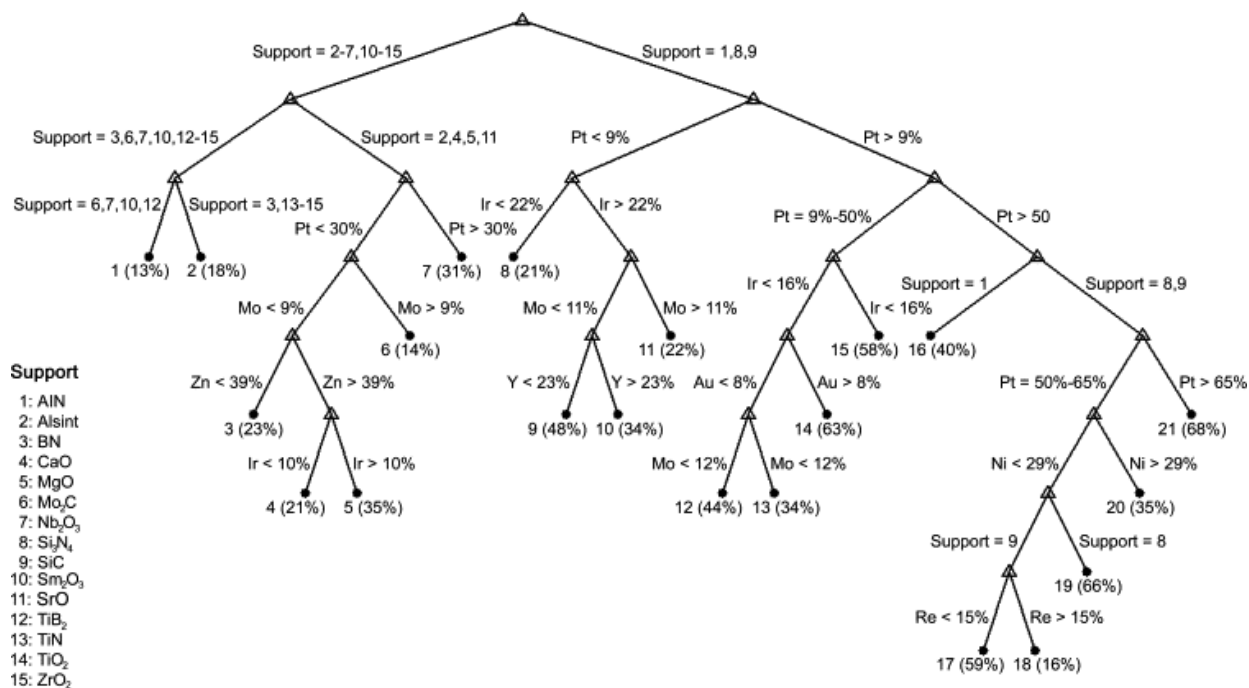
Figure 4. Regression tree obtained for the regression of HCN yield on different supports and on the relative amounts of 11 metal additives (number in parenthesis represents Pt loading, number next to metals represents relative metal loading while number next to Y represents HCN yield) [12].

Schimdt et al. illustrated the effects of multiple factors on HCN synthesis by methane conversion over Pt–Rh gauzes in adiabatic bench scale reactor [21]. Contact time, pressure, feed gases ratio, and catalyst activation were demonstrated to show a significant effect on HCN selectivity and methane conversion. For instance, it was shown that increasing the $(CH_4+NH_3)/O_2$ ratio led to a significant decrease in the conversion of both NH_3 and CH_4. It was also shown that increasing the methane to ammonia ratio in the feed gas resulted in a decrease in HCN selectivity and an increase in the reactants conversion and HCN yield.

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Conclusion

The conversion of methane to Hydrogen Cyanide through different processes was illustrated. Industrially the production of HCN is mostly carried out by the endothermic oxygen free BMA process and the exothermic oxygen assisted Andrussow process. In these two-process methane and ammonia are converted to HCN at high temperatures using supported platinum in BMA and Pt-Rh gauzes in the Andrussow process. The reaction mechanism of these two processes has been extensively studied throughout the years. It is proposed that in both processes the reaction starts with the dehydrogenation of NH_3 and CH_4. In the Andrussow process, the presence of oxygen induces the formation of NO which then reacts with adsorbed dehydrogenated methane forming HCN. In the BMA process, rather simpler mechanism is proposed in which free ammonia reacts with adsorbed dehydrogenated methane forming a complex which desorbs as methyleneimine and later dehydrogenates to form HCN. In both processes, the reaction takes place at very high temperatures reacting 1000 °C. This creates an economic burden on the industrial application specifically the endothermic BMA process. In order to decrease the required energy input, several studies were performed. The studies involved process conditions' optimization, catalyst performance enhancement or replacement and alternative methane conversion processes. New methane conversion process involving the utilization of NO as the only oxidant showed the ability to produce HCN at a relatively low temperature of 425 °C. Other studies involving the utilization of non-thermal plasma of CH_4/NH_3 mixture exhibited high selectivity for HCN and were able to produce it at a temperature of 400 °C. To enhance the performance of the platinum catalyst, addition of metal promoters such as Ir and Re was shown to increase the selectivity and yield of HCN. Optimization of factors such as methane to ammonia ratio, and the ratio of oxygen to methane and ammonia can significantly affect the efficiency of the process, hence the optimization of such conditions is of great importance. It was shown in some studies that the decomposition of methane causes the formation of coke leading to catalyst poisoning or deactivation. Although there have been several studies to increase the selectivity of platinum catalyst and reduce the temperature required for reaction, information on catalyst poisoning and coke formation are lacking. Further research should be implemented to understand and minimize catalyst deactivation.

Conflicts of Interest: The author declares no competing interests.

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