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HCN synthesis from methane and ammonia over platinum

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Abstract

The mechanism of the HCN formation from ammonia and methane over Pt black was investigated using a temporal analysis of products (TAPs) reactor system. At 1173 K the hydrogen cyanide production rate depends on the order of introducing the reactants. HCN is formed rapidly on the methane pulse just after introducing ammonia. However, a slow formation of HCN is observed on the ammonia pulse that follows a methane pulse. Moreover the form of the HCN response resembles closely that of the nitrogen and hydrogen also released during the ammonia pulse. Thus, the rate-determining step for the formation of HCN is the decomposition rate of ammonia. A reaction sequence based on elementary steps is proposed for the HCN synthesis. The formation of HCN after pulsing H_2 points to a pool of surface intermediate species that are hydrogenated to HCN.

Keywords: Temporal analysis of products; CN coupling; Reaction mechanism; Ammonia dehydrogenation; Methane decomposition

1. Introduction

Two different catalytic processes are presently used for the production of HCN, an important intermediate for nylon and clear acrylic ester polymers [1]. One route is the Andrussow process that consists of reacting ammonia, methane and oxygen over Pt/Rh gauzes at temperatures as high as 1373 K at atmospheric pressures with contact times of a few milliseconds. The addition of sub-stoichiometric amounts of oxygen leads to a net exothermic reaction. The second route is by feeding a mixture of methane and ammonia through an array of ceramic tubes coated internally with a platinum-based catalyst layer (Degussa process or BMA process). The tubes are heated externally to 1473–1573 K by directly burning natural gas. The reaction is highly endothermic and most of the reaction occurs in a short section of the tube under mass-transfer limitations [1]. The advantages of the Degussa process are the high HCN yields and the useful hydrogen waste gas, but it requires the high investment and maintenance costs. Moreover the exothermicity of the Andrussow process allows shorter contact time than that of the Degussa process. It reduces the extent of unwanted side reaction such NH_3 and CH_4 decomposition into N_2 and coke, respectively. Reaction kinetic studies in the laboratory under these conditions represent a formidable challenge and most mechanistic insights stem from surface science studies under low-pressure conditions [2–4]. Despite the pressure-gap these models predict the conversion and selectivity of commercial reactors quite well [5]. However, detailed mechanistic information is still lacking.

Especially, no consensus has been reached on the species involved in the surface formation of the HCN precursor from CH_4 and NH_3. The data of Schmidt and co-workers [3,4] do not allow discriminating between two possible pathways to HCN, namely: (1) formation of CN surface species through the surface coupling reaction of C and N adspecies followed by hydrogenation to HCN and (2) the surface reaction between CH_x and NH_x species to form adsorbed CNH_z species that are then dehydrogenated to form HCN. Diefenbach et al. performed Pt^+ mediated coupling experiments of methane and ammonia and they proposed the second route to occur over platinum [6]. Horn et al. have performed in situ studies of the Pt-catalyzed formation of HCN at 1573 K by means of beam mass spectrometry and they proposed the second route to describe the homogeneous contribution to the reaction mechanism [7]. Recently, Herceg and Trenary by using TPD experiments and spectroscopic studies argue in favor of the first route [8].

Temporal analysis of product (TAP) experiments are carried out by pulsing small amounts (on the order of a few nanomols) of reactants over a packed bed microreactor containing the catalyst sample [9]. The microreactor is maintained under vacuum conditions. The effluents are analyzed by a quadrupole

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mass spectrometer located just underneath the reactor outlet. A specially designed vacuum chamber assures efficient pumping speed thus avoiding backscattering of the molecules to the mass spectrometer. At the low pressures applied in the TAP reactor the gas transport takes place by Knudsen diffusion. A purely diffusion process implies the absence of all external mass transfer limitations as well as radial concentration gradients. Even for very exothermal reactions the adiabatic temperature rise is very small due to the small quantity of reactants introduced in the reactor. This allows a good isothermal catalyst operation. TAP experiments have for these reasons been applied to study fast reactions over real catalyst samples [10–14] giving mechanistic information not easily accessible by other methods.

2. Experimental

2.1. TAP experiments

Typically experimental formats are used in the TAP study. Multipulse experiments consist of introducing a train of pulses of one of the reactants only. These experiments will alter the surface state of the catalysts and typically will reveal information on the capacity of the catalyst to store certain species. The other experimental format is referred to as a pump-probe experiment where both reactants are admitted from two separate pulse valves. The time interval between their introductions can be varied and these experiments allow identifying the reactive surface species as well as the individual reactions step that occur. Pump-probe experiments are carried out in a cyclic fashion and thus species left on the surface during the probe pulse can interact with the reactants of the next pump pulse. In this study we have used a modified pump-probe experiment were three species were pulsed consecutively (NH_3, CH_4 and H_2 in different orders).

For the experiments the high-temperature TAP reactor [12] was slightly modified. It contains a quartz tube that is 40 mm long and with an inner diameter of 3 mm kept between two stainless steel flanges with water-cooled O-ring seals. Either 10 mg or 20 mg of platinum black (Good Fellow) was positioned in between two layers of quartz in the isothermal zone of the high-temperature TAP reactor. Platinum black is believed to be representative of the wall-coated platinum used in the industrial process. Moreover, as it is used in powder form, its quantity can be easily varied and it allows a regular bed packing. Methane and ammonia were diluted with inert gases (Ar or Xe) and pulsed independently by two high-speed pulse valves. Hydrogen was pulsed without dilution from a third independent pulse valve. Before the pulse experiments the catalyst was out gassed under vacuum for several hours at 1173 °C. The experiments were performed between 1073 and 1173 °C.

The number of molecules that were admitted per pulse varied between 1×10^{15} and 5×10^{15}. At least four sequences per atomic mass unit (AMU) value were monitored and averaged to improve the signal to noise ratio. The following AMUs were monitored to follow all reactants and products: H_2 2, N_2 CH_4 HCN 14, NH_3 CH_4 15, NH_3 CH_4 16, C_2H_4 25, HCN C_2H_4 26, HCN C_2H_4 27, N_2 C_2H_4 28, C_2N_2 52. The fragmentation patterns were established by pulsing separately all reactants and products at low temperatures except those of HCN. HCN was quantified by assuming that it has the same mass spectrometer response coefficient as N_2.

3. Results

3.1. Single pulse experiments

The experiments were carried out between 1073 K and 1173 K. Below 1123 K no formation of HCN has been observed. We report here the experiments performed at 1173 K. Negligible conversion of ammonia and methane takes place over quartz at 1173 K. Fig. 1 shows the transient responses of methane and ammonia over quartz at 1173 K. However, the ammonia pulse showed significant broadening compared to argon due to the strong reversible adsorption on the quartz particles. Single pulses of ammonia over platinum black resulted in the formation of hydrogen and nitrogen. A complete ammonia conversion was observed but both the nitrogen and hydrogen mass balances were deficient, indicating strong ammonia adsorption. Single methane pulses yielded hydrogen with a methane conversion of 0.7 over 10 mg of catalyst and a closed hydrogen mass balance.

3.2. Pump-probe experiments

The interaction between ammonia and methane was further investigated by pulsing both reactants at various time intervals consecutively. The ratio of the two reactants has also been investigated. The use of excess methane leads to a slow deactivation (on the order of several hundreds of pulses) of the

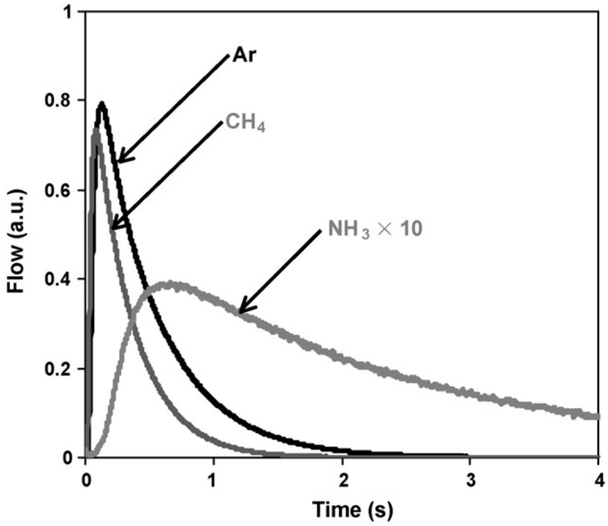

Fig. 1. Transient responses of Ar (AMU 40), CH_4 (AMU 15), NH_3 (AMU 17) at 1173 K during single pulsing of CH_4 and NH_3 over quartz. Pulses size of NH_3 and CH_4 $\sim 10^{15}$ (NH_3/CH_4 = 1.1).

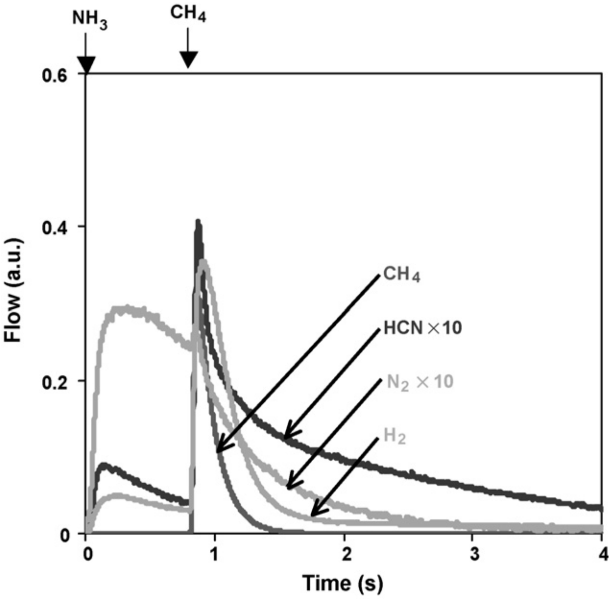

Fig. 2. Transient responses of CH_4 (AMU 15), H_2 (AMU 2), N_2 (AMU 28) and HCN (AMU 27) at 1173 K during sequential pulsing of NH_3 and CH_4 with a pulse delay of 0.8 s and a pulse spacing of 5 s. Pulses size of NH_3 and CH_4 $\sim 10^{15}$ ($NH_3/CH_4 = 1.1$).

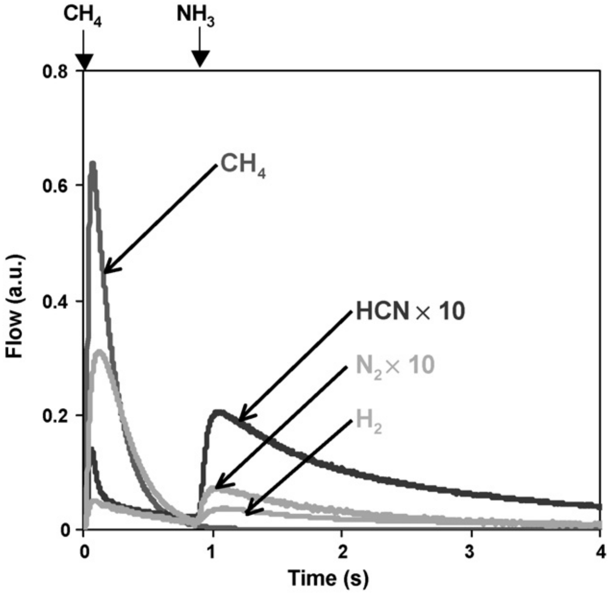

Fig. 3. Transient responses of CH_4 (AMU 15), H_2 (AMU 2), N_2 (AMU 28) and HCN (AMU 27) at 1173 K during sequential pulsing of CH_4 and NH_3 with a pulse delay of 0.8 s and a pulse spacing of 5 s. Pulses size of NH_3 and CH_4 $\sim 10^{15}$ ($NH_3/CH_4 = 1.4$).

platinum black catalyst. Apparently carbon species accumulated slowly on the surface thus reducing the number of active sites. This situation was characterized by an incomplete ammonia conversion. Only at high carbon coverages a very small pulse response at AMU 25 was observed on the methane pulse, possibly indicating the formation of traces of C–C coupling products. This was not the case under regular reaction conditions reported here.

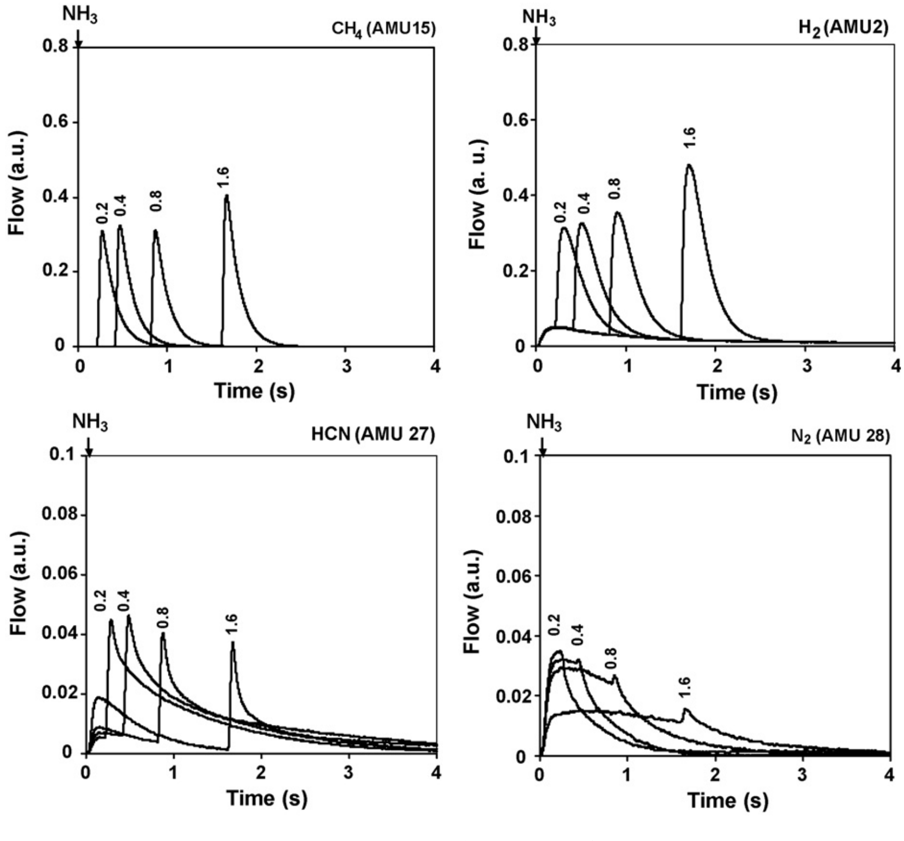

Fig. 4. Influence of the delay between NH_3 and CH_4 pulses on transient responses of CH_4 (AMU 15), H_2 (AMU 2), N_2 (AMU 28) and HCN (AMU 27) at 1173 K for a pulse spacing of 5 s. Pulses size of NH_3 and $CH_4$$\sim 10^{15}$ ($NH_3/CH_4 = 1.1$).

Fig. 2 shows the transient responses of methane, hydrogen, nitrogen and hydrogen cyanide on the introduction of a pulse of ammonia, followed 0.8 s later by a pulse of methane.

A slow formation of hydrogen is observed on the ammonia pulse followed by a much faster production on the methane pulse. A slow formation of nitrogen is seen on the introduction of ammonia that drops down after the introduction of methane. A small slow formation of HCN occurs on the ammonia pulse that sharply increases on the methane introduction and then shows a long tailing. In Fig. 3 are shown the transient responses of methane and the products when the two reactants are inverted. In this case the methane conversion is slightly lower (50% versus 67% for the former experiment) possibly due to the large amount of platinum sites occupied by adsorbed ammonia derived species. Similar (inversed) hydrogen responses are observed as in Fig. 2. A small amount of nitrogen is observed on the methane pulse followed by a more important production on the ammonia. The amount of nitrogen formed in this experiment is much smaller than that in the experiment shown in Fig. 2. The HCN shows a sharp transient response on the methane followed by a much broader response on the ammonia. In both experiments the ammonia conversion was complete. The formation of HCN on the first pulse in both experiments stems from respectively carbon species and nitrogen containing species that were formed on the second pulse. Thus, both carbon and nitrogen containing species have a long surface lifetime (at least 10 s) even at 1173 K. In fact the amount of hydrogen and hydrogen cyanide produced on the ammonia pulse in Fig. 3 represents approximately 70% of the hydrogen balance, assuming complete ammonia conversion. Thus, the nitrogen containing species are probably present in the form of adsorbed NH_x species. By varying the time interval between the ammonia and methane (Fig. 4) or between methane and ammonia (Fig. 5) the influence of the surface lifetime of the various species on the reaction products has been further studied. In both series of experiments the quantity of the second reactant pulsed increases slightly with increasing time interval. The pulse at a time spacing of 1.6 s presents 25% more than that at 0.2 s. In Fig. 4 it is shown that by increasing the time between the ammonia and methane injection the yield of HCN formed on the methane decreases whereas the N_2 formed on the ammonia pulse increases. Apparently the formation of HCN and N_2 are two coupled parallel routes. The amount of HCN on the NH_3 pulse increases with increasing time interval due to the decreasing yields of HCN, thus more carbon species are left on the surface after the methane pulse. Both the methane and ammonia conversion are constant as well as the amount of hydrogen. The data presented in Fig. 5 show that in case of the

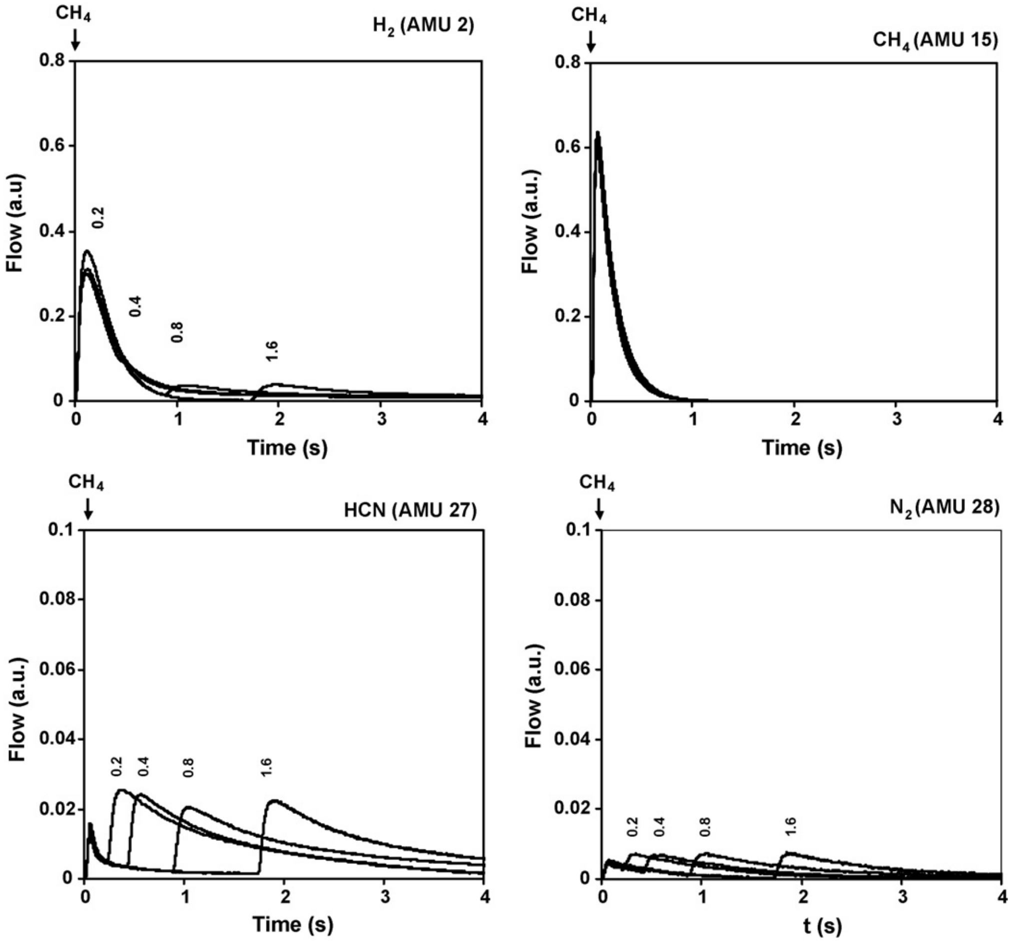

Fig. 5. Influence of the delay between CH_4 and NH_3 pulses on transient responses of CH_4 (AMU 15), H_2 (AMU 2), N_2 (AMU 28) and HCN (AMU 27) at 1173 K for a pulse spacing of 5 s. Pulses size of NH_3 and CH_4 $\sim 10^{15}$ (NH_3/CH_4 = 1.4).

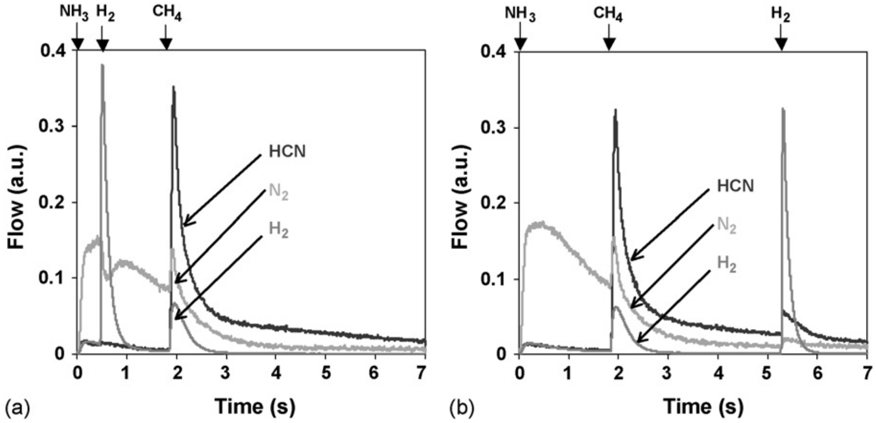

Fig. 6. Transient responses of H_2 (AMU 2), N_2 (AMU 28) and HCN (AMU 27) at 1173 K during sequential pulsing of NH_3 and CH_4 with a pulse delay of 1.6 s and a pulse spacing of 10 s by adding a hydrogen pulse either after NH_3 pulse (a) or after CH_4 pulse (b).

methane/ammonia pulse sequence the yields of HCN, N_2 and hydrogen are approximately constant for all time intervals. Moreover the conversions of methane and ammonia do not change either.

The influence of hydrogen on the HCN production was studied by adding a pulse of hydrogen to the ammonia/methane pump-probe experiment either right after the ammonia pulse or after the methane pulse. Fig. 6 shows the transient responses of hydrogen, nitrogen and hydrogen cyanide for these two experiments. Introducing H_2 after the ammonia pulse results in a decrease of the nitrogen production rate and hardly increases the HCN level. Addition of hydrogen after the methane pulse leads to an increase in the HCN production and to a smaller extend an increase in N_2.

4. General discussion

Few studies in the literature [6] report on the reaction mechanism of HCN synthesis over platinum based on elementary steps. However, ammonia activation and decomposition over platinum has been studied experimentally [15] as well theoretically [16,17] and reaction schemes have been proposed. The study of Weinberg et al. showed that NH_3 decomposition takes place through consecutive dehydrogenation steps. Exchange with deuterium yields NH_2D through ND_3, thus indicating that all NH_x species exists on the surface. Theoretical studies confirm this [16,17]. A pulse of NH_3 over bare platinum thus yields hydrogen and nitrogen through a series of consecutive dehydrogenation steps followed by the recombination of adsorbed N adatoms to form N_2 of H atoms to form H_2. At 1173 K this is a slow process as can be seen in Fig. 2. Both the hydrogen and nitrogen transient responses are very broad and they resemble one another. From the TAP experiments it is estimated that the surface lifetime of the NH_x species are at least on the order of 10 s.

Methane decomposition over platinum at 1173 K on the other hand is much faster. Pulses of methane yield hydrogen responses that have similar full width at half height as a direct pulse of hydrogen. Methane decomposition is reported to yield CH adspecies on platinum at 370 K that can be hydrogenated back by D_2 to CHD_3 and CD_4 [18]. Above 500 K C-species are formed as well as CCH species at high carbon coverages. Above 650 K the latter one is further dehydrogenated. The following reaction sequence can be proposed for the introduction of NH_3 and CH_4:

$$NH_3 + * \rightleftarrows NH_3* \tag{1}$$

$$NH_3* + * \rightleftarrows NH_2* + H* \tag{2}$$

$$NH_2* + * \rightleftarrows NH* + H* \tag{3}$$

$$NH* + * \rightleftarrows N* + H* \tag{4}$$

$$CH_4 + 5* \rightleftarrows CH* + 4H* \tag{5}$$

$$2N* \rightleftarrows N_2 + 2* \tag{6}$$

$$2H* \rightleftarrows H_2 + 2* \tag{7}$$

Step (1) through (4) are reversible, as the deuterium exchange studies of Vajo et al. [15] have indicated, in agreement with the decrease in the nitrogen production when an ammonia pulse is followed by the introduction of hydrogen in the TAP reactor. Moreover, theoretical studies show that the activations energies for the dehydrogenation step are similar for reactions (2), (3) and (4). Van Santen and co-workers and Ricart and co-workers calculated the activation energies of the successive ammonia dehydrogenation steps to be 92, 110, 118 kJ/mol [16] and 100, 105, 92 kJ/mol [15], respectively.

Methane decomposition (step (5)) into carbon and hydrogen has been simplified, as this proceeds in several steps involving CH_x species. However, as discussed above the most stable species at these temperatures are the carbon, C*, species.

The hydrogen cyanide production during pump-probe experiments shows two distinct rates: A slow rate of production is observed on the introduction of the ammonia that continues well beyond the time of the TAP experiment. The second production rate is much faster and occurs both on the introduction of methane as well as hydrogen. This is nicely illustrated by the HCN response curve in Fig. 3 with $\Delta t = 1.6$ s. On the ammonia pulse, there is still a lot of carbon species on the surface, as the HCN production was low on the previous

CH_4 pulse. As a consequence a large HCN production is observed on the ammonia pulse. Before the introduction of the methane pulse the HCN production rate has dropped to almost zero due to the depletion of surface carbon species. On the methane pulse the HCN production increases sharply due to fast decomposition of methane that delivers both surface carbon and surface hydrogen species. However, this enhanced HCN production rate decreases rapidly after the introduction of methane. This is due to a limited number of active sites that is available for the methane decomposition [19]. Thus, the hydrogen cyanide production rate seems to correlate with the availability of hydrogen as hydrogen is slowly released from adsorbed ammonia species but rapidly from methane. Another feature of the HCN production is the strong coupling with the nitrogen formation, evidenced by the drop in the nitrogen response upon the introduction of methane (Fig. 2).

Although the production of HCN may proceed through two (or more) routes the difference in hydrogen supply is compatible with one single route. However, a pool of intermediate species must be present on the surface that can be hydrogenated rapidly to explain the formation of HCN by pulsing hydrogen. This pool of intermediates are either adsorbed carbon species that form CH* species and then react with adsorbed nitrogen atoms (or NH_x* species) according to the following reactions:

$$C* + H* \rightleftarrows CH* \quad (8)$$

$$N* + CH* \rightarrow HCN + 2* \quad (9)$$

or adsorbed CN* species issued from the surface reaction between N* (or NH_x*) and C*:

$$N* + C* \rightleftarrows CN* + * \quad (10)$$

$$CN* + H* \rightarrow HCN + 2* \quad (11)$$

van Hardeveld et al. [20] reached a similar conclusion for the HCN formation over Rh proposing the hydrogenation of CN* species (step (11)) as well as the reaction step (9).

Notice that reaction steps (9) and (10) compete with reaction step (6) for N* adatoms, thus providing a coupling between the production rates of N_2 and HCN. Apparently reactions steps (9) or (10) are must faster than step (6) in the presence of surface carbon yielding high selectivities to HCN.

A third possible reaction path consist of the reaction between NH_x and CH_x species leading to a surface reaction intermediate that yields HCN after dehydrogenation. This reaction path cannot be discarded but the dehydrogenation is not rate limited, as a similar HCN response would be expected on the introduction of NH_3 and CH_4. For the same reason the desorption step for HCN is not the rate-limiting step and thus left out in the above reaction sequence.

The study was carried out at 1173 K, whereas the temperature of the Degussa process is between 1473 and 1573 K. Nevertheless, the mechanism found at 1173 K could be representative of the mechanism of the real process. The experiments show good HCN selectivities (compare the N_2 and HCN yields in Fig. 4) that are comparable to those of the industrial process. Moreover due to the strong endothermicity of the reaction the catalyst surface under industrial conditions will be at a much lower temperature. However, the conclusion on the rate-determining step of the ammonia decomposition depends strongly on the temperature.

5. Conclusions

TAP experiments have been conducted for the synthesis of HCN from ammonia and methane over platinum black. The decomposition of ammonia into nitrogen and hydrogen is a relatively slow, kinetically reversible, step at 1173 K. Methane decomposition on the other hand is very fast. Consequently, two distinct HCN production rates are observed. HCN is formed slowly on the ammonia pulse but much faster on the methane pulse. In addition HCN can be produced by injecting hydrogen after the NH_3–CH_4 pump-probe experiment. The most probable reaction path for HCN synthesis is through a hydrogenation step of either C* or CN* surface species. HCN is a stable product and its desorption is fast.

Excess methane leads to a slow catalyst deactivation, probably by a slow build-up of inactive carbon.

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