Mechanistic aspects of the Andrussow process over Pt–Rh gauzes. Pathways of formation and consumption of HCN

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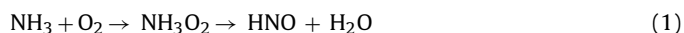
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ABSTRACT

Reaction pathways governing HCN selectivity in the oxidative coupling of methane and ammonia were investigated over three commercial Pt–Rh gauzes (fresh, activated, and spent) in the temporal analysis of products reactor with submillisecond-time resolution using isotopic traces. These gauzes differed in the extent of reaction-induced restructuring as well as impurity content. The ability of the gauzes to form HCN in the dual interactions of CH_4 with NH_3 or NO was compared considering the morphological differences of the gauzes. It was found that the progressive structural changes increased the gauze activity for methane conversion and facilitate the stabilization of methane fragments on the catalyst surface, but did not influence significantly the surface residence time of N-containing species. The well-known increase in HCN selectivity within first hours on-stream in the Andrussow process was suggested to be likely due to restructuring-induced stabilization of surface methane fragments. The decrease in the HCN selectivity after a stable phase of operation is mainly related to consecutive oxidation of HCN over iron oxide accumulated on the catalyst surface under industrial conditions of the Andrussow process.

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1. Introduction

The Andrussow process is one of the two industrially applied methods for production of hydrogen cyanide from methane and ammonia [1]. HCN finds use as a feedstock in the commercial production of synthetic fibers and plastics. Although hydrogen cyanide is industrially produced since 1940s, the mechanistic knowledge on the catalyst functioning is scare. In 1935, Andrussow extended his mechanistic concept of the Ostwald process to HCN formation via oxidative coupling of methane and ammonia [2]. He postulated the formation of intermediate nitroxyl from ammonia and oxygen (Eq. (1)) as initial step in the HCN formation. This nitroxyl species reacts with methane to methylenimine (Eq. (2)). The latter undergoes direct decomposition (Eq. (3)) or oxidation to HCN (Eq. (4)):

$$NH_3 + O_2 \rightarrow NH_3O_2 \rightarrow HNO + H_2O \qquad (1)$$

$$HNO + CH_4 \rightarrow HNOH_2CH_2 \rightarrow HNCH_2 + H_2O \qquad (2)$$

$$HNCH_2 \rightarrow HCN + H_2 \qquad (3)$$

$$2HNCH_2 + O_2 \rightarrow 2HCN + 2H_2O \qquad (4)$$

First systematic investigations of reaction pathways relevant for the formation of HCN in the Andrussow process were performed in the group of Prof. Schmidt [3–7]. According to Schmidt and Hickman

[4], the formation of HCN takes place via a stepwise dehydrogenation of methylamine (CH_3NH_2) and methylenimine (CH_2NH) formed from ammonia and methane fragments (Eq. (5)). However, these authors did not experimentally observe these intermediates. CH_3NH_2, and CH_2NH were only detected during non-oxidative ammonia and methane conversion to HCN (BMA (Blausäure aus Methan und Ammoniak) also known as Degussa process) at 1300 °C and 10^5 Pa over Pt supported on walls of a tubular flow reactor [8]:

$$CH_4 + NH_3 \xrightarrow{-H_2} H_2NCH_3 \xrightarrow{-H_2} HNCH_2 \xrightarrow{-H_2} HCN \qquad (5)$$

Herceg and Trenary [9] suggested an alternative reaction pathway of HCN formation. They investigated the formation of HCN over Pt(1 1 1) surface exposed to CH_3I and NH_3 under e^--beam irradiation. These authors observed CN under conditions, where none of the possible hydrogen-containing fragments like NH_x and CH_y can exist. Therefore, they suggested that ammonia and methane are completely dehydrogenated to N and C surface atoms, which recombine to CN (Eq. (6)). The latter species is then hydrogenated to HCN (Eq. (7)). The presence of surface species, which yield HCN reacting with hydrogen, was experimentally proven in Ref. [10]. In the latter study HCN formation was observed after H_2 pulsing over Pt black having been pretreated by NH_3 and CH_4. In addition to [9], it was suggested that HCN can be formed via coupling of nitrogen atoms and hydrogenated carbon species (Eqs. (8) and (9)):

$$C\text{-}s + N\text{-}s \rightarrow CN\text{-}s + s \qquad (6)$$

$$CN\text{-}s + H\text{-}s \rightarrow HCN + 2s \qquad (7)$$

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C-s + H-s → CH-s + s　　　　　　　　　　　　　　　(8)

CH-s + N-s → HCN + 2s　　　　　　　　　　　　　　(9)

HCN was also observed in the reaction between CH_4 and NO [6]. The latter is a product of NH_3 oxidation in the frame of the Andrussow process. The kinetics of this interaction was studied over Pt foil in a steady-state flow reactor between 330 and 1230 °C. CH_4 and NO partial pressures were varied from 0 to 530 Pa and from 13 to 530 Pa, respectively. Despite HCN was formed in this reaction, Hasenberg and Schmidt [6] concluded that this product in the Andrussow process originated mainly from direct interaction of NH_3 and CH_4. However, they suggested that the reaction of NO and CH_4 may contribute to the overall HCN formation at high conversion levels of NH_3 and CH_4.

Mechanistic studies of HCN decomposition were mainly performed over well-defined Pt single crystals under UHV conditions [11–15]. A part of hydrogen cyanide adsorbed over Pt(1 1 1) dissociates above −170 °C [13,14]. At nearly 30 °C, hydrogen atoms react with non-dissociated HCN molecules yielding new surface species. However, the assignment of these species is still controversial. Jentz et al. [14,15] related them to aminomethylidyne (CNH_2). In another FT-RAIRS study of HCN decomposition over polycrystalline Pt foil [16] these species were ascribed to trans −HC=NH. Non-dissociated HCN and H_2 desorb at temperatures between 70 and 230 °C [11,13]. CN species formed via HCN dissociation stay on the Pt surface up to 330 °C. At higher temperatures they recombine yielding gas-phase C_2N_2 [11–13]. Since gas-phase N_2 was not detected upon HCN decomposition, it was concluded that Pt was not able to break the strong C–N bond under vacuum conditions. This is also valid for decomposition of CH_3NH_2 over Pt(1 1 1) [17] as well as for conversion of C_2N_2 over Pt(1 0 0) [18], and stepped Pt(1 1 1) [19]. Rh should possess higher activity towards rupture of CN bond, since N_2 was formed in the C_2N_2 decomposition over Rh(1 1 0) [20,21]. N_2 desorbed starting from 300 °C, while carbon atoms stayed on the surface up to 800 °C [21].

It should be stressed that the above studies did not use commercial catalysts and, therefore, did not aim to elucidate if the developed mechanistic schemes depended on reaction-induced morphological changes of Pt–Rh gauzes. The reaction-induced catalyst restructuring is typical for the Andrussow process [1] and is accompanied by changes in time on-stream production of HCN [22]. In a previous study of this author [23], the mechanistic aspects of primary O_2 and NH_3–CH_4 interactions were investigated over three commercial Pt–Rh gauzes (fresh, activated, and spent) having been used for different times on-stream in the Andrussow process. The fresh Pt–Rh gauze was not used for HCN synthesis and therefore was not restructured. The surface of activated catalyst possessed strong reaction-induced morphological changes. It revealed also the highest HCN selectivity under transient conditions. The spent one was the mostly restructured. Moreover, a lot of iron oxide was accumulated on its surface. It possessed the lowest selectivity towards HCN formation. Despite these strong morphological dissimilarities, the sequence of product formation from NH_3 and CH_4 in the presence of oxygen did not depend on the reaction-induced changes of catalyst morphology. It was suggested that nitric oxide primarily formed from ammonia reacted further with methane and ammonia yielding hydrogen cyanide and nitrogen, respectively.

From a fundamental point of view, there is still a lack in mechanistic understanding of the relationships between the reaction-induced catalyst restructuring and different HCN selectivity of these gauzes. Therefore, it is highly important to identify individual reaction pathways determining HCN selectivity and to establish their relation with structural characteristics of commercial Pt–Rh gauze catalysts. In the present study, NH_3–CH_4 and NO–CH_4 interactions as well as oxidative and non-oxidative HCN decomposition were studied in TAP reactor over the Pt–Rh

gauzes used in Ref. [23]. This study enabled to relate morphological changes of these catalysts to selectivity-determining reaction pathways.

2. Experimental

2.1. Catalytic materials

Woven Pt–Rh (10% Rh) gauzes used as catalysts were supplied by Evonik. In the manuscript the gauzes are denoted as fresh, activated, and spent. They were previously characterized with respect to their surface morphology and chemical composition using various characterization methods (Kr-BET, and SEM combined with EDX). It was established that the catalysts underwent severe reaction-induced morphological restructuring, which resulted in an increase in their surface area. For the fresh, activated, and spent gauzes, the specific surface areas were amounted to 0.002, 0.003, and 0.118 m^2/g, respectively. Moreover, the gauze restructuring was accompanied by an accumulation of various impurities on the catalyst surface. Content and type of these impurities possessed local variations. Iron oxide dominated on the surface of the spent Pt–Rh gauze and determined the highest surface area of this catalyst. The near-to-surface Pt/Rh ratio of the deposit-free areas was nearly the same for all the gauzes studied. However, these areas were strongly faceted on the spent Pt–Rh gauze. More details can be found in Ref. [23].

2.2. Transient experiments

Transient experiments were performed in the TAP-2 reactor system (for details see [24]). The present system was equipped with an in-house-developed quartz-glass microreactor (d = 6 mm, L = 40 mm). The gauze catalyst was packed between two layers of quartz particles (250–350 μm) in the isothermal zone of the microreactor. A new gauze sample with a weight between 40 and 50 mg was used in each of the following experiments:

- Single pulsing of NH_3–CH_4 (NH_3:CH_4:Kr or Ar = 1:1:1) mixture between 750 and 1000 °C with 50 °C intervals.
- Sequential pulsing of ^{15}NO (^{15}NO:Ne = 1:1) and CD_4 (CD_4:Kr = 1:1) and vise versa with time delays of 0.1, 0.2, 0.5, and 1 s at 750, 850, and 950 °C.
- Single pulsing of HCN (10% HCN in N_2:Ar = 1:1) between 850 and 1000 °C with 50 °C intervals. Subsequent sequential pulsing of HCN (10% HCN in N_2:Ar = 1:1) and $^{18}O_2$ ($^{18}O_2$:Ne = 1:1) with a time delay of 0.5 s between 850 and 1000 °C with 50 °C intervals.

NH_3 (2.5), CH_4 (4.5), ^{15}NO (2.5), $^{18}O_2$ (95–98%), NO (2.5), N_2O (2.5), N_2 (4.9), 10% HCN in N_2 (95–99%), CO_2 (4.5), CO (4.7), H_2 (5.0), Kr (4.0), Ar (5.0), and Ne (5.0) were used without further purification. Isotopically labeled methane (CD_4), oxygen ($^{18}O_2$), and nitric oxide (^{15}NO) were purchased from ISOTEC, ISOCOM, and Linde, respectively. The isotopically labeled molecules were used for proper mass-spectroscopic identification of reaction products, which spectra are otherwise overlapping.

Transient responses were recorded at the reactor outlet using a quadrupole mass spectrometer (HAL RC 301 Hiden Analytical). The following atomic mass units (AMUs) were used for the identification of different compounds: 52.0, 38.0 (C_2N_2), 48.0, 30.0 ($C^{18}O_2$), 46.0, 32.0, 28.0 ($N_2^{18}O$), 46.0, 31.0, 30.0 ($^{15}N_2O$), 36.0 ($^{18}O_2$), 32.0 ($N^{18}O$), 31.0 (^{15}NO, CH_3NH_2), 30.0 ($C^{18}O$, $^{15}N_2$), 30.0, 29.0, 28.0, 27.0, 26.0 (C_2H_6), 28.0, 27.0, 26.0 (C_2H_4), 28.0 (N_2), 29.0 ($DC^{15}N$, CH_2NH), 27.0, 26.0 (HCN), 20.0, 19.0 ($H_2^{18}O$), 20.0, 18.0, 16.0, 14.0 (CD_4), 15.0 (NH_3, CH_4), 13.0 (CH_4), 2.0 (H_2), 84.0 (Kr), 40.0 (Ar), and 20.0 (Ne). In the performed experiments, pulses were repeated 10 times for each AMU and averaged to improve the signal-to-