

Liquid-Phase Catalytic Decomposition of Novel Ammonia Precursor Solutions for the Selective Catalytic Reduction of NO_x

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Abstract Aqueous solutions of NH_3 -precursor compounds (i.e. urea and methanamide) were catalytically hydrolyzed in the liquid phase by applying a pressure of 50 bar during contact with the catalyst in a heated tube. Methanamide could be hydrolyzed on an Au/TiO_2 catalyst to yield not only NH_3 , but also H_2 . Decomposition of urea under high pressure in the liquid phase could even be achieved without the addition of a catalyst. Due to the large excess of water present during decomposition, side products could be avoided. As the reactor tube is electrically heated, the presented method provides a possibility to reliably transform NH_3 -precursor compounds into gaseous NH_3 independent of the engine exhaust gas temperature. The NH_3 -flow can be added to the main exhaust duct to enable the selective catalytic reduction of NO_x at the light-off of the SCR catalyst.

Keywords Selective catalytic reduction (SCR) · NH_3 -precursor · Hydrolysis

1 Introduction

Selective catalytic reduction (SCR) of NO_x with ammonia (NH_3) is a widespread technique for the elimination of harmful NO_x emissions from lean combustion sources [1]. In mobile applications the required NH_3 must be stored and released from NH_3 -precursor compounds due to safety regulations. Reliable release of the NH_3 from the precursor compounds without the formation of harmful or undesired side products is becoming increasingly difficult as the thermal energy contained in the exhaust gas is constantly reduced.

Hydrolysis of the precursor in an external device operating independently of the exhaust gas temperature could provide gaseous NH_3 even at exhaust gas temperatures significantly lower than those required for the reliable evaporation of aqueous urea solution sprayed into the main exhaust duct [2]. Also, solutions of alternative NH_3 -precursor compounds would become an option to produce gaseous NH_3 [3].

In this study, we present results on the generation of gaseous NH_3 from aqueous urea solution or aqueous methanamide solution by the catalytic decomposition in the liquid phase under elevated pressure and temperature.

2 Experimental

2.1 Catalyst Preparation and Characterization

In Table 1 the catalytic materials used in this study are listed. 32.5 % urea solution and 40 % methanamide solution were prepared by dissolving the corresponding pure substances in de-ionized water.

Au/TiO_2 was prepared by a deposition–precipitation procedure described in literature [4] using a cut-out TiO_2 monolith sample provided by Porzellanfabrik Frauenthal GmbH, which was loaded with 1.5 % of gold relative to the TiO_2 mass and fitted into the reactor tube. The other catalysts, which were used for the decomposition of urea solution, were filled into the reactor without prior processing.

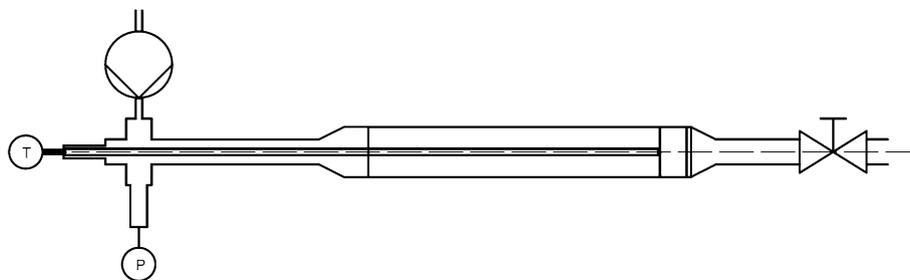
3 Setup for Decomposition of NH_3 -Precursor Solutions

The decomposition of the NH_3 -precursor solutions was intended to proceed in the liquid phase. As the aqueous

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Table 1 List of used catalytic materials

Material	Producer	Shape	Size	Amount (g)	BET surface (m ² /g)
TiO ₂ (anatase)	Porzellanfabrik Frauenthal	Crushed monolith	240–270 μm	9.51	70
ZrO ₂	Unknown	Cylindrical pellets	2.9 × 3.2 mm	16.42	33
γ-Al ₂ O ₃	Zeochem AG Uetikon	Powder	0.8–1.0 mm	7.57	243
1.5 % Au/TiO ₂	in-house (doping at PSI)	400 cpsi monolith	7.5 × 125 mm	3.87	100

Fig. 1 Scheme of the high-pressure NH₃-generator used to convert NH₃-precursor compound solutions into gaseous NH₃

solutions would boil under atmospheric pressure, a pressure valve with a set pressure of 50 bar was positioned downstream of the stainless steel reactor tube (Fig. 1). The catalyst bed was fixed inside the reactor by a porous metal frit with 60 μm pores. A thermocouple placed inside the catalytic bed was used to record the reaction temperature and for feedback control of the heating wire wrapped around the reactor tube, while a pressure sensor was installed upstream of the reactor to guarantee constant pressure of 50 bar inside the reactor. The NH₃-precursor solutions were fed using a high pressure liquid chromatography (HPLC) pump with a constant flow rate of 5 mL/min.

Before the pressure was released by the outlet valve, the gases were cooled so they could be quantitatively quenched in water. The mass of collected sample and the corresponding amount of consumed NH₃-precursor solution per sampling interval was recorded and used for the evaluation.

4 Analytics

For evaluation of the nitrogen balance of the decomposition reactions, the main product NH₃ was quantified by photometric determination, whereas side products or undecomposed NH₃-precursor compounds were determined by HPLC analysis.

The photometric measurement of NH₃ was adopted from the indophenol method for the quantification of NH₃ in solution according to the VDI method 2461 [5]. By the addition of phenol and sodium hypochlorite, sodium nitroprusside catalytically transformed NH₃ into the blue indophenol dye. The quantification was performed by UV–Vis spectroscopy at 630 nm. Calibration solutions were prepared using ammonium chloride, while the blank value

was determined from de-ionized water. As the method is extremely sensitive the collected samples needed to be diluted depending on the amount of contained NH₃.

The liquid samples obtained from the quenched product gases were diluted with 5 mM phosphate buffer (adjusted to pH 7 with NaOH) in order to prepare them for HPLC analysis [6]. Typical side products including isocyanic acid (HNCO), biuret, cyanuric acid, ammeline, ammelide or melamine could be quantified by an in-house developed HPLC analysis procedure using an anion-exchange column for separation and detection of the components in the UV wavelength range [7]. However, only HNCO and biuret were found in the course of the presented experiments. The undecomposed NH₃-precursor compounds urea and methanamide could also be determined quantitatively and were found to represent more than 97 % of the molar amount of nitrogen not emitted as NH₃ in all experiments.

In addition to analysis of the gas quenching solution, the gaseous reaction products of methanamide decomposition on Au/TiO₂ at 150 °C which were not soluble in water were captured in a gas collecting tube and subsequently analyzed by feeding them into a quadrupole mass spectrometer. By this measure, it was intended to capture eventually formed CO or H₂, which could evolve during decomposition of methanamide [8]. The analysis provided only a crude quantitative result, as CO₂ was also contained in the gas sample even though it was mostly quenched in the solution due to the high amount of dissolved NH₃.

5 Results

The amount of NH₃ from decomposition and the amount of emitted NH₃-precursor compounds during the experiments

are plotted in Fig. 2. Both, decomposition of urea solution on catalysts or in the empty reactor and the decomposition of methanamide solution on Au/TiO₂ are shown.

The amount of unconverted NH₃-precursor and yielded NH₃ evolve in opposite directions and add up to around 100 %, indicating only a small amount of side product formation. Figure 3 shows all additionally detected compounds containing nitrogen, i.e. any side products reducing the yield of NH₃ from conversion of the NH₃-precursors. In case of methanamide solution no products containing nitrogen besides NH₃ or methanamide could be found. During decomposition of methanamide solution at 150 °C 80 % H₂, 20 % CO₂ and 0.1 % CO could be detected in the gas-phase. NH₃ could also be measured in trace amounts of approximately 60 ppm, indicating an efficient absorption of NH₃ in water. The obtained H₂ suggests decomposition of the intermediate formic acid to H₂ and CO₂ rather than H₂O and CO [9].

The most striking feature of Figs. 2 and 3 is that the results of all urea decomposition experiments are quite similar, including the experiment without catalyst in the reactor. This observation is in contrast to the decomposition in the gas phase, which is negligible without catalyst up to 200 °C, but shows conversions larger than 90 % with any of the tested catalysts.

In order to compare liquid phase and gas phase decomposition, pseudo first-order rate constants according to Formula 1 were calculated and compared with literature values. The Arrhenius plot for liquid phase decomposition is shown in Fig. 4.

$$k = -\frac{V^*}{W} \ln(1 - X) [\text{cm}^3 \text{g}^{-1} \text{s}^{-1}] \quad (1)$$

(V* = volumetric flow through reactor; W = catalyst weight; X = urea conversion)

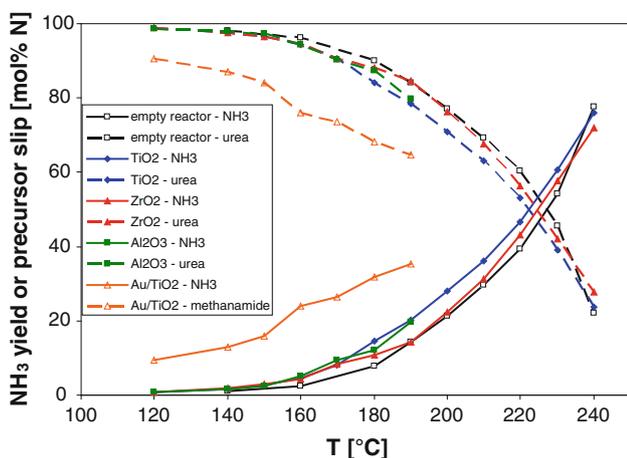


Fig. 2 Results from decomposition of urea or methanamide solution under pressure

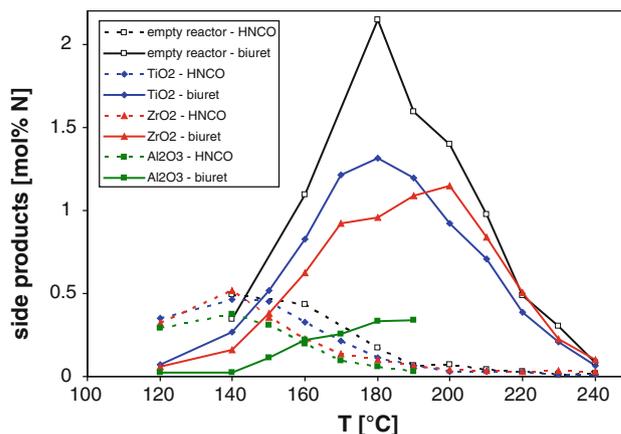


Fig. 3 Side product formation from decomposition of urea solution under pressure

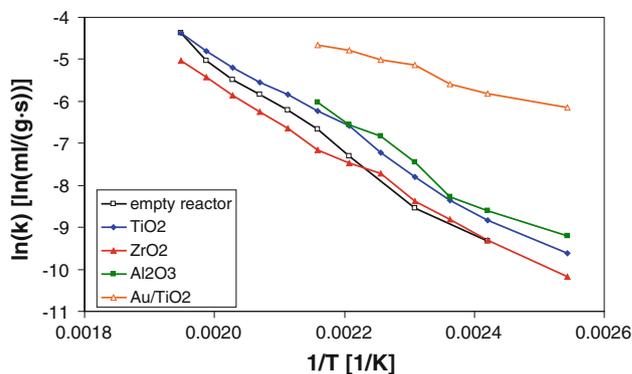


Fig. 4 Arrhenius plot of decomposition in the liquid phase. Apparent activation energies (E_A) for the hydrolysis reaction are 87 kJ/mol (empty reactor), 75 kJ/mol (TiO₂), 72 kJ/mol (ZrO₂), 72 kJ/mol (Al₂O₃) and 34 kJ/mol (Au/TiO₂)

If compared with values for the gas phase decomposition of urea or HNCO on these catalytic materials (e.g. E_A HNCO hydrolysis on TiO₂ = 73 kJ/mol [10]), the activation energies for urea hydrolysis are similar, while the pre-exponential factors are smaller by two orders of magnitude [11]. In contrast to the gas phase decomposition though, the entire volumetric flow consists of aqueous urea, while it mostly consists of carrier gas for gas phase decomposition. Therefore, the smaller reaction rates can be overcompensated by the much smaller reactor volume for liquid phase decomposition.

The low activation energy of 34 kJ/mol for methanamide decomposition could point towards a diffusion limitation in the liquid phase. As a 400 cpsi extruded TiO₂ monolith with a pitch of 1.27 mm rather than a packed bed was used for the experiment, the maximum diffusion distance of 0.635 mm could indeed be too long for the low diffusion rates in the liquid phase. Consequently, superior catalytic decomposition could be feasible when using a more dense catalyst in the reactor.

6 Conclusion

The decomposition of urea in the liquid phase was—in contrast to the decomposition in the gas phase—not accelerated significantly by any of the tested catalytic materials. Comparison of the rate constants for urea decomposition on hydrolysis catalysts in the liquid phase with values from the gas phase show that gas phase decomposition proceeds approximately 100 times faster. However, the reactor size is much more compact for the liquid phase, thereby overcompensating the low reaction rates.

Consequently, the presented result could lead to the development of a new method to reliably provide gaseous NH_3 from NH_3 -precursor compound solutions without the formation of side products, enabling direct injection into the main exhaust duct upstream of an SCR catalyst [12].

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