Chapter 16
Ammonia Storage and Release in SCR Systems for Mobile Applications

Daniel Peitz, Andreas Bernhard and Oliver Kröcher

16.1 Introduction

The SCR reaction requires ammonia for the reduction of nitrogen oxides. While compressed or liquefied ammonia is used for the supply of ammonia in stationary applications, the odorous ammonia gas had to be replaced in mobile SCR applications by an ammonia precursor compound for the safe storage and reliable release of ammonia in the right quantities and right dynamics. Thus, significant innovation was needed before mobile SCR systems could be realized, even though commercial operation of ammonia SCR systems in coal power plants (>250 MW) started already around 1980 [1]. After the invention of HC-SCR for mobile NO_x sources, to avoid handling NH_3 [2], and the discovery of cyanuric acid as a safe NH_3 storage compound, [3] urea was proposed as a storage material for NH_3 in 1988 [4]. By then, urea was already known to work as an NH_3 precursor for SCR in stationary applications for 3 years [5]. First results on mobile urea-based SCR were publically presented in 1990, already showing NO_x conversions above 90 % from 250 °C at gas hourly space velocities (GHSV) of 12,900 h^{-1} [6]. The first patented mobile applications of urea solutions for SCR were registered in 1990 [7].

Due to the large-scale production of urea as a bulk commodity, it is readily available in large quantities. Since the involved reactants CO_2 and NH_3 needed for urea synthesis are bulk chemicals that are produced directly from air and natural gas, using the well-known industrial Haber–Bosch process, urea can be produced at a low price [8]. Also, urea is nontoxic, noncorrosive and can easily be handled as aqueous solutions, such as a 32.5 wt % solution with the trade name AdBlue®.

D. Peitz · A. Bernhard · O. Kröcher (✉)
Bioenergy and Catalysis Laboratory, Paul Scherrer Institut, OVGA/112 5232 Villigen PSI, Switzerland
e-mail: oliver.kroecher@psi.ch

O. Kröcher
École polytechnique fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

I. Nova and E. Tronconi (eds.), *Urea-SCR Technology for deNOx After Treatment of Diesel Exhausts*, Fundamental and Applied Catalysis,
DOI: 10.1007/978-1-4899-8071-7_16,

Usually, urea solution is directly dosed into the main exhaust pipe, where it decomposes due to the elevated temperature and on the SCR catalyst to yield the actual reducing agent NH_3 [9, 10]. These advantages have made urea the most important NH_3 precursor compound used today for the $DeNO_x$ aftertreatment of Diesel exhausts by SCR.

However, some challenges related to the use of urea remain. Urea solution is more difficult to dose and to mix with the exhaust gas than NH_3 gas-urea may decompose incompletely, form deposits and even deactivate the SCR catalyst [11–13]. These issues are subject of ongoing research and will be treated in Sect. 16.2.

Furthermore, the NH_3 storage density of AdBlue® solution is only one-third compared to liquefied NH_3, the freezing point of -11 °C is too high to reliably avoid freezing in many parts of the world [14] and the stability when stored at elevated temperature is limited [15]. Improved NH_3 storage density, freezing and storage stability can be achieved by using alternative NH_3 storage compounds, which will be treated in Sect. 16.3.

16.2 Urea as Ammonia Precursor Compound

16.2.1 Solid Urea

The NH_3 storage density (gravimetric and volumetric) of solid urea is very high, but the dosing is technically challenging. In order to release all the stored NH_3, urea needs to be contacted with a catalyst, and this is quite difficult to achieve during dynamic operation of a vehicle [16]. In order to dose solid urea, urea is pressed into spherical pellets of defined diameter. The pellets are then dispensed from the storage tank by a star feeder [17] and shot onto a hydrolysis catalyst-coated heated plate using pressurized air [18]. The catalyst-coated plate constituted an external reactor in a bypass flow of the main exhaust for the conversion of solid urea to NH_3 gas [19]. Later modifications of the reactor place the unit in the main exhaust pipe, downstream of an oxidation catalyst, in order to harvest heat from the exhaust gas for the decomposition of the dosed urea, rather than using solely electric heating [20].

Still, the handling and dosing of solid urea in mobile SCR systems remains complicated, as small amounts of solids are hard to dose as dynamically as the NO_x emissions from the engine varies [16]. Handling is made even more difficult by the high deliquescence of solid urea, which easily transforms the single solid urea pellets into larger aggregates of solid urea that no longer pass the solid transfer sections [21].

16.2.2 Urea Solution

In order to simplify the dosage of urea into the main exhaust pipe, urea-water-solutions (UWS) were introduced. A concentration of 32.5 % (by mass) urea in H_2O was chosen for mobile applications as a standardized solution due to the eutectic nature with a melting point of −11 °C. The trade name AdBlue® was introduced in many countries, in others the solution became known as Diesel Exhaust Fluid (DEF) or as Aqueous Urea Solution (AUS) [22]. For the exhaust gas aftertreatment of Diesel engines in large ships a more concentrated solution of 40 % urea is used, as the stored urea solution is not exposed to low temperatures in the ship's engine room. As the temperature in many parts of the world falls regularly below −11 °C in winter, the AdBlue® tank of vehicles must be equipped with a heating system. Most frequently, the heating system is a combination of electric heating and a heat exchanger drawing off heat from the engine cooling fluid [23]. High-temperature stability of AdBlue® is also restricted, as urea in the aqueous solution will start decomposing, thereby building up pressure in the storage tank. AdBlue® containments and transport lines are not generally certified to withstand pressures higher than 50 mbar relative to ambient pressure. However, AdBlue® in a sealed vessel will build up a pressure of 70 mbar under storage at 40 °C. The shelf life when stored between 30 and 35 °C is reduced to just 6 months [23].

The easy release of NH_3 from the precursor compound clearly becomes a disadvantage for the application of AdBlue® in Mediterranean up to tropical areas.

The NH_3 storage potential of AdBlue® amounts to 0.201 kg/L (0.184 kg/kg) NH_3/solution [22] compared to solid urea with 0.567 kg/kg (0.749 kg/L solid block or 0.42 kg/L pellets).

Since the commercial introduction of AdBlue® in 2004 [24], it has been adopted worldwide for heavy-duty applications of Diesel engines equipped with SCR systems, and is considered the most promising system for the Diesel engine passenger car market [25].

16.2.3 Urea Thermolysis and Evaporation

As urea is the predominant NH_3 precursor compound, its decomposition will be discussed in detail. In general, urea decomposes in the hot exhaust gas via a two-step reaction to yield the actual SCR reducing agent NH_3 [9].

Urea thermolysis:	$CO(NH_2)_2 \rightarrow NH_3 + HNCO$
Isocyanic acid hydrolysis:	$HNCO + H_2O \rightarrow NH_3 + CO_2$
Overall reaction:	$CO(NH_2)_2 + H_2O \rightarrow 2\ NH_3 + CO_2$

Before these chemical reactions occur, the dosed UWS aerosol is heated up by the surrounding exhaust gas and the contained water evaporates. The exact state of aggregation of urea during decomposition is still uncertain [26, 27]. Two recent theoretical studies [28, 29] relying on experimental data [30–33] point toward urea evaporation from liquid aerosols and decomposition in the gas phase. However, another recent study supposed the mentioned chemical reactions take place in solid aerosols [34].

Urea thermolysis is usually considered a solely thermal reaction, whereas the intermediate isocyanic acid (HNCO) is stable in the gas phase but hydrolyzes on the SCR catalyst or on a dedicated hydrolysis catalyst [9]. Catalytic reactions will be discussed later; this section is focusing on thermal decomposition.

Back in 1966, Schmidt described a process to thermolyze urea into NH_3 and HNCO gas on an industrial scale [35]. In this process, solid urea was blown into a fluidized bed of inert material, which was heated above 300 °C. The produced HNCO gas was used for melamine synthesis.

HNCO is stable in the gas phase at conditions relevant for SCR [9], but is highly reactive with respect to byproduct formation in the condensed state [36]. Figure 16.1 shows a reaction scheme for urea decomposition, including the two byproducts biuret and cyanuric acid which are formed first [37].

Basic investigations of urea thermolysis, including the formation and decomposition of byproducts, have been performed using thermogravimetric analysis (TGA) and/or differential scanning calorimetry (DSC) [11, 13, 36, 38]. The DSC data consistently show a sharp feature at 133 °C, the melting point of urea. Further features strongly depend on experimental conditions, like the type of sample administration [11, 38].

Typically, solid urea was administrated in a crucible. Inside a crucible, volatile compounds produced within the urea melt have to reach the surface of the liquid, desorb to the gas phase, and finally leave the crucible by gas diffusion and convection. The slow mass transport of gaseous compounds to leave the crucible leads to long residence times of, e.g., the reactive HNCO inside the crucible, resulting in extensive byproduct formation [11]. Since HNCO is consumed during byproduct formation, the observed HNCO concentration in the gas phase is largely reduced compared to the NH_3 concentration below 300 °C [11, 38]. On the other hand, mainly HNCO is observed in the gas phase above 300 °C due to cyanuric acid decomposition [11, 38]. In addition to experiments using a crucible, Lundström et al. [10] performed DSC experiments with cordierite monoliths, impregnated with urea [38]. Due to the large monolith surface, HNCO desorption was faster than cyanuric acid formation, resulting in virtually similar curves for the gas phase concentration of NH_3 and HNCO.

Improving the mass transport further by increasing the space velocity and decreasing the amount of urea on the monolith relative to the gas flow through the channels, allows urea evaporation to be even faster than urea thermolysis [39]. In other words, the urea evaporated in the temperature programmed desorption (TPD) experiments, before the temperature was high enough for urea thermolysis [39]. Urea sublimation under vacuum has been known for decades and gaseous urea exists in monomolecular form [32, 40, 41]. Recent studies have shown that gaseous urea also exists in monomolecular form under atmospheric pressure and that diluted urea vapor is sufficiently stable to be measured by Fourier transform infrared (FTIR) spectroscopy in a gas cell heated to 180 °C [39, 42]. Comparing

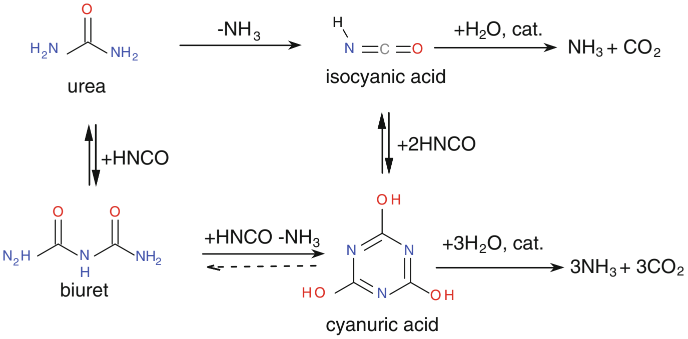

Fig. 16.1 Reaction scheme for urea decomposition, including the two byproducts biuret and cyanuric acid

the saturation vapor pressure of urea [39, 40] with raw NO_x emissions of 200–300 ppm of a modern Diesel engine [14] reveals that a temperature of only about 120 °C is sufficient for complete evaporation of the required urea (assuming quantitative urea decomposition and NO_x reduction). Of course, urea-SCR at just 120 °C is not feasible due to kinetics, however, one should keep in mind that a significant fraction of the dosed urea may reach the catalyst as urea vapor in addition to NH_3, HNCO and urea aerosols.

More realistic urea decomposition experiments were performed with single UWS droplets on a quartz fiber [33]. Even contact-free experiments are possible with UWS droplets in an acoustical levitator [43]. Experiments with single UWS droplets also provide information about water evaporation from the UWS droplets as shown in Ref. [33, 43]. These data are a valuable input for modeling work, but real UWS aerosols are much smaller than the droplets used in these studies [33, 43]. It is plausible that, in analogy to the TGA, DSC, and TPD experiments mentioned above [11, 36, 38, 39], smaller aerosols with faster mass transport to the surrounding gas favor the desorption of HNCO and/or urea vapor over byproduct formation inside the aerosols.

16.2.4 *Urea Decomposition Byproducts and Catalyst Deactivation*

The byproducts biuret and cyanuric acid are observed in the largest quantity at low and moderate temperatures up to about 300 °C [36]; however, additional byproducts form in smaller amounts as shown in Fig. 16.2 [11, 36, 37]. Substitution of the OH groups of cyanuric acid by NH_3 yields the more stable triazines ammelide, ammeline, and melamine [36]. Ammelide may also be formed by the reaction of biuret with HNCO, if water is eliminated instead of NH_3 [11]. Melamine may also be produced by trimerization of cyanamide [36] since cyanamide is an intermediate in melamine synthesis [35]. Cyanamide was not observed in a

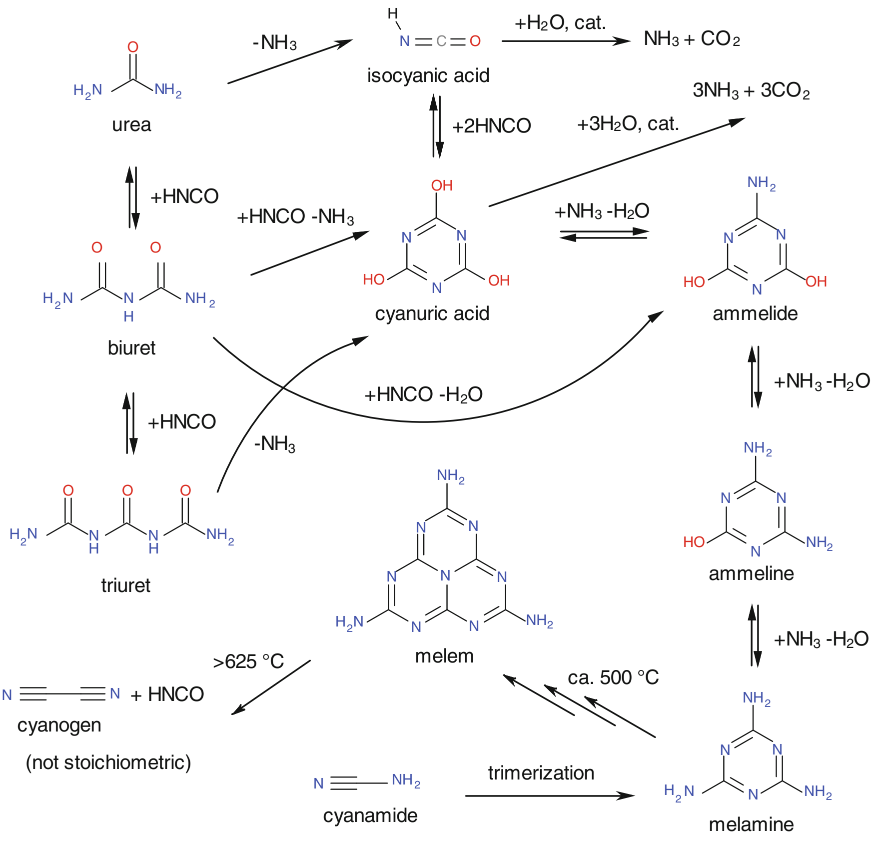

Fig. 16.2 Reaction scheme showing the formation of minor byproducts from urea [11, 36, 37]

prominent study on urea decomposition [36], but it was observed on TiO2 catalysts in other studies, where cyanamide may have been formed by disproportionation of HNCO [44, 45]. Melamine is more stable than cyanuric acid; it slowly sublimes rather than decomposes at temperatures around 300 °C [36, 37]. At higher temperatures, melamine polymerizes to form melem and melon [11]. Polymeric melamine is water-insoluble and decomposes only above 625 °C [11, 13].

Of course, byproduct formation is unwanted in the urea-SCR application. One crucial measure to limit byproduct formation is realizing a high spray quality [13, 46]. In addition, the presence of a catalyst is favorable. Since HNCO, originating from urea thermolysis, plays a key role in byproduct formation, a catalyst can largely reduce byproduct formation by HNCO hydrolysis [10, 11, 37]. The best hydrolysis catalyst known for the urea-SCR application is anatase TiO_2 [10, 37, 47–49]. Also, $V_2O_5/WO_3\text{-}TiO_2$ [13, 50] and zeolite-based [10, 11, 51] SCR catalysts provide high hydrolysis activities.

If byproducts form on the catalyst in spite of its hydrolysis activity, or if byproduct-containing aerosols are deposited on the catalyst, even these byproducts can be hydrolyzed catalytically. According to a recent work [37], a temperature around 200 °C is sufficient already to hydrolyze biuret, cyanuric acid, ammelide, ammeline, and melamine on anatase TiO_2. Cyanuric acid, melamine and even melem can be hydrolyzed on Al_2O_3 [52]. Eichelbaum et al. [11] found that urea induces a reversible deactivation of an iron-exchanged Beta catalyst [12]. The SCR reaction at 250 °C was strongly inhibited by cyanuric acid and ammelide, but the activity could be largely restored at 300 °C or completely at 500 °C [12]. In a urea-SCR application, regeneration of the SCR catalyst due to its own hydrolysis activity may often be sufficient. If the urea-induced catalyst deactivation is too fast, this deactivation may be avoided by a dedicated hydrolysis catalyst upstream of the SCR catalyst.

16.2.5 Catalytic Urea Decomposition

As mentioned above, urea thermolysis into NH_3 and HNCO is usually considered a solely thermal reaction. If urea thermolyzes completely upstream of the catalyst or if urea thermolysis on the catalyst is very fast, catalytic HNCO hydrolysis would be the rate determining step in the overall urea hydrolysis reaction. Catalytic HNCO hydrolysis has been investigated by both experimental and theoretical studies [45, 47–51, 53, 54] and is, therefore, well understood. Pure anatase TiO_2 is the best hydrolysis catalyst, apart from ZrO_2, which is sensitive to sulfur poisoning and consequently not used in urea-SCR applications [54]. The addition of V_2O_5 and/or WO_3 to TiO_2 decreases its hydrolysis activity [50, 54]. Also, zeolite catalysts show lower hydrolysis activity than pure TiO_2 [51, 54]. Still, HNCO hydrolysis on SCR catalysts is faster than the actual SCR reaction, indicating that increasing the size of the SCR catalyst is better than placing a hydrolysis catalyst in front of it [50]. However, in a urea-SCR application, a large fraction of the dosed urea remains intact before it enters the catalyst [9]. Therefore, interaction of molecular urea with catalysts deserves a closer look.

Urea thermolysis is usually thought to be a solely thermal reaction, but there have been some studies pointing toward catalytic urea thermolysis [10, 11, 13, 55]. Previously, Bernhard et al. [37] reported catalytic urea thermolysis as well as hydrolysis under steady-state conditions [42, 56]. Figures 16.3 and 16.4 show a catalyst screening, using the data of Ref. [56]. To reveal differences between the catalysts rather than performing mass transport limited reactions, small amounts of the catalysts (roughly 10 g/L) were coated on cordierite monoliths with a high cell density (600 cpsi). The space velocity was 91,000 h^{-1}. Urea solution was dosed as a very fine spray, using the setup described in Ref. [57]. In addition to UWS, water-free organic urea solutions were dosed to investigate the thermolysis reaction alone, without subsequent HNCO hydrolysis (Fig. 16.3a).

In the absence of water, urea was catalytically thermolyzed, yielding HNCO with high selectivity (Fig. 16.3a). In the presence of water, urea was efficiently

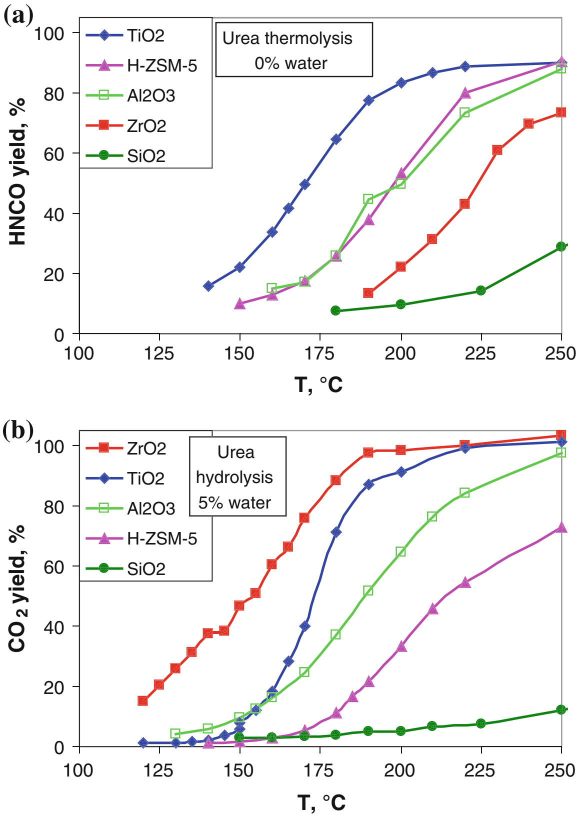

Fig. 16.3 Catalyst screening for urea decomposition. Parameters: 100 ppm urea, 10 % O_2 in N_2, total gas flow = 500 L/h at STP, GHSV = 91,000 h^{-1}, active masses: 45 mg anatase TiO_2, 52 mg ZrO_2, 48 mg H-ZSM-5 (H-MFI 27), 64 mg Al_2O_3, 55 mg SiO_2. **a** Water-free experiments with 0.31 % ethanol in the gas phase. **b** Hydrolysis with 5 % water in the gas phase [58]

hydrolyzed as shown in Fig. 16.3b. The order of catalyst activities according to [42, 56] is:

Urea thermolysis: $TiO_2 > \text{H-ZSM-5} > Al_2O_3 > ZrO_2 > SiO_2$
Urea hydrolysis: $ZrO_2 > TiO_2 > Al_2O_3 > \text{H-ZSM-5} > SiO_2$

As for HNCO hydrolysis, ZrO_2 was most active for urea hydrolysis, but since ZrO_2 is sensitive to sulfur poisoning [54], TiO_2 is the best for urea-SCR applications.

Figure 16.4a shows the slip of the intermediate HNCO produced during urea hydrolysis. Interestingly, TiO_2, H-ZSM-5 and Al_2O_3 showed significant local maxima in the HNCO slip. Local maxima of the intermediate HNCO are in agreement with the assumed two-step mechanism (urea thermolysis and HNCO hydrolysis). However, pure HNCO hydrolyzed much faster on the same catalysts (Fig. 16.4b). The comparatively slow hydrolysis of the HNCO originating from urea thermolysis indicates that urea strongly inhibits HNCO hydrolysis. Inhibition of HNCO hydrolysis on TiO_2 by NH_3, originating from urea thermolysis, cannot explain the HNCO peak in Fig. 16.4a, because NH_3-inhibition on of HNCO hydrolysis was found to be negligible above 150 °C by Refs. [53, 54].

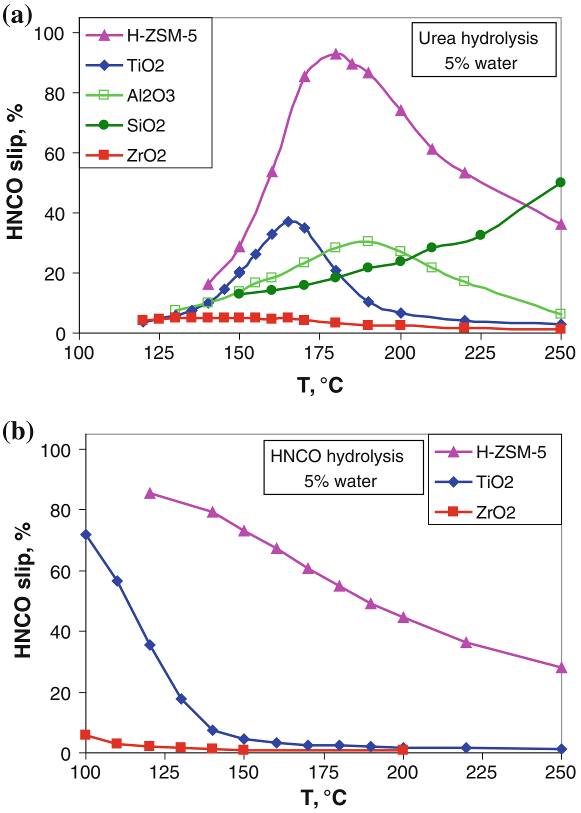

Fig. 16.4 Urea hydrolysis (**a**) versus HNCO hydrolysis (**b**). Parameters: 100 ppm urea or HNCO, 10 % O_2 in N_2, total gas flow = 500 L/h at STP, GHSV = 91,000 h^{-1}, active masses: 45 mg anatase TiO_2, 52 mg ZrO_2, 48 mg H-ZSM-5 (H-MFI 27), 64 mg Al_2O_3, 55 mg SiO_2 [58]

The presented studies [56, 58] will not be the last on catalytic urea decomposition, yet the results already clearly show that urea thermolysis is catalyzed and that catalytic urea hydrolysis is much slower than the hydrolysis of pure HNCO. Taking into account the risk of urea-induced deactivation of the SCR catalyst [12], the ongoing trend for lower exhaust gas temperatures and the good properties of TiO_2 for byproduct decomposition [37], using a dedicated hydrolysis catalyst may be a good option for some urea-SCR applications.

16.3 Alternative Ammonia Precursor Compounds

16.3.1 Cyanuric Acid

Historically, cyanuric acid can be considered one of the first ammonia precursor compounds. As far back as 1977, a Japanese patent mentions the possibility of replacing NH_3 in power plant exhaust gas aftertreatment with inorganic ammonium salts, urea or cyanuric acid granules of 0.1–10 mm diameter [59]. However, almost one decade later, in 1986, the publication of Perry and Siebers on high NO conversion, when directing a Diesel engine exhaust flow through a heated bed of cyanuric acid, still received much attention [3]. Their intention in using cyanuric acid was to release isocyanic acid upon heating above 330 °C. They believed the evolved HNCO to be the active reactant in reduction of NO [60]. Indeed, they were able to reliably decompose cyanuric acid to HNCO. NO was converted to N_2 in their setup when flowing through a stainless steel beads bed with the produced HNCO. These results led to several patents on the utilization of cyanuric acid in mobile exhaust gas aftertreatment, the process was named RAPRENO$_x$ (RAPid REduction of NO$_x$) [3, 61, 62]. However, it was later shown that the stainless steel beads used as reactor filling material actually catalyzed the decomposition of HNCO [63], leading to the production of NH_3, which was the actual reducing agent. During this time, first experiments were conducted with solid urea as NH_3 storage compound, and a direct comparison showed urea to be advantageous for multiple applications [64].

16.3.2 Ammonium Formate

In the course of optimizing the low-temperature stability of aqueous urea solution, various anti-freeze additives were tested. For example, typical engine coolant antifreeze additives such as ethanol [65], propylene glycol or methanol [66] were added to aqueous urea. However, the freezing point depression was not very significant (<10 K) and the emission of the additionally introduced hydrocarbons in the exhaust was not acceptable [66]. In contrast, ammonium formate addition to aqueous urea solution caused a depression of the freezing point down to −30 °C, and it could even contribute to the NH_3 storage capacity [67]. Inorganic ammonium salts have already been proposed for application in fossil fuel power plant SCR systems [59], but ammonium formate was only mentioned in previous disclosures concerning the selective non-catalytic reduction (SNCR) of NO$_x$ in these units [68]. The use of ammonium formate as an additive to urea solution has brought the benefit of decreasing the melting point [69], and yet increased the amount of stored NH_3 in the solution [70]. Depending on the application, high NH_3-containing solutions could also be prepared that showed comparable low-temperature stability to AdBlue® [71]. The most preferable solutions are named Denoxium-20 or Denoxium-30 with freezing points around −20 and −30 °C, respectively. The NH_3-releasing capacity amounts to 0.207 kg/kg (0.232 kg/L) for Denoxium-30 and to 0.205 kg/kg (0.228 kg/L) for Denoxium-20. Denoxium-20 is only advantageous to Denoxium-30 in so far that it contains less of the more expensive ammonium formate, while containing approximately the same amount of stored NH_3. The melting point of Denoxium-30 is actually not exactly −30 °C—the solution shows a hysteresis of freezing as low as −31 °C and melting as high as −26 °C [72]. Until now, only the Denoxium-30 solution has been commercially employed, either under the name Denoxium®, or, in Canada, the USA and Mexico, under the name

TerraCairPlus®, due to a license agreement between Denoxium® owner Kemira Oyj with Terra Environmental Technologies Inc [73].

There is already interest in modeling the evaporation of ammonium formate urea solution droplets in the exhaust gas pipe [74]. Ammonium formate will split into ammonia and formic acid in the hot exhaust [70]. While ammonia is the desired product that is consumed in the SCR reaction, formic acid constitutes an undesired emission. In fact, formic acid is the most corrosive halogen-free organic acid, and its corrosive effect on metals is further enhanced by O_2 [75]. The corrosion of steel by formic acid is a function of the acid concentration and the temperature [76], but in contrast to inorganic acids, formic acid does not form a passivating film on the metals during corrosion [77]. In the past, the corrosive effect on various types of steel was investigated (type 304 [78], type 430 [79], SUS 329J1 [80], AISI-316 [81]); however, the experiments did not include corrosion by hot formic acid vapors.

In addition to the immediate corrosive effect of formic acid, there is an additional danger of forming undesired side products from the reaction of formic acid with compounds in the exhaust gas. One possible side reaction is the formation of methanamide by a condensation with NH_3 [82]. Methanamide is considered to be teratogenic [83], though it must be noted that while some animal studies did show teratogenic effects [84], others (with different application doses) did not observe a teratogenic effect [85].

From methanamide hydrogen cyanide (HCN) can also be formed by the removal of another water molecule. As HCN is a very toxic compound, its emissions must be avoided, even though there is no immediate legal regulation on the concentration of HCN in internal combustion engine exhaust gas. The formation of HCN from methanamide will be discussed in more detail later.

16.3.3 Ammonium Carbamate

In order to avoid freezing issues altogether, solid precursor compounds are a good substitute for solutions of NH_3 precursor compounds. However, the handling of solid NH_3 precursors is more complicated, especially if they also need to be contacted with a decomposition catalyst like solid urea (as discussed in Sect. 16.2.1).

There are, however, also solid substances which do not need a catalyst to yield NH_3, and only need to be heated for NH_3 release. One compound in this category is ammonium carbamate. Ammonium carbamate is the ammonium salt of the instable carbamic acid, and it can be transformed to urea by a condensation of the salt [86]. Another compound which can be decomposed to yield NH_3 without a catalyst is ammonium carbonate [87]. However, ammonium carbonate stores less NH_3 per mass and volume, because it contains an additional molecule of water with respect to ammonium carbamate. In detail, ammonium carbamate stores 0.436 kg NH_3/kg (0.698 kg/L), while ammonium carbonate stores 0.354 kg NH_3/kg (0.531 kg/L).

The decomposition of ammonium carbamate or ammonium carbonate in order to yield NH_3 are both thought to proceed via a two-step reaction. For ammonium carbamate, the reaction proceeds as shown below via the instable carbamic acid [86].

$$NH_4COONH_2 \rightarrow NH_3 + HCOONH_2$$

$$HCOONH_2 \rightarrow NH_3 + CO_2$$

The decomposition of ammonium carbonate is considered to proceed via the stable ammonium bicarbonate intermediate [87].

$$(NH_4)_2CO_3 \rightarrow NH_3 + (NH_4)HCO_3$$

$$(NH_4)HCO_3 \rightarrow NH_3 + CO_2 + H_2O$$

In addition, the condensation of ammonium carbamate to yield urea and water can occur as the following side reaction [88].

$$NH_4COONH_2 \rightarrow NH_2CONH_2 + H_2O$$

As all the above reactions are also reversible, the repeated cycling between heating and cooling during the SCR system operation can lead to the presence of all the mentioned compounds in the storage tank. This can become an issue if H_2O condenses during cooling inside the tank, because it can lead to an uncontrolled production of NH_3 from ammonium carbamate and with it a sudden pressure increase in the storage tank [82]. This becomes relevant for the decomposition of ammonium carbonate, because H_2O is released, but commercial ammonium carbonate usually also contains ammonium carbamate as well [89].

As ammonium carbamate stores more NH_3, does not produce H_2O during decomposition and needs less heat for decomposition, it is preferred over ammonium carbonate. Despite the difficulties associated with the dynamically controlled decomposition of ammonium carbamate, the system was tested for commercial applications [90, 91]. A light-duty application on a 5.9 L Diesel engine was presented and the use of ammonium carbamate was protected by the name Solid SCR® [92].

However, until now, ammonium carbamate does not seem to be commercially applied as NH_3 precursor in mobile or stationary SCR applications.

16.3.4 Metal Ammine Chlorides

A completely different approach in storing NH_3 is the reversible coordination of NH_3 as a ligand to metal atoms [93]. Since the absorption of ammonia as a ligand is exothermic, and its release is endothermic, the idea is to first store NH_3 in metal ammine chlorides, so it can be later released by heating the salt. Salts of particular interest for NH_3 release are $Mg(NH_3)_6Cl_2$, $Ca(NH_3)_8Cl_2$ and $Sr(NH_3)_8Cl_2$, due to the high amount of NH_3 they can store [69]. Even though $CaCl_2$ and $SrCl_2$ would be advantageous compared to $MgCl_2$ because of their higher NH_3 storage capacity, these compounds are less attractive for practical applications. This is not because of economic considerations, but because of the high NH_3 vapor pressure exhibited by $Ca(NH_3)_8Cl_2$ and $Sr(NH_3)_8Cl_2$. The NH_3 vapor pressure of $Ca(NH_3)_8Cl_2$ at 25 °C is 630 mbar, and that of $Sr(NH_3)_8Cl_2$ is 550 mbar [94], both of which are rather high for handling or even storing in a sealed container, as there would be significant leakage of NH_3 in the case of a container rupture in an accident [95]. The storage and release of NH_3 into or from these salts is proceeding successively, with decreasing enthalpies of adsorption or desorption as the amount of coordinated NH_3 increases. The individual reactions for $MgCl_2$ are the following:

$$MgCl_{2(s)} + NH_{3(g)} \leftrightarrow Mg(NH_3)Cl_{2(s)} \qquad \Delta H_r = -87.0\ \text{kJ/mol}\ NH_3$$
$$Mg(NH_3)Cl_{2(s)} + NH_{3(g)} \leftrightarrow Mg(NH_3)_2Cl_{2(s)} \qquad \Delta H_r = -74.9\ \text{kJ/mol}\ NH_3$$
$$Mg(NH_3)_2Cl_{2(s)} + 4\ NH_{3(g)} \leftrightarrow Mg(NH_3)_6Cl_{2(s)} \qquad \Delta H_r = -55.6\ \text{kJ/mol}\ NH_3$$

All reactions are exothermic, but reaction enthalpies are different [96]. Using the Van't Hoff equation, the releasing temperature for NH_3 at a constant reservoir pressure of 1.5 bar can be calculated.

$$\ln P_{NH_3,eq} = \frac{-\Delta H_{r,k}}{RT} + \frac{\Delta S_{r,k}}{R}$$

The index k identifies the reaction of the NH_3 absorption or desorption process, R is the gas constant, T the temperature, $\Delta H_{r,k}$ the corresponding desorption enthalpy per mole NH_3 and $\Delta S_{r,k}$ the corresponding desorption entropy of the reaction. The calculated temperatures for release of the last 4 absorbed NH_3 molecules are 150 °C, 298 °C for the second, and 387 °C for the first molecule. From these calculated values, the full release of all six stored NH_3 molecules is impractical because of the high temperatures needed. This reduces the amount of practically stored NH_3 to two-thirds of the theoretical value. Another factor that reduces the amount of stored NH_3 is that a powder, and not a single crystal, is used. Typically void fraction of 45–50 % are present in the storage container, which not only decreases NH_3-storage capacity but also reduces heat transfer [95]. Since heat transfer is crucial for the dynamic release of NH_3 gas from the salt, the powder is compacted under high pressure [97]. Bulk densities of 97 % of the solid density can be achieved, approaching 93 % of the volumetric NH_3 storage capacity of liquefied NH_3 [95]. As the ammine salt releases NH_3 gas, its density is reduced and NH_3 gas diffusion is not hindered. When the salts are exhausted of NH_3, they can be recharged with NH_3. During absorption, the pressurized cylinders are first heated so that the NH_3 evenly distributes within the bulk material [98].

Recently, the Danish company Amminex announced the launch of a production part approval process for exchangeable cylinders filled with metal ammine salts for NH_3 storage, the total investment amounted to 50 million € [99]. Also, the US-based Navistar and French Faurecia invested in Amminex's technology, promising rapid utilization in mobile applications [100]. Interestingly, Amminex is using $SrCl_2$ rather than $MgCl_2$ as NH_3 absorbant, because it has the advantage of requiring only 80 °C for the release of seven molecules of NH_3 [101]. This can be achieved by using the engine coolant as heat source. The cartridges filled with charged $Sr(NH_3)_8Cl_2$ are not classified as dangerous goods, in spite of the 550 mbar of NH_3 vapor pressure present at 25 °C. During the operation, pressures of 6 bar are achieved in the cartridge, so there is a need for robust containers. So far, no comments have been made regarding the possibility of transporting the storage salt during NH_3 dosage onto the SCR catalyst. In this case the SCR catalyst could be deactivated due to its sensitivity toward earth-alkaline metals [102, 103]. In addition to the application as a NH_3 source for SCR, the cartridges are proposed as storage cylinders for NH_3 which will be converted to H_2 and used to power a fuel cell [104].

16.3.5 Methanamide

Analogous to urea being the condensation product of ammonium carbamate, methanamide (formamide) is the condensation product of ammonium formate. At ambient conditions (20 °C, 1 atm), methanamide is a liquid with a vapor pressure of 30 mbar and a melting point of 2 °C [105]. However, if mixed with water, an aqueous 80 % methanamide solution has a melting point of −28 °C, and remains stable at temperatures up to 100 °C [82]. This solution is known as Admide(R) and is also proposed as an NH_3 precursor for mobile applications. In addition to the excellent temperature stability, the solution with 0.30 kg/kg (0.33 kg/L) also stores 50 % more NH_3 than AdBlue® [14]. In contrast to urea, methanamide will molecularly vaporize without decomposition. Admide(R) was further determined to be biodegradable, but was also found to correlate with teratogenic effects in some animal tests [84], though not in all [85]. As the general perception of methanamide was that it indeed causes defects to the unborn child, the introduction of Admide(R) to the automotive market was cancelled [83]. Today's gasoline fuel contains up to 1 % (by volume) of benzene [106] also due to the substitution of lead-based anti-knocking agents, even though benzene is known as a teratogenic substance [107]. Therefore, the handling of Admide(R) solution by trained personnel during the regular service of a vehicle could be an option, considering the great advantages of using the solution.

Under certain conditions, such as overdosage of the reducing agent at low temperature, emissions of molecular methanamide rather than the decomposition products, can occur. Additionally, during decomposition methanamide also yields upon hydrolysis formic acid, which, as previously mentioned, is a corrosive compound. Decomposition of formic acid may either lead to CO and H_2O, or to CO_2 and H_2. Unfortunately, the preferred latter decomposition reaction products are not the main products, but rather CO and H_2O. Another possible reaction that occurs at very high temperatures during methanamide decomposition is the removal of water to yield HCN. As previously mentioned, there is no immediate legal regulation on the emission of HCN in exhaust gas, but due to the toxicity of the compound it should be avoided.

Currently, the use of Admide(R) as a NH_3 precursor solution is protected by MAN Truck & Bus [108], but seems not to be commercially used.

16.3.6 Guanidinium Salts

In urea, two amine groups are attached to a carbonyl moiety. If the carbonyl is replaced by an imine function, one obtains guanidine. Guanidine is an instable compound with one of the highest basicities for organic compounds. Both properties are driven by the stabilization of the guanidinium cation by three amine functions connected to the central carbon atom. Due to the symmetric structure, the guanidinium cation is a very stable compound in combination with an anion [109]. For the utilization of guanidinium salts in exhaust gas aftertreatment, small organic anions are preferred which decompose completely to gaseous products. The most promising compounds are therefore guanidinium carbonate, guanidinium hydrogen carbonate, guanidinium formate, and guanidinium oxalate. Besides the preference of CO_2 as decomposition product for the anion, the solubility of the salt in water is also an essential factor, which needs to be observed. Here, the solubility of guanidinium formate, with up to 6.19 kg dissolving in 1 L of water is unrivaled [110]. However, in order to achieve good thermal stability, significantly less salt is dissolved in water. An aqueous 60 % guanidinium formate solution can be stored for several months at a temperature of 60 °C, and can be supercooled to a temperature of −30 °C without freezing [111]. The low amount of water contained in the solution compared to AdBlue® is an advantage, because significantly less water needs to be evaporated by the hot exhaust gas [112]. In this solution, again, approximately 1.5 times the amount of NH_3 is stored compared to AdBlue®. However, due to the high stability of the compound, its catalytic decomposition below 200 °C is incomplete [14]. The decomposition of guanidinium carbonate and guanidinium bicarbonate is occurring at lower temperatures, but the solubility of the salt is much lower—not even the NH_3 storage capacity of AdBlue® is achieved, which makes it largely irrelevant [14].

The decomposition of guanidinium formate is best achieved on a dedicated hydrolysis catalyst, and since higher temperatures than those found in the exhaust gas pipe are needed, the decomposition in a side stream reactor with the possibility of external heating is preferred [14]. The conditions for the catalytic decomposition of guanidinium formate, including the necessary temperature, space velocity and catalyst material, were determined in the framework of a PhD thesis [113].

16.3.7 Catalytic Decomposition of Alternative NH_3 Precursor Compounds

Anatase TiO_2 is an excellent catalyst for HNCO hydrolysis [47, 50, 54] and for urea decomposition [10, 37]. In an early study of alternative ammonia precursor compounds, TiO_2 also showed promising results for the decomposition of guanidinium salts above 300 °C [14]. Interestingly, ZrO_2, which is even more active for HNCO hydrolysis than TiO_2, but sensitive to sulfur poisoning [54], showed only low guanidinium hydrolysis activity [14]. Unlike guanidinium formate, methanamide could also be decomposed fairly well under SCR conditions on a V_2O_5/WO_3-TiO_2 or on a Fe-ZSM5 catalyst around 250 °C [14]. However, depending on the temperature, there were concerns about incomplete decomposition, emission of corrosive formic acid and of toxic CO as well as HCN.

In the course of a recent research project, a novel TiO_2 supported Au catalyst was developed to enable the targeted decomposition of alternative NH_3 precursor compounds without side product formation. Due to the Au deposited (0.5–1.5 % by mass) on the hydrolysis catalyst TiO_2, formic acid derived side products such as formic acid, CO, methanamide or HCN are efficiently decomposed to CO_2 (and NH_3 if applicable), without any oxidation of the released NH_3 [113].

The Au/TiO_2 catalyst was also tested concerning its hydrothermal resistivity under authentic operating conditions and its behavior after modeled long-term poisoning by sulfur compounds. In all aging experiments, the catalyst performance even after severe treatment such as hydrothermal aging at up to 850 °C or 200 ppm of SO_2 in the gas feed still maintained acceptable activity for catalytic decomposition of NH_3 precursor compounds [113].

In case of 60 % guanidinium formate solution, temperatures around 250 °C were necessary for quantitative conversion to NH_3 and CO_2 at a gas hourly space velocity (GHSV) of 20,000 h^{-1}. The decomposition was, however, mainly limited by the hydrolysis activity of TiO_2, as formic acid could be decomposed to CO_2 even at just 130 °C.

An aqueous solution containing 80 % (by mass) methanamide could be converted to NH_3 and CO_2 in a temperature window ranging from 130 to 340 °C at a GHSV of 20,000 h^{-1} on a 1.0 % Au/TiO_2 catalyst, thereby outperforming state of the art SCR catalysts concerning the light-off temperature [113]. Further increasing of the space velocity in order to shrink the catalyst size, however, will result in higher light-off temperatures. Still, the low temperature requirements for quantitative decomposition enable the direct dosing of the NH_3 precursor solution into the main exhaust pipe. On the other hand, a side stream reactor concept with a very small decomposition catalyst would be feasible to provide a concentrated flow of NH_3 rich gas to the main exhaust gas flux.

Similar to methanamide, ammonium formate decomposition proceeded in a wide temperature window. As ammonium formate does in fact not need to be hydrolyzed, formic acid decomposition is the limiting reaction for the quantitative conversion of the precursor solution to NH_3 and CO_2. However, if mixtures with urea, such as Denoxium® are being used, the temperature needs to be sufficient to enable urea hydrolysis. Therefore, an in-pipe or side stream system equipped with an Au/TiO_2 hydrolysis catalyst could in fact be used to provide NH_3 from either AdBlue®, Denoxium® or Admide(R). This would enable the flexibility to ensure efficient NH_3 production, and, consequently, NO_x reduction, even in cold climates or during long refill intervals. Guanidinium formate solution would also be an optional NH_3 precursor solution for a side stream reactor if the reactor could be electrically heated at temperatures below 250 °C, but would not qualify for direct injection into the main exhaust pipe.

The multiple choices for NH_3 precursor solutions, and possibility to even use mixtures thereof, represent valuable advantages for the introduction of a dedicated hydrolysis catalyst based on Au/TiO_2.

References

1. Cichanowicz JE, Muzio LJ Twenty-Five (2001) Years of SCR Evolution: Implications For US Application And Operation. In: U.S EPA-DOE-EPRI, Chicago
2. Held W, König A (1986) Verfahren und Vorrichtung zur Reduktion von Stickoxiden. DE3,642,018
3. Perry RA, Siebers DL (1986) Rapid reduction of nitrogen oxides in exhaust gas streams. Nature 324(6098):657–658
4. Held W, König A, Puppe L (1988) Verfahren zur Reduktion von in Abgasen enthaltenen Stickoxiden mittels eines zeolithhaltigen Katalysators. DE3830045
5. Bowers WE (1988) Reduction of nitrogen-based pollutants through the use of urea solutions containing oxygenated hydrocarbon solvents. US Patent 4,719,092
6. Held W, König A, Richter T et al (1990) Catalytic NO_x Reduction in Net Oxidizing Exhaust Gas. SAE Technical Paper 900496
7. Jacob E (1990) Process and device for selective catalytic NO_x reduction in exhaust gases containing oxygen. EP487,886
8. Fromm D, Lützow D (1979) Moderne Verfahren der Großchemie: Harnstoff. Chem unserer Zeit 13(3):78–81
9. Koebel M, Elsener M, Kleemann M (2000) Urea-SCR: a promising technique to reduce NO_x emissions from automotive diesel engines. Catal Today 59(3–4):335–345
10. Lundström A, Snelling T, Morsing P et al (2011) Urea Decomposition and HNCO Hydrolysis Studied over Titanium dioxide, Fe-Beta and γ-Alumina. Appl Catal B 106:273–279
11. Eichelbaum M, Farrauto RJ, Castaldi MJ (2010) The impact of urea on the performance of metal exchanged zeolites for the selective catalytic reduction of NO_x: Part I. Pyrolysis and hydrolysis of urea over zeolite catalysts. Appl Catal B 97(1–2):90–97
12. Eichelbaum M, Siemer AB, Farrauto RJ et al (2010) The impact of urea on the performance of metal-exchanged zeolites for the selective catalytic reduction of NO_x: Part II. Catalytic, FTIR, and NMR studies. Appl Catal B 97(1–2):98–107
13. Fang HL, DaCosta HFM (2003) Urea thermolysis and NO_x reduction with and without SCR catalysts. Appl Catal B 46:17–34
14. Kröcher O, Elsener M, Jacob E (2009) A model gas study of ammonium formate, methanamide and guanidinium formate as alternative ammonia precursor compounds for the selective catalytic reduction of nitrogen oxides in diesel exhaust gas. Appl Catal B 88(1–2):66–82
15. ISO (2008) Diesel engines - NO_x reduction agent AUS 32 - Part 3: Handling, transportation and storage. vol ISO 22241–3
16. Weisweiler W, Buchholz F (2001) Fester Harnstoff als Ammoniakquelle für die katalysierte Stickstoffoxid-Minderung in Dieselabgasen nach dem SCR-Verfahren. Chem Ing Tech 73(7):882–887
17. Käfer S, Müller W, Herr A et al (2004) Vorrichtung und Verfahren zur Dosierung und Förderung von trockenem Harnstoff, insbesondere bei der Durchführung des SCR-Verfahrens in Kraftfahrzeugen. DE10,251,498A1
18. Müller W, Herr A, Käfer S et al (2004) SCR using solid urea. In: 3rd Internation Exhaust Gas and Particulate Emissions Forum, Sinsheim

19. Jacob E, Müller W, Herr A et al (2002) Vorrichtung zur Reduktion von Stickoxiden im Abgas von Brennkraftmaschinen. DE10,206,028
20. Dismon H, Lappan R, Nowak M et al (2006) Vorrichtung zur Reduktion von Stickoxiden im Abgas von Brennkraftmaschinen. DE102,006,004,170
21. Berliner JFT (1936) Crystal Urea: Industrial Development and Properties. Ind Eng Chem 28(5):517–522
22. ISO (2006) Diesel engines - NO_x reduction agent AUS 32 - Part 1: Quality requirements. vol ISO 22241–1
23. Thompson J, Op De Beeck J, Joubert E et al (2008) Case Studies of Urea SCR Integration on Passenger Cars Monitoring of Urea Inside the Tank During Hot and Cold Environment Test Missions. SAE Technical Paper 2008-01-1181
24. Gabrielsson PLT (2004) Urea-SCR in Automotive Applications. Top Catal 28(1):177–184
25. Granger P, Parvulescu VI (2011) Catalytic NO_x Abatement Systems for Mobile Sources: From Three-Way to Lean Burn after-Treatment Technologies. Chem Rev 111:3155–3207
26. Birkhold F, Meingast U, Wassermann P et al (2007) Modeling and simulation of the injection of urea-water-solution for automotive SCR DeNOx-systems. Appl Catal B 70(1–4):119–127
27. Ström H, Lundström A, Andersson B (2009) Choice of urea-spray models in CFD simulations of urea-SCR systems. Chem Eng J 150(1):69–82
28. Abu-Ramadan E, Saha K, Li X (2011) Modeling the depleting mechanism of urea-water-solution droplet for automotive selective catalytic reduction systems. AlChE J 57(11):3210–3225
29. Lundström A, Waldheim B, Ström H et al (2011) Modelling of urea gas phase thermolysis and theoretical details on urea evaporation. Paper presented at the Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering
30. Della Gatta G, Ferrq D (1987) Enthalpies of fusion and solid-to-solid transition, entropies of fusion for urea and twelve alkylureas. Thermochim Acta 122(1):143–152
31. Emel'yanenko VN, Kabo GJ, Verevkin SP (2005) Measurement and Prediction of Thermochemical Properties: Improved Increments for the Estimation of Enthalpies of Sublimation and Standard Enthalpies of Formation of Alkyl Derivatives of Urea. J Chem Eng Data 51(1):79–87
32. Ferro D, Barone G, Della Gatta G et al (1987) Vapour pressures and sublimation enthalpies of urea and some of its derivatives. J Chem Thermodyn 19(9):915–923
33. Wang TJ, Baek SW, Lee SY et al (2009) Experimental investigation on evaporation of urea-water-solution droplet for SCR applications. AIChE J 55(12):3267–3276
34. Ebrahimian V, Nicolle A, Habchi C (2012) Detailed modeling of the evaporation and thermal decomposition of urea-water solution in SCR systems. AIChE J 58:1998–2009
35. Schmidt A (1966) Herstellung von Melamin aus Harnstoff bei Atmosphärendruck. Chem Ing Tech 38(11):1140–1144
36. Schaber PA, Colson J, Higgins S et al (2004) Thermal decomposition (pyrolysis) of urea in an open reaction vessel. Thermochim Acta 424(1–2):131–142
37. Bernhard AM, Peitz D, Elsener M et al (2012) Hydrolysis and thermolysis of urea and its decomposition byproducts biuret, cyanuric acid and melamine over anatase TiO_2. Appl Catal B 115–116:129–137
38. Lundström A, Andersson B, Olsson L (2009) Urea thermolysis studied under flow reactor conditions using DSC and FT-IR. Chem Eng J 150 (2–3):544–550
39. Bernhard AM, Czekaj I, Elsener M et al (2011) Evaporation of Urea at Atmospheric Pressure. J Phys Chem A 115(12):2581–2589
40. Krasulin AP, Kozyro AA, Kabo GY (1987) Saturation vapor pressure of urea in the temperature range 329–403 K. J Appl Chem USSR 60 (1 pt 1):96–99
41. Langer J, Schrader B, Bastian V et al (1995) Infrared-spectra and force-constants of urea in the gaseous-phase. Fresenius J Anal Chem 352(5):489–495
42. Bernhard AM, Peitz D, Elsener M et al (2013) Quantification of gaseous urea by FTIR spectroscopy and its application in catalytic urea thermolysis. Top Catal 56:130–133

43. Kontin S, Höfler A, Koch R et al (2010) Heat and Mass Transfer accompanied by Crystallisation of single Particles containing Urea-water-solution. In: 23rd Annual Conference on Liquid Atomization and Spray Systems, Brno
44. Bernhard AM, Czekaj I, Elsener M et al (2013) Adsorption and catalytic thermolysis of gaseous urea on anatase TiO_2 studied by HPLC analysis, DRIFT spectroscopy and DFT calculations. Appl Catal B 134–135:316–323
45. Hauck P, Jentys A, Lercher JA (2007) On the quantitative aspects of hydrolysis of isocyanic acid on TiO_2. Catal Today 127:165–175
46. Dong H, Shuai S, Wang J (2008) Effect of Urea Thermal Decomposition on Diesel NO_x-SCR Aftertreatment Systems. SAE Technical Paper 2008-01-1544
47. Hauck P, Jentys A, Lercher JA (2007) Surface chemistry and kinetics of the hydrolysis of isocyanic acid on anatase. Appl Catal B 70(1–4):91–99
48. Piazzesi G, Kröcher O, Elsener M et al (2006) Adsorption and hydrolysis of isocyanic acid on TiO_2. Appl Catal B 65(1–2):55–61
49. Czekaj I, Kröcher O (2009) Decomposition of Urea in the SCR Process: Combination of DFT Calculations and Experimental Results on the Catalytic Hydrolysis of Isocyanic Acid on TiO_2 and Al_2O_3. Top Catal 52(13):1740–1745
50. Kleemann M, Elsener M, Koebel M et al (2000) Hydrolysis of isocyanic acid on SCR catalysts. Ind Eng Chem Res 39(11):4120–4126
51. Piazzesi G, Devadas M, Kröcher O et al (2006) Isocyanic acid hydrolysis over Fe-ZSM5 in urea-SCR. Catal Commun 7(8):600–603
52. Zhan Z, Müllner M, Lercher JA (1996) Catalytic hydrolysis of s-triazine compounds over Al_2O_3. Catal Today 27(1–2):167–173
53. Czekaj I, Kröcher O, Piazzesi G (2008) DFT calculations, DRIFT spectroscopy and kinetic studies on the hydrolysis of isocyanic acid on the TiO_2-anatase (1 0 1) surface. J Mol Catal A 280(1–2):68–80
54. Piazzesi G (2006) The Catalytic Hydrolysis of Isocyanic Acid (HNCO) in the Urea-SCR Process. Dissertation No. 16693, ETH Zurich
55. Larrubia MA, Ramis G, Busca G (2000) An FT-IR study of the adsorption of urea and ammonia over V_2O_5-MoO_3-TiO_2 SCR catalysts. Appl Catal B 27(3):L145–L151
56. Bernhard AM, Peitz D, Elsener M et al (2013) Catalytic urea hydrolysis in the selective catalytic reduction of NO_x: Catalyst screening and kinetics on anatase TiO_2 and ZrO_2. Catal Sci Technol 3(4):942-951
57. Peitz D, Bernhard A, Elsener M et al (2011) Laboratory test reactor for the investigation of liquid reducing agents in the selective catalytic reduction of NO_x. Rev Sci Instrum 82(8):084101
58. Bernhard AM (2012) Urea evaporation and catalytic urea decomposition in the selective catalytic reduction of NO_x. Dissertation No. 20813, ETH Zurich
59. Wada Y, Yamatsuta K (1977) Treating exhaust gases contg. nitrogen oxide(s) - by adding granules of cyanuric acid, urea or ammonium cpd., and an organic cpd. having nitrile gp. JP54,028,771
60. Perry RA (1985) Kinetics of the reactions of NCO radicals with H_2 and NO using laser photolysis–laser induced fluorescence. J Chem Phys 82:5485–5488
61. Gardner-Chavis RA, May MP (1990) Catalytic decomposition of cyanuric acid and use of product to reduce nitrogen oxide emissions. US5,087,431
62. Perry RA (1987) System for NO reduction using sublimation of cyanuric acid. US4,800,068
63. Siebers DL, Caton JA (1990) Removal of nitric oxide from exhaust gas with cyanuric acid. Combust Flame 79(1):31-46
64. Caton JA, Siebers DL (1989) Comparison of Nitric Oxide Removal by Cyanuric Acid and by Ammonia. Combust Sci Technol 65(4–6):277–293
65. Mao FF, Li CG (2000) Urea-Ethanol-Water Solution Properties for Diesel NOx Control Using Urea. In: Presentations of the 6th Diesel Engine Emissions Reduction (DEER) Workshop, San Diego

66. Lambert C, Montreuil C, Vanderslice J (2003) Application of Organic Freeze-Point Depressants in Aqueous Urea Solutions: Effect on NO_x Reduction. SAE Technical Paper 2003-01-0775
67. Solla A, Westerholm M, Söderström C et al (2005) Effect of Ammonium Formate and Mixtures of Urea and Ammonium Formate on Low Temperature Activity of SCR Systems. SAE Technical Paper 2005-01-1856
68. Lyon RK (1973) Method for the reduction of the concentration of NO in combustion effluents using ammonia. US3,900,554
69. Marko A, Wahl T, Alkemade U et al (1997) Verfahren und Vorrichtung zur selektiven katalytischen NO_x-Reduktion. DE19,728,343
70. Koebel M, Elsener M (1998) Oxidation of Diesel-Generated Volatile Organic Compounds in the Selective Catalytic Reduction Process. Ind Eng Chem Res 37(10):3864–3868
71. Nissinen T, Kukkonen J (2004) Catalytic process for reducing nitrogen oxides in flue gases and reducing agent composition. FI2,004,000,057
72. Highfield T (2011) Lower Freezing DEF For Higher NO_x Reduction Attainment. In: Presentations of the Directions in Engine-Efficiency and Emissions Research (DEER) Conference, Detroit
73. Savara A, Li MJ, Sachtler WMH et al (2008) Catalytic reduction of NH_4NO_3 by NO: Effects of solid acids and implications for low temperature DeNOx processes. Appl Catal B 81(3–4):251–257
74. Lee SY, Baek SW (2011) Experimental Study on Evaporation Characteristics of Ammonium Formate-Urea-Water Solution Droplet for Selective Catalytic Reduction Applications. Ind Eng Chem Res 50(13):8285–8294
75. Gassen R, Göhr H, Müller N et al (1986) Korrosion in Carbonsäuren Teil II: Das Korrosionsverhalten hochlegierter Stähle, zweier Nickellegierungen und von Titan in Ameisensäure. Materialwiss Werkstofftech 17(6):218–225
76. Singh MM, Gupta A (1996) Corrosion behaviour of mild steel in formic acid solutions. Mater Chem Phys 46(1):15–22
77. Singh SK, Mukherjee AK, Singh MM (2011) Kinetics of mild steel corrosion in aqueous formic acid solutions. Can Metall Quart 50:186–194
78. Sekine I, Chinda A (1984) Comparison of the Corrosion Behavior of Pure Fe, Ni, Cr, and Type 304 Stainless Steel in Formic Acid Solution. Corrosion 40:95–100
79. Sekine I, Hatakeyama S, Nakazawa Y (1987) Corrosion behaviour of type 430 stainless steel in formic and acetic acids. Corros Sci 27:275–288
80. Sekine I, Momoi K (1988) Corrosion Behavior of SUS 329J1 Stainless Steel in Formic Acid Solution. Corrosion 44:136–142
81. Sekine I, Masuko A, Senoo K (1987) Corrosion Behavior of AISI 316 Stainless Steel in Formic and Acetic Acid Solutions. Corrosion 43:553–560
82. Kröcher O, Elsener M, Jacob E (2008) Neue Reduktionsmittel für die Low-NO_x-SCR-Technik/New reducing agents for the low-NO_x SCR technology. In: Proceedings of the 5th International Exhaust Gas and Particulate Emissions Forum, Ludwigsburg
83. Kennedy GL (2001) Biological effects of acetamide, formamide, and their mono and dimethyl derivatives: an update. Crit Rev Toxicol 31:139–222
84. Dresser TH, Rivera ER, Hoffmann FJ et al (1992) Teratogenic assessment of four solvents using the Frog Embryo Teratogenesis Assay–Xenopus (FETAX). J Appl Toxicol 12:49–56
85. Fail PA, George JD, Grizzle TB et al (1998) Formamide and dimethylformamide: reproductive assessment by continuous breeding in mice. Reprod Toxicol 12(3):317–332
86. Ramachandran BR, Halpern AM, Glendening ED (1998) Kinetics and Mechanism of the Reversible Dissociation of Ammonium Carbamate: Involvement of Carbamic Acid. J Phys Chem A 102(22):3934–3941
87. Fulks G, Fisher G, Rahmoeller K et al (2009) A Review of Solid Materials as Alternative Ammonia Sources for Lean NO_x Reduction with SCR. SAE Technical Paper 2009-01-0907
88. Irazoqui HA, Isla MA (1993) Simulation of a Urea Synthesis Reactor - 2. Reactor Model. Ind Eng Chem Res 32:2671–2680

89. Sclar CB, Carrison LC (1963) Phase Composition of Commercial “Ammonium Carbonate”. Science 140:1205–1207
90. Krüger M, Nisius P, Scholz V et al (2003) A Compact Solid SCR System for NO_x Reduction in Passenger Cars and Light Duty Trucks. MTZ Worldwide Edition 2003-06
91. Tatur M, Tomazic D, Lacin F et al (2009) Solid SCR Demonstation Truck Application. In: Directions in Engine-Efficiency and Emissions Research Conference, Dearborn
92. Lacin F, Kotrba A, Hayworth G et al (2011) SOLID SCR®: Demonstrating an Improved Approach to NO_x Reduction via a Solid Reductant. SAE Technical Paper 2011-01-2207
93. Lepinasse E, Spinner B (1994) Cold production through coupling of solid-gas reactors I: Performance analysis. Int J Refrig 17(5):309–322
94. Vegge T, Sørensen RZ, Klerke A et al (2008) Indirect Hydrogen Storage in Metal Ammines, Part 4: Chemically Bound Hydrogen Storage. In: Solid-State Hydrogen Storage: Materials and Chemistry, Woodhead Publishing Limited, Cambrige, pp 533–564
95. Elmøe TD, Sørensen RZ, Quaade U et al (2006) A high-density ammonia storage/delivery system based on $Mg(NH_3)_6Cl_2$ for SCR-DeNOx in vehicles. Chem Eng Sci 61(8):2618–2625
96. Liu CY, Aika K-I (2004) Ammonia Absorption on Alkaline Earth Halides as Ammonia Separation and Storage Procedure. B Chem Soc Jpn 77:123–131
97. Johannessen T, Christensen CH, Norskov JK et al (2005) High density storage of ammonia. WO2,006,081,824
98. Johannessen T, Schmidt H, Svagin J et al (2008) Ammonia Storage and Delivery Systems for Automotive NO_x Aftertreatment. SAE Technical Paper 2008-01-1027
99. Johannessen T (2011) Next generation SCR system for fuel-efficient NO_x reduction. In: IQPC Conference Selective Catalytic Reduction, Wiesbaden
100. Navistar (2009) Navistar to Invest in Danish Technology Company. http://media.navistar.com/index.php?s=43&item=343. Accessed 10 Feb 2014
101. Johannessen T (2010) Compact ammonia storage systems for fuelefficient NO_x emissions reduction. In: CTI conference on SCR Systems, Stuttgart
102. Nicosia D, Czekaj I, Kröcher O (2008) Chemical deactivation of V_2O_5/WO_3-TiO_2 SCR catalysts by additives and impurities from fuels, lubrication oils, and urea solution: Part II. Characterization study of the effect of alkali and alkaline earth metals. Appl Catal B 77:228–236
103. Tang F, Xu B, Shi H et al (2010) The poisoning effect of Na^+ and Ca^{2+} ions doped on the V_2O_5/TiO_2 catalysts for selective catalytic reduction of NO by NH_3. Appl Catal B 94:71–76
104. Christensen CH, Sørensen RZ, Johannessen T et al (2005) Metal ammine complexes for hydrogen storage. J Mater Chem 15:4106–4108
105. Koebel M (1999) Comparative Study on the Use of Various Selective Reducing Agents in Automotive DeNOx Systems.
106. Smeets PJ, Meng Q, Corthals S et al (2008) Co-ZSM-5 catalysts in the decomposition of N_2O and the SCR of NO with CH_4: Influence of preparation method and cobalt loading. Appl Catal B 84(3–4):505–513
107. Gist GL, Burg JR (1997) Benzene - a review of the literature from a health effects perspective. Toxicol Ind Health 13(6):661–714
108. Jacob E (2005) Ammoniakvorläufersubstanz und Verfahren zur selektiven katalytischen Reduktion von Stickoxiden in sauerstoffhaltigen Abgasen von Fahrzeugen. DE102,005,059,250
109. Günther T, Mertschenk B, Schulz B (2006) Guanidine and derivatives. In: Ullmann’s Encyclopedia of Industrial Chemistry. Wiley-VCH, Weinheim, pp 175–188
110. Gerhart C (2011) NO_x-Reduzierung im motorischen Abgas mit Guanidinsalzen (NORA), Report No. NAZ-823-08, Bavarian Research Foundation
111. Kröcher O, Elsener M, Glückert U et al (2008) Guanidiniumformiat als neues Reduktionsmittel für die Low-NO_x-SCR-Technik. In: Proceedings of the 2nd Conference MinNOx - Minimization of NO_x Emissions Through Exhaust Gas Aftertreatment, Berlin

112. Koebel M, Strutz EA (2003) Thermal and hydrolytic decomposition of urea for automotive selective catalytic reduction systems: Thermochemical and practical aspects. Ind Eng Chem Res 42(10):2093–2100
113. Peitz D (2012) Investigation on the catalytic decomposition of guanidinium formate, ammonium formate and methanamide as NH_3-precursors for the selective catalytic reduction of NO_x. Dissertation No. 20568, ETH Zurich