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ORIGINAL PAPER

# Quantification of Gaseous Urea by FT-IR Spectroscopy and Its Application in Catalytic Urea Thermolysis

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**Abstract** An analysis method was developed for the quantification of gaseous urea in model exhaust gases by FT-IR spectroscopy. The method was applied for the investigation of the catalytic thermolysis of urea, which is used as ammonia storage compound in the selective catalytic reduction of $NO_x$ in diesel engines.

**Keywords** FT-IR spectroscopy · Gaseous urea · Catalytic urea thermolysis · Urea-SCR

## 1 Introduction

Aqueous urea solution is widely used as a safe $NH_3$ storage compound for the selective catalytic reduction of $NO_x$ (urea-SCR) [1]. Urea decomposes in the hot exhaust gas after-treatment system according the overall reaction Eq. (1):

$$CO(NH_2)_2 + H_2O \rightarrow 2\ NH_3 + CO_2 \quad (1)$$

The first decomposition step is the thermolysis of urea to $NH_3$ and HNCO Eq. (2):

$$CO(NH_2)_2 \rightarrow NH_3 + HNCO \quad (2)$$

Due to the continuing trend for lower exhaust temperatures, urea decomposition is becoming increasingly difficult to accomplish. The importance of urea decomposition in the urea-SCR process raises the need for measuring unreacted urea in the gas phase. One known method involves a liquid-quench of the exhaust gas mixture to absorb urea, followed by HPLC analysis of the quenching solution [2]. The HPLC method also enables the quantification of urea decomposition byproducts with high molecular weight like cyanuric acid [2, 3]. On the other hand, HPLC is not an online method.

FT-IR spectroscopy is a widespread online method for gas analysis in exhaust gas aftertreatment [1, 4]. Provided that the spectrometer is carefully calibrated, a wide range of compounds with low molecular weight, including $CO_x$, $NO_x$, $NH_3$, HCN and HNCO, can be quantified simultaneously. However, to the extent of our knowledge no FT-IR spectroscopy method is available for the quantification of urea in the gas phase.

FT-IR spectra of gaseous urea have been reported in the literature for both, vacuum [5] and atmospheric pressure [3] conditions. Since urea has a rather low vapor pressure [3, 6, 7] and a limited stability [8–10], its quantification in the gas phase is a challenging task. However, previous results in our group on urea evaporation show that gaseous urea is more stable than expected and that an FT-IR spectrum of urea can be recorded at atmospheric pressure [3], which motivated us to develop an FT-IR spectroscopy method for the quantification of urea. We were able to integrate urea in a multi-component FT-IR spectroscopy method, which allows the online analysis of urea in model exhaust gases.

The suitability of the new method was demonstrated by a catalyst screening for urea thermolysis. Urea thermolysis Eq. (2) is generally considered to be a non-catalytic reaction [11], but scattered information in the literature about the behavior of urea on catalysts suggests catalytic urea thermolysis [12–15]. In this study, we report about steady-state experiments, which clearly show that urea thermolysis is a catalyzed reaction. A more detailed study of catalytic urea decomposition, including urea hydrolysis, was previously published elsewhere [16].

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## 2 Experimental

### 2.1 Catalyst Samples

Urea solutions were prepared by dissolving solid urea (Merck, ≥99.5 % purity) in ethanol (Merck, ≥99.9 % purity). Catalyst-coated cordierite monoliths with 600 cells per square inch (cpsi) were prepared as described in [17], using the catalysts shown in Table 1. For coating of the cordierite monoliths all catalysts were suspended in de-ionized water, except $TiO_2$, which was suspended in diluted $NH_3$ solution.

### 2.2 Setup

Experiments were carried out using the lab-scale setup described in [18]. Urea solution was constantly dosed into a tubular glass reactor by a gas-assisted spray nozzle. The catalyst-coated cordierite monoliths were directly fitted into the reactor, 9 cm downstream of the urea spray nozzle. A reactor with an inner diameter of 20.4 mm was used to measure the fast catalytic urea thermolysis at a high gas hourly space velocity (GHSV) of 91,000 $h^{-1}$. The reactor exit was open to atmospheric pressure. From the total gas flow of 500 L/h at standard temperature and pressure (STP: 0 °C, 1,013 hPa), 180 L/h at STP were extracted for gas analysis by FT-IR spectroscopy. The constant and aerosol-free gas flow was provided by a membrane gas pump (KNF Neuberger N 012 ST.26 E), followed by a PTFE membrane filter with 5 μm pore diameter (Sartorius). In order to avoid condensation of corrosive and sticky gases like water vapor, $NO_x$ and $NH_3$, the filter and all tubes, made of stainless steel, were heated to 170 °C. The gas pump and the FT-IR gas cell were heated to 180 °C. Since urea can on one side easily condensate at low temperatures and on the other side decompose at too high temperatures, the experimental conditions described in Ref. [18] had to be optimized for urea gas phase analysis: The reactor exit was heated to 170 °C instead of 220 °C, the extraction capillary was heated to 150 °C instead of 190 °C and the glass wool condenser was removed. To maintain a gas flow of 180 L/h at STP for gas analysis, a stainless steel tube with an outer diameter of 3 mm and an additional restriction was used at the entrance of the extraction capillary to provide the necessary pressure drop.

**Table 1** Catalysts

| Material | Producer, product name | BET surface ($m^2$/g) | Considered $p/p_0$ |
|---|---|---|---|
| Anatase $TiO_2$ | Crystal global, DT-51 | 89 | 0.05–0.3 |
| $ZrO_2$ | MEL chemicals, XZO881 | 67 | 0.05–0.3 |
| $Al_2O_3$ | Condea, disperal S | 200 | 0.05–0.3 |
| H-ZSM-5 | Süd-chemie, H-MFI 27 | 420 | 0.01–0.1 |
| $SiO_2$ | Davison catalysts, davicat® SI 1452 | 380 | 0.05–0.3 |

Gaseous reaction products of low molecular weight were analyzed with an Antaris IGS FT-IR spectrometer from ThermoFisher equipped with a 2 m multi-path gas cell (V = 240 mL) and a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. The temperature of the gas cell was kept at 180 °C in order to not compromise the validity of the existing quantification method. The Quant-pad-software (Version 6.1, ThermoNicolet), which is designed for the development of multi-component gas analysis methods allowing for correction of cross-sensitivities between the gas components, was used for quantification of the compounds NO, $NO_2$, $N_2O$, $NH_3$, $H_2O$, CO, $CO_2$, HNCO, formic acid, HCN, formaldehyde, methanamide and $HNO_3$ [18] and was extended in this study with the components urea and ethanol. For both, the FT-IR measurements and the method calibration, the spectral resolution was 0.5 $cm^{-1}$ and 64 spectrometer scans were averaged, resulting in a time resolution of 75 s.

### 2.3 Urea Calibration

The experimental setup described above was used to record urea spectra when spraying a solution of 4 wt% urea in ethanol into the empty reactor. Ethanol was chosen as solvent instead of water, because water exhibits very strong and broad absorption bands, which interfere much more with the urea infrared signals than ethanol (Fig. 1a). To obtain a gas mixture containing 100 ppm of gaseous urea, the urea solution was dosed at a rate of 70.4 μL/min into a gas flow of 10 % $O_2$ in $N_2$ (500 L/h at STP). The reactor was heated to 170 °C, which induced complete evaporation of the urea solution. According to the saturation vapor pressure of urea [3, 7], a temperature of only 116 °C should have been sufficient to achieve evaporation of 100 ppm urea. The need for higher temperatures may have been due to heat transfer limitations in the spray. At the moderate temperatures applied (≤180 °C), most of the dosed urea remained unreacted till the exit of the FT-IR gas cell. We did not test urea concentrations above 100 ppm to limit the risk of deposits of urea decomposition byproducts on the windows or the mirrors of the gas cell.

Reference spectra of urea were recorded at six logarithmically equidistant concentrations in the range of 14–100 ppm by varying the dosing rate of the urea solution, while keeping constant the gas flow and the reactor temperature. The measured spectra were corrected by subtracting the spectra of ethanol, $NH_3$ and water. HNCO and $CO_2$ spectra were not subtracted because their absorption bands do not interfere with those of urea.

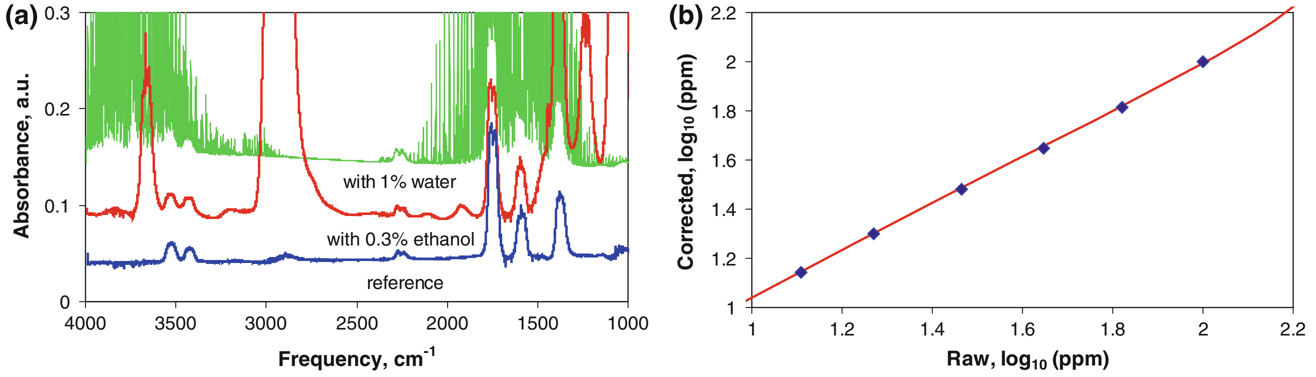

**Fig. 1** **a** FT-IR spectra of 100 ppm urea after subtraction of ethanol, $NH_3$ and water (*blue*); raw spectrum with 0.3 % ethanol before any subtraction (*red*); raw spectrum with 1 % water (*green*). **b** Calibration curve for urea, plotted at a double logarithmic scale

Figure 1a shows the corrected reference spectrum of 100 ppm urea and two raw spectra for comparison.

Using the highest absorption peak of urea for quantification (1,700–1,840 $cm^{-1}$), a calibration curve was calculated using a 3rd order polynom, forced through the intercept. The calibration curve (Fig. 1b) was close to linear and the average error was 1.4 %. The method was not used to measure urea concentrations higher than 100 ppm. Ethanol was quantified at 2,550–3,100 $cm^{-1}$.

A significant drawback of the method was the cross-sensitivity of water on urea, which could not be completely eliminated by the multi-component correction of the Quantpad-software, causing too low urea concentrations. Therefore, we calculated corrections for water concentrations of 3, 5 and 8 % using well-defined linear regression lines. At 5 % water concentration, the correction formula was $y = 1.13x + 3.65$, where $x$ = measured urea concentration (ppm). The presence of water did not only change the measured urea concentration but also induced scattering. At 5 % water concentration, the detection limit for urea was roughly 10 ppm (estimate, based on comparison with HPLC results).

## 3 Results and Discussion

The new FT-IR spectroscopy method was applied to water-free urea thermolysis experiments. Under these conditions, urea decomposes according to Eq. (2) to $NH_3$ and HNCO, which does not hydrolyze further due to the absence of water. Please note that under the humid conditions in real exhaust gas, HNCO will rapidly hydrolyze to $NH_3$ and $CO_2$ [11, 19, 20].

Figure 2a shows catalytic urea thermolysis into $NH_3$ and HNCO. When urea solution was sprayed into the empty reactor, only little urea conversion was observed (dashed line in Fig. 2a). The high HNCO yields obtained with the different catalyst-coated monoliths strongly indicate catalytic thermolysis.

The urea slip, measured by the new FT-IR spectroscopy method (Fig. 2b) was in good agreement with the corresponding values measured by HPLC (not shown). By summing up the HNCO, urea and $CO_2$ amounts ($CO_2$ mostly <5 % due to hydrolysis by unavoidable water traces), the carbon balance could be usually closed within 4 % accuracy (not shown).

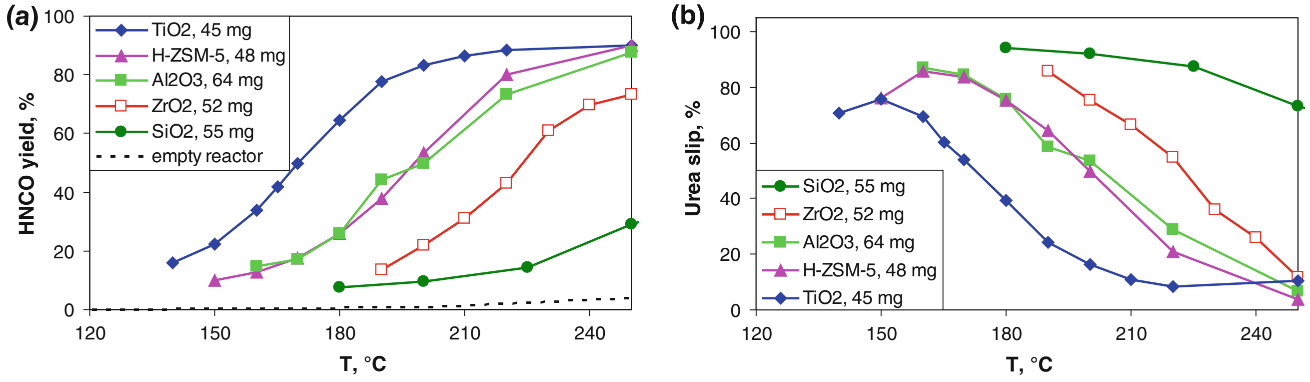

**Fig. 2** Catalytic urea thermolysis with 100 ppm urea in the gas phase. Gas composition: 0.3 % ethanol, 10 % $O_2$ in $N_2$. Total gas flow = 500 L/h at STP. GHSV = 91,000 $h^{-1}$. Gas analysis by FT-IR spectroscopy

Other products could not be found in the FT-IR spectra even at high magnification, excluding side-reactions due to the presence of ethanol. Moreover, if condensation of ethanol to diethyl ether had occurred, higher $CO_2$ yield would have been found due to water released by the condensation reaction.

## 4 Conclusions

Urea was successfully integrated into a multi-component FT-IR spectroscopy method. Urea concentrations up to 100 ppm could be reliably analyzed with the new method in water-free experiments on catalytic urea thermolysis. The observed urea thermolysis activities were in the order $TiO_2 > \text{H-ZSM-5} \approx Al_2O_3 > ZrO_2 > SiO_2$. When applying a cross sensitivity correction for water, the method also proved useful for the analysis of humid product gases. With additional efforts for temperature optimization and downscaling of void volumes, significantly higher urea concentration may become accessible while keeping urea decomposition insignificant. The volume of the FT-IR gas cell may be largely decreased by using the cell design presented in [21].

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