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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

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ABSTRACT

Urea-SCR over metal exchanged zeolites is one of the leading catalytic technologies to abate NO_x emissions in diesel exhaust. Ideally, urea injected into the diesel exhaust upstream of the SCR catalyst decomposes only to the gaseous products CO_2 and NH_3, where the latter gas can react with NO_x emissions to form harmless N_2 and H_2O. However, solid by-products can be formed as well, and if deposited on the catalyst harm the long-term catalytic performance. In order to identify the impact of various urea decomposition products on the catalytic activity, we studied the pyrolysis and hydrolysis of neat urea and of urea over different zeolites (H-Y, Cu-Y, H-Beta, Na-Beta, and Fe-Beta). The experiments were run in dry and steam-containing N_2 between 20 and 750 °C by using simultaneous thermogravimetric analysis (TGA), differential thermoanalysis (DTA), and online GC/MS evolved gas analysis. Solid intermediate products at different decomposition temperatures were identified by means of ATR-FTIR and luminescence spectroscopy. As for neat urea, CO_2, NH_3 and HNCO could be detected as major gaseous products. At 270 °C significant amounts of cyanuric acid and ammelide and at 500 °C of melem and melon were identified as solid intermediates. Above 625 °C, all solid residues decomposed to cyanogen and isocyanic acid. Furthermore, it could be shown clearly that the investigated zeolites significantly accelerate the pyrolysis of urea and cyanuric acid, and the hydrolysis of HNCO, by shifting the decomposition processes to lower temperatures and by inhibiting the formation of solid by-products. In addition, the presence of steam in the feed gas can prevent even further the formation of solid residues and the high temperature adsorption of gaseous products.

1. Introduction

Diesel engines are an attractive alternative to gasoline internal combustion engines because they operate with high compression ratios and lean air–fuel mixtures making them 20–40% more fuel efficient. However, due to the large amounts of excess air in the exhaust the gaseous, liquid, and solid emissions cannot be abated by simply using the three-way catalyst strategy of gasoline cars [1–3]. The simultaneous abatement of both nitrogen oxides (NO_x) and particulate matter is challenging, a problem that apparently cannot be solved by improved engine management alone [3]. NO_x causes ground level ozone (smog), induces the formation of toxic chemicals as well as acid rain, and it is therefore regulated in the U.S. by the Environmental Protection Agency (EPA). As NO_x standards are becoming more stringent for diesel motor vehicles under the EPA Tier 2 program as well as under EURO V and VI regulations in Europe, and since there is a trade-off between low NO_x emissions and low fuel consumption, the need for NO_x abatement technology is growing [1,2,4].

In power plants and stationary sources, selective catalytic reduction (SCR) by NH_3, which transforms NO_x into harmless N_2 and water vapor, has already proven itself for the successful reduction of NO_x emissions in flue gases [5,6]. Furthermore, the installation of a powerful catalytic NO_x abatement technology can reduce diesel fuel consumption by as much as 7% by allowing the engine to be optimized on fuel economy [4]. Thus, a successful implementation of SCR in diesel cars and trucks bears the potential for building vehicles that emit not only less NO_x, but generate significantly less of the greenhouse gas CO_2 as well.

Since NH_3 is a reactive and toxic gas it is proposed to use an aqueous urea solution containing 32.5% by weight (wt.%) urea (also

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referred to as AdBlue®) as the NH_3 source for SCR in transportation applications due to its non-toxicity and the ability to be carried on board much more easily and safely [3,4,7,8]. For stationary sources and originally also for mobile diesel applications vanadia-based catalysts have been used as NH_3-SCR catalysts [5]. However, the low activity at low temperatures, the low selectivity at high temperatures, and the problems associated with the release of toxic vanadium during operation have triggered many research activities to find better urea-SCR catalysts for mobile diesel applications. Metal-exchanged zeolites such as copper- and iron-based ZSM-5 [3,9–11] show very high activities and selectivities towards urea-SCR over a broad temperature range. Fe-exchanged BEA zeolites have superior SCR activities even outperforming typical vanadia on anatase catalysts [12].

After the injection of urea solution into the hot diesel exhaust upstream of the catalyst water evaporates and urea decomposes first into equimolar amounts of gaseous NH_3 and isocyanic acid (HNCO) [8,13–16].

$$NH_2\text{–}CO\text{–}NH_2(aq) \rightarrow NH_3(g) + HNCO(g) + xH_2O. \qquad (1)$$

In a subsequent reaction HNCO has to react with water forming NH_3 and CO_2[8,13–16].

$$HNCO(g) + H_2O \rightarrow NH_3(g) + CO_2(g). \qquad (2)$$

However, reaction (2) is rather slow at typical diesel exhaust temperatures, and thus demands an additional hydrolysis catalyst. Fortunately, common oxide catalysts used for SCR can catalyze this reaction making a hydrolysis catalyst redundant [17–19].

However, it has been reported that solid components such as cyanuric acid (CyA), ammelide, ammeline or melamine can be formed during urea pyrolysis, too [13,14,16,20,21]. White or pale beige precipitates were even identified on SCR catalysts subsequent to engine or lab reactor tests with urea injection [14,22,23]. Furthermore, Cheng et al. and Xu et al. simulated the urea decomposition on SCR catalysts by spraying aqueous urea solution on monolithic Cu-exchanged zeolites followed by a hydrothermal treatment at temperatures above 700 °C and observed a diminished SCR activity [23,24]. The urea-induced deactivation of the catalyst was beyond that found by hydrothermal aging alone. The formation of unwanted by-products could not only decrease the amount of NH_3 formed by urea decomposition, but could also poison the SCR catalyst and thus could significantly decrease its lifetime. Heavy-duty diesel vehicles must fulfill the NO_x emission standards even after much more than 400,000 miles of driving. Consequently, even a slight negative impact of urea might seriously affect the catalytic performance after such long operation times. Hence, the detailed investigation of the urea decomposition on SCR catalysts is required to understand any possible catalyst deactivation mechanisms and to develop strategies preventing a negative influence of urea for the long-term performance of diesel SCR catalysts for optimum NO_x abatement. So far only the effect of vanadia-based catalysts on urea decomposition was studied [14], whereas the impact of zeolite-based SCR catalysts has to the best of our knowledge not been thoroughly investigated yet.

We studied the decomposition of neat urea and of urea/zeolite mixtures. The investigated zeolites were H-Y, Cu-Y, H-Beta, Na-Beta, and Fe-Beta. Urea decomposition was investigated by means of simultaneous thermogravimetric (TG) and differential thermoanalysis (DTA) in the temperature range between 20 and 750 °C in both dry and steam-containing N_2. The gases evolved during the reactions were detected by online GC/MS. Solid intermediates of the decomposition at 270, 300, and 500 °C were characterized by attenuated total reflection (ATR) FTIR and luminescence spectroscopy. The impact of the deposits on the SCR performance of metal exchanged zeolite catalysts is reported in part II of the companion paper [25].

2. Experimental

2.1. Sample preparation

32.5 wt.% aqueous urea solution for impregnation was prepared by dissolving the appropriate amount of urea (Fisher Scientific) in deionized (D.I.) water. The zeolites H-Y, Cu-Y, H-Beta, Na-Beta, and Fe-Beta were prepared by ion exchange of the NH_4-forms of the appropriate zeolites. For impregnation with urea typically 1.0 g of the catalyst powder was wetted with the appropriate amount of 32.5 wt.% aqueous urea solution followed by drying the sample under ambient conditions. Alternatively, samples were prepared by mechanically mixing the catalyst with appropriate amounts of dry solid urea. Catalyst/cyanuric acid (98%, Acros Organics) mixtures were prepared in a similar way with the dry components being the starting materials.

2.2. Characterization techniques

Thermogravimetric and differential thermoanalysis in dry atmospheres was performed with a TG-DTA/DSC apparatus (Netzsch STA 409 PC Luxx) equipped with a TG/DTA sample carrier using corundum pans. As purge and protective gas dry N_2 (UHP grade) was used. The flow rate was set to 80 ml/min. TG experiments in humid atmospheres were done with the TG-DTA/DSC instrument Netzsch STA 449 F3 Jupiter with steam furnace equipped with a TG sample carrier and corundum sample pans. The desired amounts of steam were provided by a saturator operated at controlled temperatures. The steam concentration in the purge gas was monitored by means of an online dew point measurement (EdgeTech DewPrime I). The flow rate was controlled by mass flow controllers (Aalborg GCF17) and set to 200 ml/min. Alternatively, measurements were run in dry atmospheres with the same apparatus and equivalent flow rates, but by using the dry purge gas without saturating it with water. Both TG instruments could be connected to a GC/MS system (gas chromatograph Agilent 6890 series equipped with a fused silica column (Varian CP7447), and coupled to the mass selective detector Agilent 5973Network) by heated transfer lines to analyze evolved gases. For this purpose experiments were first run in scan MS mode to identify all gaseous decomposition products. The data shown were acquired by using the single ion mode (SIM) to monitor the mass/charge ratios 17 (NH_3), 18 (H_2O), 43 (HNCO), 44 (CO_2), and 52 ($(CN)_2$) with highest sensitivity.

Solid decomposition products were characterized with a Bio-Rad FTS 6000 FTIR spectrometer equipped with a DuraSamplIR™ Diamond ATR (attenuated total reflection) unit.

Photoluminescence spectra of the urea residues were recorded at room temperature with the Ocean Optics HR2000 spectrometer equipped with a Schott KV370 long pass filter to suppress excitation light. Excitation was carried out with the pulsed N_2-laser MNL 103-PD from Lasertechnik Berlin (wavelength: 337.1 nm, pulse energy: 80 νJ, repetition rate: 20 Hz, pulse duration: 3.5 ns).

3. Results and discussion

3.1. Pyrolysis of neat urea

In order to understand the impact of urea deposited on SCR catalysts it is necessary to study the decomposition under conditions as close to real conditions in the diesel exhaust stream as possible. Even though several studies regarding the pyrolysis of urea have been published [13–16,20,21], the influence of