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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.

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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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