The impact of urea on the performance of metal-exchanged zeolites for the selective catalytic reduction of NO\textsubscript{x}—Part II. Catalytic, FTIR, and NMR studies

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\begin{abstract}
The selective catalytic reduction (SCR) with urea over metal-exchanged zeolites is one of the most promising contenders for the reduction of NO\textsubscript{x} emissions in diesel exhaust. However, one major concern – a possible deactivation of the catalyst by urea deposits – has not been investigated sufficiently as yet. The formation of urea deposits on the catalyst after long-term operation was simulated by impregnating Fe–beta zeolite powder with 32.5 wt.% aqueous urea solution followed by hydrothermal aging at temperatures between 250 and 750 °C. The SCR activity was measured after each hydrothermal aging step. It could be shown that Fe–beta can be reversibly deactivated by urea deposits such as cyanuric acid and ammelide (as identified by ATR-FTIR) if the impregnated catalyst was hydrothermally aged at temperatures not higher than 250 °C. Upon steaming at 500 °C a complete regeneration of the SCR activity as well as a total decomposition of urea deposits left on the catalyst was observed. In addition, MAS \textsuperscript{29}Al and \textsuperscript{29}Si NMR experiments clearly show that no detrimental changes of the Si/Al zeolite framework were induced by urea-impregnation followed by steaming at 750 °C compared to the dealumination observed for hydrothermal aging alone. Thus, the urea-induced deactivation is fully reversible since no permanent structural changes in the zeolite could be identified.

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1. Introduction

Nitrogen oxides (NO\textsubscript{x}, x = 1/2, 1, 2) are major air pollutants generated by anthropogenic activities. NO\textsubscript{2} is not only a toxic gas by itself, but can react in the atmosphere to form ground level ozone (smog) and acid rain [1]. Most of the NO\textsubscript{x} is produced during the combustion of fossil fuels due to the oxidation of atmospheric N\textsubscript{2} at very high temperatures (thermal NO\textsubscript{x}). Organic nitrogen as source for NO\textsubscript{x} is less important since the content of N-containing species in gasoline and diesel fuels has been reduced significantly over the last years. Without catalytic aftertreatment diesel engines generate less NO\textsubscript{x} than their gasoline counterparts due to lower combustion temperatures [2,3]. However, the successful implementation of the three-way catalyst (TWC) in gasoline cars to simultaneously abate NO\textsubscript{x}, CO, and unburned hydrocarbons (HC) has led to the situation that today NO\textsubscript{x} from diesel exhaust contributes to about 75% of the total NO\textsubscript{x} from road traffic [4]. Unfortunately, the TWC does not work for diesel exhaust due to the lean nature of the diesel combustion process (i.e. combustion of diesel with oxygen/air excess) [3,5,6]. In particular, the simultaneous abatement of both NO\textsubscript{x} and particulate matter emissions is challenging, a problem that apparently cannot be solved by improved engine management alone.

Selective catalytic reduction (SCR) with ammonia is a very promising technology for the abatement of NO\textsubscript{x} emissions in diesel vehicles. SCR is the reaction between NH\textsubscript{3} and NO\textsubscript{x} on an appropriate catalyst to form harmless N\textsubscript{2} and H\textsubscript{2}O. It has been proven for stationary applications such as the abatement of NO\textsubscript{x} in flue gases of power or waste-to-energy plants [7,8]. Furthermore, the implementation of SCR in diesel vehicles, which has already been accomplished by some major car and truck companies, can reduce the fuel consumption by 7% since the engine could then be optimized on fuel economy [9]. Consequently, with SCR cars and trucks are not only able to emit less NO\textsubscript{x}, but smaller amounts of the combustion product and greenhouse gas CO\textsubscript{2} as well.

NO\textsubscript{x} in diesel exhaust of light-duty engines usually consists of more than 90% NO and only of a minor fraction of NO\textsubscript{2}. Therefore, the basic reaction taking place is the so-called standard SCR [6,10]:

\begin{equation}
4\text{NH}_3 + 3\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}.
\end{equation}

If the exhaust contains significant amounts of NO\textsubscript{2}, ideally an NO/NO\textsubscript{2} mixture of 1:1, the following reaction becomes dominant,