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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

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ABSTRACT

The selective catalytic reduction (SCR) with urea over metal-exchanged zeolites is one of the most promising contenders for the reduction of NO_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 ^{27}Al and ^{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_x, $x = 1/2, 1, 2$) are major air pollutants generated by anthropogenic activities. NO_x 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_x is produced during the combustion of fossil fuels due to the oxidation of atmospheric N_2 at very high temperatures (thermal NO_x). Organic nitrogen as source for NO_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_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_x, CO, and unburned hydrocarbons (HC) has led to the situation that today NO_x from diesel exhaust contributes to about 75% of the total NO_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_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_x emissions in diesel vehicles. SCR is the reaction between NH_3 and NO_x on an appropriate catalyst to form harmless N_2 and H_2O. It has been proven for stationary applications such as the abatement of NO_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_x, but smaller amounts of the combustion product and greenhouse gas CO_2 as well.

NO_x in diesel exhaust of light-duty engines usually consists of more than 90% NO and only of a minor fraction of NO_2. Therefore, the basic reaction taking place is the so-called standard SCR [6,10]:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O. \quad (1)$$

If the exhaust contains significant amounts of NO_2, ideally an NO/NO_2 mixture of 1:1, the following reaction becomes dominant,

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