An innovative route to enhance low-temperature catalyst performance in the selective catalytic reduction (SCR) of NO by NH_3

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Introduction

The removal NO_x at low temperature is a significant challenge for flue gas of industry and gas exhaust of Diesel engines. An efficient solution can be provided by selective catalytic reduction (SCR) using catalysts operating already at temperatures below 250°C. Many studies have been devoted to the development of traditional metal oxide catalysts for low- temperature SCR applications, e.g. Cu zeolites, unsupported and supported Mn oxides [1-3]. Recently, Stakheev et al. [4] have introduced catalyst combinations as a non-conventional principle. They consist of mechanical mixture of an oxidation catalyst with a SCR catalyst. This idea is based on the fact that the SCR of NO/NO_2 mixtures (eq. (1)) is much faster than the SCR of NO alone (eq. (2)). Therefore, a catalyst selectively oxiziding NO to NO_2 would be beneficial to promote "in situ" fast-SCR reaction.

$$NO + NO_2 + 2\,NH_3 \rightarrow 2\,N_2 + 3H_2O \qquad (1),\ \text{"fast SCR"}$$

$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad (2),\ \text{"standard SCR"}$$

Materials and Methods

SCR of NO by NH_3 was investigated over mechanical mixtures consisting of 0.4 wt-% Fe-ZSM-5 (FeZ) and 0.5 wt-% V_2O_5/10 wt-% WO_3/TiO_2 (VTi) as components active for SCR and an oxidation catalyst at weight ratio 1:1. Oxidation components used included several metal oxides M´O_x, where M´ is Mn, Mn-Cu, Ce-Zr, Mn/Ce-Zr, etc.. Among them, MnO_x was aged by thermal treatment in a temperature range between 350-850°C. The individual components were evaluated in SCR at GHSV of 600,000 h^{-1} and combined catalysts at 300,000 h^{-1}, using a reactant mixture consisting of 1000 ppmv NO, 1000 ppmv NH_3, 2 vol-% O_2, balance – He in a temperature range of 100-600°C. After the measurement at 600 °C, the reactors were cooled down and a second identical run was carried out in order to provide an initial insight into the stability. NO oxidation was also carried out over the individual components using similar conditions, just in absence of NH_3. The samples were characterized by XRD, BET, chemical analysis and some of them by XPS.

Results and Discussion

By comparison of SCR rates and selectivities of the mixtures ("combined catalysts") with those of their individual components significant and sometimes dramatic synergistic effects between both components were established. Mn-based oxidation components, which provide high SCR activity on their own, were improved with respect to selectivity towards N_2 by the presence of both Fe-ZSM-5 and $V_2O_5/WO_3/TiO_2$. The improved N_2 selectivity remained when the SCR activity of pure Mn oxide components was suppressed by thermal ageing as shown in **Figure 1**. The mixed Cu-Mn oxide showed poor N_2 selectivity which excludes it from practical applications. With the Ce-Zr oxidation component, very high selectivities were achieved; however at lower NO conversion, which was boosted in the low temperature range by adding Mn.

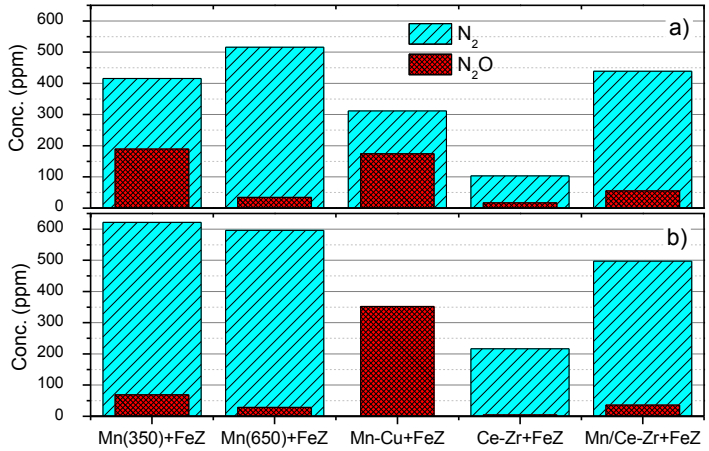

Figure. 1. Comparison of NH_3-SCR performances of combined catalysts at 250 °C. a) fresh catalysts (first run); b) aged catalysts (second run).

The measurement of NO oxidation rates showed general parallel tendencies with SCR activities, which complies with the idea of oxidation catalysts providing NO_2 to open the fast SCR path catalyzed by Fe-ZSM-5 or $V_2O_5/WO_3/TiO_2$. There are, however, contradictions to the above mentioned tendency, which can be probably explained by solid-state reactions between zeolite and admixed oxidation catalyst, and different influences of the (inhibiting) effect of NH_3 on NO_2 formation under SCR conditions.

Significance

The recently proposed combined catalyst approach [4] for improved NO reduction rates and N_2 selectivities at low temperature was explored by combining various oxidation and SCR functions. The MnO_x oxidation component could provide an adequate NO_2 production to trigger the fast SCR reaction. Mn-combined systems can be optimized by aging the Mn-component or by adjusting ratios between oxidation and SCR functions.

References

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