Structure-activity relationship for HC-SCR over Ag/Al₂O₃ with cyclic and aromatic reductants

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Introduction
Ag/Al₂O₃ is a promising catalyst for selective catalytic reduction of NOₓ with hydrocarbons (HC-SCR). However, most studies have used straight alkanes or alkenes as reductants [1] (and references herein). Studies using e.g. cyclic or aromatic hydrocarbons are scarce, despite the detrimental effect on the activity [2,3] and the fact that such hydrocarbons are commonly present in diesel fuel. Therefore, this study examines the influence of the nature of the reductant, and the effect of silver particle size and morphology in regard to the HC-SCR activity. The silver particle size and morphology on one hand, and the nature of the reductant on the other hand are investigated towards their dependence for HC-SCR over Ag/Al₂O₃.

Materials and Methods
Ag/Al₂O₃ samples with either 2 or 6 wt% silver loading were prepared, using a sol-gel method including freeze-drying [1,4]. The catalytic performance of the samples was evaluated by flow reactor experiments, with paraffins, olefins and aromatics of different nature as reductants. X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of silver. The silver particle size distribution was analyzed by scanning transmission electron microscopy/high angle annular dark field imaging (STEM/HAADF). The ratio between step and terrace silver sites was determined by the construction of Wulff shapes of Ag particles in the corresponding size range. Turnover frequencies for HC-SCR over the step- and terrace sites were calculated.

Results and Discussion
The activity for lean NOₓ reduction by hydrocarbons over Ag/Al₂O₃ is highly dependent on the nature of the reducing agent (Figure 1, right). For alkylated cyclic paraffins (methylcyclohexane) and alkylated aromatics (toluene, cumene) a higher NOₓ reduction is observed compared to the corresponding non-alkylated cyclic or aromatic hydrocarbons. Moreover, the activity increases with increasing chain length of the alkyl group. For alkylated cycloparaffinic and alkylated aromatic hydrocarbons, the NOₓ reduction is clearly higher at temperatures below 500 °C for the 6 wt% Ag/Al₂O₃ sample, than for the 2 wt% sample. In addition, the NOₓ reduction over the catalyst is not only dependent on the nature of the reducing agent, but also on the silver loading and morphology. The STEM/HAADF analysis (not shown) show that the 6 wt% sample contains a higher total number of silver particles than the 2 wt% sample, and also a much higher fraction of silver particles in the 5 nm range. Further, the 2 wt% sample contains a higher fraction of small, 2–3 nm particles. Together with the observed differences in NOₓ reduction below 500 °C, this strongly indicates that the HC-SCR reaction is dependent on the ratio between step- and terrace silver sites (Figure 1, left). Moreover, calculated rates (not shown) over the different sites for NOₓ reduction and HC oxidation manifests that the overall NOₓ reduction rate is a function of the nature of the reducing agent and the silver morphology.

Significance
It is shown that the HC-SCR activity is dependent on the reducing agent and silver morphology, which needs to be considered when designing highly active diesel-SCR catalysts.

References

Figure 1. Left: Step/terrace atomic ratio over silver particle size. Constructed Wulff shapes for 2 and 5 nm silver particles. Right: NOₓ reduction vs. temperature over the Ag/Al₂O₃ samples for different reductants. Gas feed: 500 ppm NO, 6 vol.% O₂, 10 vol.% CO₂, 350 ppm CO, 12 vol.% H₂O, He bal. C/N=6. Total flow: 500 ml/min. GHSV = 60 000 h⁻¹.