

Lean NO_x reduction with methanol over Ag-Al₂O₃ - influence of hydrogen and characteristics of silver species

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Introduction

Lean NO_x reduction over Ag-Al₂O₃ has been widely studied for several types of reducing agents [1]. However, there are only a limited number of detailed reports on methanol as reductant for NO_x [2]. Methanol is today one of the most promising renewable fuels for transports both on land and at the sea. In addition, methanol is a small molecule and thus methanol-SCR provides a model system for investigations of HC-SCR reactions in general.

The objective of the present study is to investigate the activity and selectivity, and the influence of hydrogen, for lean NO_x reduction with methanol over Ag-Al₂O₃. The results are discussed in relation to silver loading, availability of different types of silver species and their properties. The aim is to contribute to a fundamental understanding of methanol-SCR reactions over Ag-Al₂O₃.

Materials and Methods

Ag-Al₂O₃ samples with 1-4 wt% silver were prepared according to the sol-gel method including freeze-drying, described by Kannisto et al. [3]. The catalytic performance of coated monolith samples was studied in a continuous flow reactor where the outlet gas composition was analyzed by gas-phase FTIR spectroscopy [4]. Calculations of the N₂ yield, i.e. conversion of NO_x to N₂, has been described previously [4]. The silver species in the samples were characterized by temperature programmed reduction with hydrogen (H₂-TPR) and UV-Vis spectroscopy.

Results and Discussion

Figure 1a shows a step-response experiment where H₂ is introduced and removed from the feed gas composition. The results show that H₂ is formed during methanol-SCR conditions. In accordance with Johnson et al. [5], this availability of H₂ is suggested to contribute to the high low-temperature activity often observed when using alcohols as reducing agents, in comparison with hydrocarbons which do not contain oxygen.

When H₂ is added to the feed, for all three gas mixtures (**Figure 1a**), more oxidized reaction products are formed. Interestingly, only diminutive amounts of HCHO and CO are observed during methanol oxidation, compared to during SCR conditions. Consequently their formation must be highly influenced by the presence of NO, and maybe part of the NO_x reduction reactions. Moreover, the addition of H₂ results in a temperature increase in the catalyst, likely to a large extent owing to oxidation of H₂ to H₂O. However, it is concluded from the methanol-SCR experiments during temperature ramps in **Figure 1b**, that not only the temperature increase is causing the higher NO_x reduction to N₂ observed in the presence of H₂.

Comparison of the H₂ consumption during H₂-TPR (not shown) with the N₂ formation during the methanol-SCR experiments in **Figure 1b**, shows that the silver species

reduced by H₂ cannot be directly associated with the N₂ formation. Furthermore, the UV-Vis analysis indicates a higher proportion of large metallic particles in the high-loaded samples, which can explain the lower N₂ formation at high temperatures, owing to a more extensive combustion of the reducing agent.

In the present study we show that H₂ is formed during methanol-SCR conditions. This availability of hydrogen is suggested to result in a similar effect as H₂ addition to HC-SCR, when not using an oxygenated reducing agent.

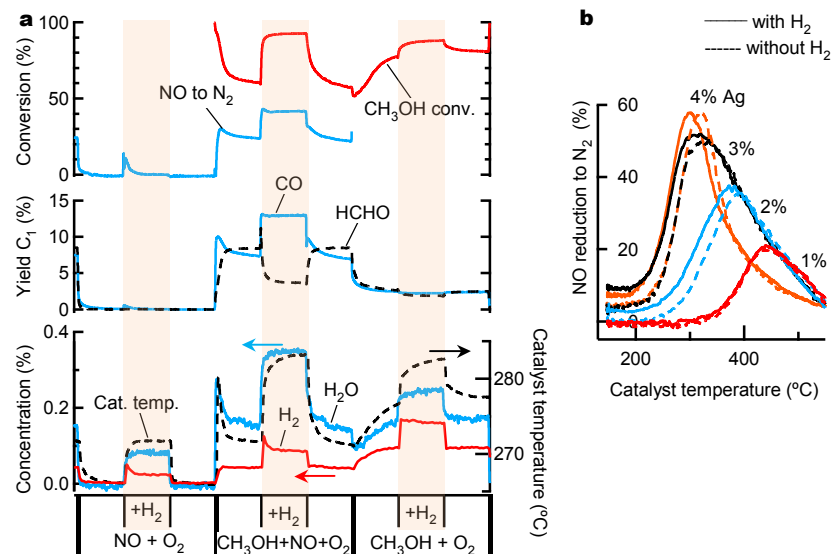


Figure 1. a) Step-response experiment with (3 wt% Ag) Ag-Al₂O₃ at 260 °C (inlet temperature). b) Methanol-SCR experiments during cooling ramp, with and without H₂, over Ag-Al₂O₃ (1-4% Ag). Inlet gas mixture: 10 % O₂, 1,700 ppm methanol (when used), 500 ppm NO (when used), 1000 ppm H₂ (when used), Ar bal.

Significance

Fundamental knowledge of catalytic reactions is important when developing new catalysts, here specifically addressing bio-fuel applications with focus on methanol, in combination with the low exhaust gas temperatures of fuel-efficient engines.

References

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