Impact of physico-chemical properties of transition metal oxide based TiO₂ catalysts on the low-temperature selective catalytic reduction of NO by NH₃

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Abstract: The relationship between catalytic activity, redox behavior, acidity and NOₓ adsorption ability of MOₓ/TiO₂ (M: Co, Cu, Ce, Fe, Ni and Mn) catalysts was investigated for the low-temperature selective catalytic reduction of NOₓ in the presence of NH₃.

Keywords: selective catalytic reduction, NOₓ, transition metal oxides

Introduction

Nitrogen oxides (NOₓ) are hazardous gases that cause problems such as photochemical smog, formation of fine particles, acid rain, ozone depletion and act as of greenhouse gases to the environment. Today, selective catalytic reduction (SCR) using ammonia is the most widely used technology for removal NOₓ emitted from stationary sources, such as coal fired power plants and gas turbines. V₂O₅-WO₃/TiO₂ (VWT) catalysts have been commercialized for SCR and operate under moderate temperatures of about 320-450°C. However, some problems are still evident with the use of this catalyst: V oxide is highly toxic and successive dust pollution of the catalyst will eventually result from the upstream flue gas, which can cause the deactivation of VWT catalyst at the low temperature operation window (150-250 °C) [1]. In this temperature range MnOₓ based catalysts supported on titania dioxide are suitable for the NH₃ system and possess excellent SCR activity [2]. Additionally, this catalytic system cause also very high yield of N₂O as an undesired product of the NH₃-SCR reaction. The impact of transition metal oxide (TMO) on the behavior of SCR catalysts is still not fully understood [1,2]. The present study focuses on the investigation of the effects of TMOs by comparing the SCR activity and physico-chemical properties for catalysts with identical molar ratio of M:Ti.

Experimental

A series of Mn, Fe, Cu, Ce, Co and Ni oxide catalysts supported on TiO₂ (Anatase, P25) were prepared by wet impregnation. The content of active metal was kept at a constant molar ratio of M:Ti = 0.4. The prepared catalysts were characterized by XRD, N₂-sorption, H₂-TPR, NOₓ- and NH₃-TPD. The activity of the catalysts for NH₃-SCR was studied using a model gas containing 500 ppm NO, 575 ppm NH₃ and 4 vol.-% O₂ in a fixed-bed flow-reactor in a temperature range of 120-400 °C and at a GHSV of 30,000 h⁻¹. The gaseous products were continuously analyzed by on-line NDIR-spectroscopy.

Results and discussion

The SCR studies show that Mn- and Cu/TiO₂ catalysts exhibit a high NO-conversion of 85-95 % at 180 °C (Fig.1a). However, a significant formation of N₂O with a yield of about 78 % was observed for Mn/TiO₂. In comparison, the yield of N₂O on Cu, Fe, Co, Ce and Ni containing catalysts was about 7-10 times lower, although at a lower NOₓ-conversion of 40-65 %. The dependence of the NOₓ-conversion on the TMOs for the catalysts follows the
Fig. 1. NOx-conversion and N2O-yield over prepared catalysts during NH3-SCR at 175, 210 and 260°C (a) and correlation between the main reduction temperature of the catalysts during TPR with the temperature for 50% of NOx conversion and between temperature of N2O formation by NH3-TPD (b) and 10% N2O yield (c) observed during NH3-SCR (c).

order: Mn > Cu > Co > Ni > Fe > Ce. NH3-SCR, H2-TPR, NO-TPD and NH3-TPD results show a strong correlation between the ability of the TMO containing catalysts for the oxidation of ammonia, its catalytic activity and the yield of N2O formed during SCR reaction.

Conclusion

The obtained results illustrate the importance of quantitative and qualitative assessment of NOx adsorption and catalytic oxidation of NH3 over supported TMOs for the development of new SCR catalysts. A linear correlation between the reduction temperature determined by TPR and the temperature at which a NOx-conversion of 50% occurs over the catalysts during NH3-SCR was observed (Fig.1b). This indicates that the reduction properties of the TMOs are the determining factors for the low-temperature activity during NH3-SCR (Fig. 1c).

Additionally, the adsorption of NOx in the form of weakly bonded NOx species and the oxidation activity of TMO containing catalyst are the key factors for the SCR reaction in the presence of ammonia and can be improved in a targeted manner.

Acknowledgments

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References

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