Impact of physico-chemical properties of transition metal oxide based TiO_2 catalysts on the low-temperature selective catalytic reduction of NO by NH_3

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Abstract: The relationship between catalytic activity, redox behavior, acidity and NO_x adsorption ability of MO_x/TiO_2 (M: Co, Cu, Ce, Fe, Ni and Mn) catalysts was investigated for the low-temperature selective catalytic reduction of NO_x in the presence of NH_3.

Keywords: selective catalytic reduction, NO_x, transition metal oxides

Introduction

Nitrogen oxides (NO_x) 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 NO_x emitted from stationary sources, such as coal fired power plants and gas turbines. V_2O_5-WO_3/TiO_2 (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 MnO_x based catalysts supported on titania dioxide are suitable for the NH_3 system and possess excellent SCR activity [2]. Additionally, this catalytic system cause also very high yield of N_2O as a undesired product of the NH_3-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 TiO_2 (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, N_2-sorption, H_2-TPR, NO_x- and NH_3-TPD. The activity of the catalysts for NH_3-SCR was studied using a model gas containing 500 ppm NO, 575 ppm NH_3 and 4 vol.-% O_2 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/TiO_2 catalysts exhibit a high NO-conversion of 85-95 % at 180 °C (Fig.1a). However, a significant formation of N_2O with a yield of about 78 % was observed for Mn/TiO_2. In comparison, the yield of N_2O on Cu, Fe, Co, Ce and Ni containing catalysts was about 7-10 times lower, although at a lower NO_x-conversion of 40-65 %. The dependence of the NO_x-conversion on the TMOs for the catalysts follows the

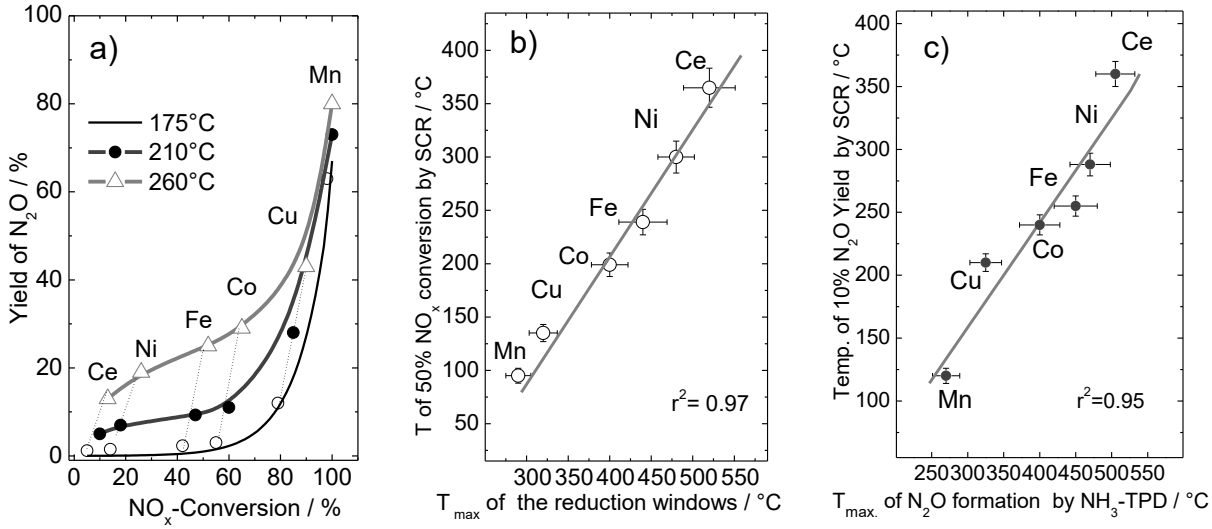

Fig. 1. NO_x-conversion and N_2O-yield over prepared catalysts during NH_3-SCR at 175, 210 and 260° (a) and correlation between the main reduction temperature of the catalysts during TPR with the temperature for 50 % of NO_x conversion and between temperature of N_2O formation by NH_3-TPD (b) and 10% N_2O yield (c) observed during NH_3-SCR (c) .

order: Mn > Cu > Co > Ni >Fe > Ce. NH_3-SCR, H_2-TPR, NO-TPD and NH_3-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 N_2O formed during SCR reaction.

Conclusion

The obtained results illustrate the importance of quantitative and qualitative assessment of NO_x adsorption and catalytic oxidation of NH_3 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 NO_x-conversion of 50 % occurs over the catalysts during NH_3-SCR was observed (Fig.1b). This indicates that the reduction properties of the TMOs are the determining factors for the low-temperature activity during NH_3-SCR (Fig. 1c). Additionally, the adsorption of NO_x in the form of weakly bonded NO_x 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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