

Selective Catalytic Reduction of NO_x by Methane over Co-H-MFI and Co-H-FER Zeolite Catalysts: Characterization and Catalytic Activity

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Introduction

The removal of nitrogen oxides from flue gases of thermal power plants is currently carried out with the so-called NH₃-SCR technology, *i.e.* the Selective Catalytic Reduction of NO by ammonia over V₂O₅-WO₃/TiO₂ or V₂O₅-MoO₃/TiO₂ catalysts.

The need of storing ammonia is one of the main drawbacks of this technology when applied to power plants. Additionally, the possibility of formation of ammonium sulphates due to reaction of SO₂, oxygen, water and ammonia and the dangerous ammonia slip may also limit the conditions for application of this process.

A valid alternative process for denitrification of exhaust gases of power plants (as NO decomposition is not yet applicable) implies the use of methane as the reducing agent. Methane as a reductant is, the preferred choice for NO_x removal from flue gases because it is already present in methane-fuelled power plants. Co-containing zeolites, such as Co-MFI and Co-FER, were found to be particularly active in CH₄-SCR in the presence of oxygen [1].

In this work Co-exchanged MFI and ferrierite (FER) zeolites obtained from NH₄⁺-zeolites were studied for CH₄-SCR. The study was aimed to obtain information on the nature of active sites, and to investigate on the role of protonic sites. To gain this purpose several characterisation techniques were employed, that can give complementary results, such as FT-IR, UV-Vis diffuse reflectance, XRD, TG-DTA, NH₃-TPD, TPR. Catalytic tests were performed in a flow laboratory plant with a fixed bed reactor operating at atmospheric pressure. The operation condition were: reacting mixture composition: NO = 1500 ppm, CH₄ = 1500 ppm, O₂ = 25000 ppm, He balance; T = 523 - 773K; GHSV = 30000 - 60000 h⁻¹. Grain dimensions of the catalysts were 150-212 μm. The analysis of NO, NO₂, N₂O was performed by a continuous spectrophotometer analyser ABB URAS 14 equipped with a NO₂ converter. CH₄, N₂, CO, CO₂ concentrations were measured by a HP 5890 gas chromatograph with a TCD detector and a molecular sieves 5A-Porapak Q double packed column.

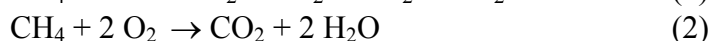
Results and Discussion

The presence of Co cations in exchanged sites in the zeolite cavities has been confirmed, through UV-Vis and FT-IR spectroscopies, although the exchange of protons by Co ions also occurs on the external crystal surface.

Both Co-H-FER and Co-H-MFI retain large amount of residual protonic sites whose acidic strength seems increased by the Co exchange.

The presence of easily reducible Co oxide species has been shown by TPR measurements that also gave evidence that exchanged Co^{2+} ions were hardly reducible.

Co-H-MFI appears more active than Co-H-FER in NO and CH_4 conversions in the whole temperature range. This could suggest that exchanged Co^{2+} ions play an important role in CH_4 -SCR. Moreover both catalysts show a maximum in NO conversion, shifted to higher temperature for Co-H-FER. Similar results were reported for Co-MFI catalysts [2,3]. By contrast CH_4 conversion is always increasing with temperature, thus leading to a varying CH_4/NO reaction ratio: at temperatures lower than the maximum, this is close or slightly higher than the stoichiometric one, while at higher temperatures it reaches largely exceeding values. This clearly suggests the occurrence of side reactions, mainly methane combustion, as previously reported. The catalytic behaviour of H-zeolites was also investigated. It can be stressed out that the not-exchanged zeolite is active mainly for NO oxidation to NO_2 , that is practically the only reaction product at $T > 650$ K, and in negligible extent towards NO reduction, in agreement with results reported elsewhere. In order to obtain more information about the catalyst activity towards this reaction, tests were carried out feeding NO and O_2 in the same concentrations as during CH_4 -SCR tests, but in absence of methane. Co-H-MFI shows significant activity and that conversion to NO_2 reaches the equilibrium values starting from 650 K. At $T \leq 650$ K conversion to NO_2 is practically the same as that observed in CH_4 reduction tests, while it is lower at higher temperatures. This suggests that under CH_4 -SCR conditions NO oxidation competes with the main reaction, being prevailing at low temperature; NO reduction seems to be favoured only at higher temperature where oxidation to NO_2 is thermodynamically limited. From the above data it can be suggested that under SCR conditions the following reactions can occur:



At low temperature reaction (3) is the main one. At high temperature, when NO oxidation is thermodynamically limited, reactions (1) and (2) become the prevailing ones. Therefore it is evident the activity of both protonic sites and cobalt species in NO oxidation. The activity for NO reduction is probably due to Co^{2+} ions. However the contribution of Co oxo-ions species can not be excluded.

References

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