Iron-catalysts for abatement of nitrous oxide under demanding conditions

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Introduction

The preferred process for the abatement of N_2O during nitric acid production is its catalytic decomposition in the ammonia burner at temperatures 750-900 °C. These high temperatures together with high content of water vapour in the gas streams represent highly demanding conditions that require structurally very stable catalysts. This study aims into the understanding of structural parameters controlling the stability of iron containing catalysts for high temperature N_2O decomposition.

Materials and Methods

The catalysts for high temperature decomposition of N_2O were prepared by wet impregnation of support material (α-, γ-alumina, SiO_2, CeO_2, and ZrO_2) or precipitation from a solution (aluminate, spinel or hexaaluminate structures). Fe-zeolites of several structural topologies were prepared using impregnation with a solution of $FeCl_3$ in acetylacetone. The activity of the catalysts for high temperature decomposition of N_2O were tested in quartz reactor at temperatures 700 - 900 °C with GHSV 100 000 and 400 000 h^{-1}. The composition of the reaction gas was 1000 ppm N_2O, 0.5% NO, 2% O_2 and 10% H_2O in He. Catalysts were aged in the ammonia burner for 290 or 580 hours.

Results and Discussion

The N_2O decomposition over Fe-zeolites was governed by the concentration of Fe(II) balanced by Al pairs in the framework cationic sites [1]. The decrease in the concentration of Fe(II) ions in cationic sites was strongly affected by the topology of zeolite structure. Fe-FER zeolites stabilized by Fe(II) in the cationic sites provided stable and high conversion in N_2O decomposition after ageing at 800 °C for 580 h. In contrast, the conversion of N_2O over Fe-ZSM-5 gradually decreased. Fe-oligomers and highly dispersed iron oxides on Al_2O_3, ZrO_2 and CeO_2 supports provided sufficient activity at 800 - 900 °C. After long time-on-stream the Fe/γ-Al_2O_3 and Fe/α-Al_2O_3 provided comparable conversions of N_2O due to the structural transformation of γ- to α-Al_2O_3. Fe species in spinels and hexaaluminate catalysts showed low versatility in valence of Fe ions and relatively close coordination sphere that result in lower activity than supported Fe_2O_3 catalysts. The comparison of Fe-zeolites and the supported catalysts (Figure 1) shoved that the turn-over-frequencies over Fe(II) ions stabilised in ferrierite zeolites is of one order higher compared to those containing dispersed small oligomeric Fe_xO_y species stabilised on oxide supports.

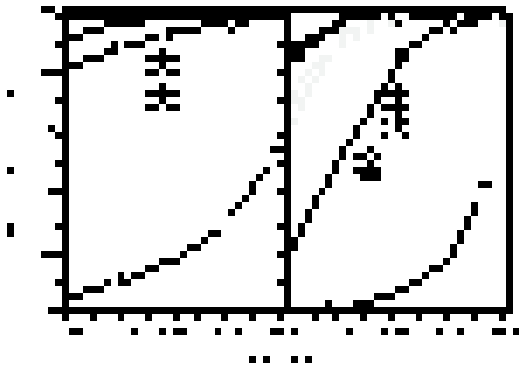

Figure 1. Effect of ageing of Fe-catalysts on conversion in high-temperature catalytic decomposition of N_2O. Comparison of fresh catalysts (filled symbols) and those after ageing in a stream of 15% H_2O, 10 NO and 2.5% O_2 in N_2 at 800 °C for 12 days (opened symbols).

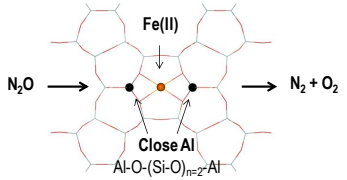

Figure 2. Structure of Fe active sites controlled by local density of aluminium in the zeolite framework in extruded Fe-FER catalyst for high temperature N_2O decomposition.

Significance

It is demonstrated that bare counter Fe ions balanced by Al-Si-Si-Al sequences in 6MRs of the framework greatly stabilize the structure of ferrierite zeolite. This cationic species undergo reversible redox Fe(III)O^-/Fe(II) cycle during N_2O decomposition and represent the most active site in the high temperature decomposition of N_2O to molecular components. Fe-FER zeolite with Fe in cationic sites provided sufficiently high structural stability and activity for total elimination of N_2O at high temperature.

Acknowledgments

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References

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