# Optimizing Co-based spinel catalysts for efficient $N_2O$ decomposition

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## Introduction

For an environmental friendly production of $HNO_3$ beside emissions of $NO_x$ the amount of $N_2O$ in the flue gas of the production plant has to be reduced drastically. Especially $N_2O$ is a strong greenhouse gas due to its participation in the depletion of the ozone layer, its high ability to adsorb IR-radiation in the atmosphere and its long lifetime in the atmosphere (150 years). So $N_2O$ has a 310 times higher global warming potential than $CO_2$. Nowadays $HNO_3$ plants are the largest single source of $N_2O$ emissions. For a reduction of emissions the catalytic decomposition of $N_2O$ into $N_2$ and $O_2$ is the most economic and ecologic way because of low costs and no secondary emissions. The only industrial applied catalyst is a Fe-ZSM-5 catalyst which achieves 50 % conversion at a temperature ($T_{50\%}$) of 430 °C [1]. Compared to the average temperatures of the tail gases (T = 250 - 500°C) the activity is still too low to achieve quantitative conversions. Due to these problems there is still the need of a more active catalyst to quantitatively decompose $N_2O$ in the conditions appearing in the tail gases of the $HNO_3$ production. Previous works showed that $Co_3O_4$ and its doping with alkali metals (especially K) leads to highly active catalysts [2]. The exchange of one cobalt atom by various metals results in a significant variation of the catalytic activity [3].

Therefore we focused on optimization of Co-based spinel catalysts for $N_2O$ decomposition and investigated the influence of type and amount of exchanged metal. Furthermore, possible doping agents have been studied and inhibition effects due to NO were reduced.

## Materials and Methods

$M_xCo_{3-x}O_4$ catalysts (M = Mg, Cu, Co, Cr, Zn; x = 0.25, 0.5, 0.75, 1) were prepared by thermal decomposition at 600 °C in air of stoichiometric mixtures of the corresponding metal nitrates. Preparation of alkaline (earth) metal doped catalysts (D = Na, K, Sr, Ba) followed the same procedure by adding the doping metal nitrate to the reactant mixture in a molar ratio between n[D]/(n[Co]+n[Cu]) = 0.01 – 0.05.

Catalytic tests were carried out in a fixed bed flow reactor. The tableted catalysts were pretreated at 400 °C in nitrogen flow for 30 min. Afterwards, the reaction gas composed of 1000 ppm $N_2O$ in nitrogen (ideal conditions) or composed of 1000 ppm $N_2O$, 200 ppm NO, was introduced into the reactor with a catalyst contact time of W/F = 0.2 g·s·ml$^{-1}$. The temperature was increased in steps of 60 K starting from 210 °C up to 690 °C. The effluent gas of the reactor was analyzed by infrared spectroscopy using a Perkin Elmer Spectrum Two equipped with a specac gas cell and the $N_2O$ conversion was determined according to $X(N_2O) = (c(N_2O)_{in} - c(N_2O)_{out}/c(N_2O)_{in})\cdot 100$ %.

## Results and Discussion

A comparison of the catalytic activity of the various $M_xCo_{3-x}O_4$ spinels showed that the use of $Mg_x$ – and $Cu_xCo_{3-x}O_4$ showed the biggest impact of the amount of M integrated in the spinel on the activity while for $Zn_x$ no dependency was found. Furthermore, the $Cu_x$ and $Mg_x$ catalysts resulted in the highest activity found for the different metals. The achieved $T_{50\%}$ values in idealized conditions are 350 °C for $Mg_{0.25}$ and 400 °C for $Cu_{0.25}$, which are 80 K and 30 K lower than the $T_{50\%}$ values of the industrial applied Fe-ZSM-5 catalyst. The results show that by choosing the right amount of integrated metal the activity can be highly optimized. Furthermore, an even more pronounced increase in activity was found for doping the spinel phase with potassium. In this way it was possible to achieve a $T_{50\%}$ value of 280 °C for $0.01K-Mg_{0.25}Co_{2.75}O_4$ and full conversion at 450 °C. In the case of the Cu integrated spinel values of $T_{50\%}$ = 300 °C and full conversion at 450 °C was found for $0.01K-Cu_{0.25}Co_{2.75}O_4$. Catalytic tests in stable reaction conditions showed stable activity for both catalyst systems over a time period of 150 h. By going to more realistic conditions, the addition of NO to the reaction mixture was found to inhibit the performance and $T_{50\%}$ increase by ca. 60 K, but during time on steam no further inhibition could be observed. Switching the conditions back to idealized NO-free conditions showed that the inhibition effect is fully reversible and the initial activity can be restored. An evolution of the activities during optimization of the $Cu_xCo_{3-x}O_4$ catalysts is shown in figure 1.
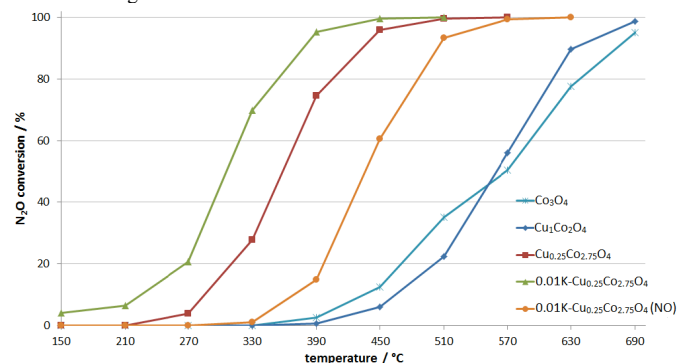


**Figure 1:** Evolution of activities during optimization of $Cu_xCo_{3-x}O_4$ catalysts. Conditions: $c(N_2O)$ = 1000 ppm in $N_2$ ; (NO): addition of 200 ppm NO; GHSV = 54000 h$^{-1}$.

## Significance

In our work we could show that partial metal exchange in combination with suitable doping agents can significantly increase the catalytic activity of spinels in the decomposition of $N_2O$. The performance of optimized cobalt based spinel catalysts during addition of NO to the gas stream indicates a high potential for industrial application. Further advantages are the easy and fast synthesis and the high thermal and mechanical stability of these catalysts.

## References

1.       J. Pérez-Ramírez, F. Kapteijn, K. Schöffel, J. A. Moulijn, Appl. Catal. B 2003, 44, 117.
2.       K. Asano, C.Ohnishi, S. Iwamoto, M. Shioya, Y. Inoue, Appl. Catal. B 2008, 78, 242.
3.       N. Russo, D. Fino, G. Saracco, V. Specchia, Catal. Today 2007, 119, 228.