Performance improvement of MgCo$_2$O$_4$ catalyst for N$_2$O decomposition

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Introduction

Nitrous oxide (N$_2$O) is an environmental pollutant that during the last decade has been recognized as a potential contributor to the destruction of ozone in the stratosphere and acknowledged as a relatively strong greenhouse gas [1]. The continuous increase in its concentration in the atmosphere, both due to natural and anthropogenic sources (0.2–0.3% per year) and longer atmospheric residence time (150 years), enforce us to develop efficient catalysts for its decomposition into nitrogen and oxygen to protect our global environment. Catalytic removal of N$_2$O from anthropogenic sources would be one of the possible solutions to protect our global environment. In recent years, spinel-type oxide based on 3d transition metals have been the subject of increasing fundamental and applied research because of their catalytic properties [2]. The synthetic process of spinel precursor compounds, which determines final oxide structure, texture, and chemical composition, plays a crucial role in ultimate performance of these spinels [3,4].

In the present paper, the synthesis method-activity relationship of MgCo$_2$O$_4$ catalyst was studied. On the basis of the obtained results, the suitability of the mentioned catalysts for industrial application will be finally discussed.

Materials and Methods

The catalysts were prepared by two different synthesis method: Solution Combustion Synthesis (SCS) from an aqueous solution of nitrates precursors and glycine (acting as a sacrificial fuel) and co-precipitation method [3,4] from an aqueous solution of 15 wt.% K$_2$CO$_3$ (about 10 ml/min) and nitrate precursors at room temperature until the pH of the solution reached 9. In the course of catalysts synthesis, the key step was to stop stirring when the color of the slurry was between red and pink. The resultant precipitate was washed until the filtrate was neutral, then dried at 100 °C for 7 hours, followed by calcinations at 400 °C in air for 2 h. The catalysts were fully characterized by BET, FESEM, XRD and TPD/R/O analyses.

The catalytic activity of the prepared materials was performed in a fixed-bed quartz micro reactor under an atmosphere of 5000 ppmv N$_2$O, with 5% or without O$_2$, balanced by He, at a rate of 100 ml/min over 50 mg catalyst (W/F = 0.02 g s cm^{-3}, GHSV ≈ 30,000 h^{-1}). The outlet gas composition was analyzed through NO$_x$/N$_2$O NDIR (ABB) and chemiluminescence NO/NO$_x$ (Ecophysics) analyzers vs the bed temperature.

Results and Discussion

The XRD spectra show for all the catalysts synthesized diffraction peaks corresponding to the desired catalysts structure. The FESEM views enlighten a very foam structure and the BET specific surface area (SSA) values ranges between 7 and 144 m^2/g.

The activity tests on powder catalysts show that MgCo$_2$O$_4$ obtained by co-precipitation method exhibits a very good progress of the catalytic performance: hence, a T$_{50}$=380°C is attained, which represents a decrease of 60°C as compared to the one observed

with the combustion synthesis method. It is generally accepted that surface vacant sites are responsible for nitrous oxide decomposition: the decomposition of nitrous oxide mainly proceeds with the decomposition of N$_2$O into N$_2$ owing to the presence of a vacant site ([ ]-M) and adsorbed surface oxygen (O-M), desorption of this surface oxygen by combination with another oxygen atom as O$_2$ to gas phase or by direct reaction with another N$_2$O molecule [1].

The high specific area attained with the co-precipitation method (see BET column in Table 1) and the amount of released oxygen , i.e. the capability to form surface vacancies (see TPD-O$_2$-desorption column in Table 1), seem to be the governing parameters for the catalytic activity, in agreement with the reaction mechanisms above reported. Quite promising results were also obtained with the catalysts deposited over a ceramic honeycomb converters. Studies are now in progress to evaluate the catalyst performance on a prototype for an industrial application for the abatement of N$_2$O emitted from an acid adipic plant.

Table 1. Results collection of the characterization tests concerning BET specific surface area, catalytic activity and temperature programmed desorption.

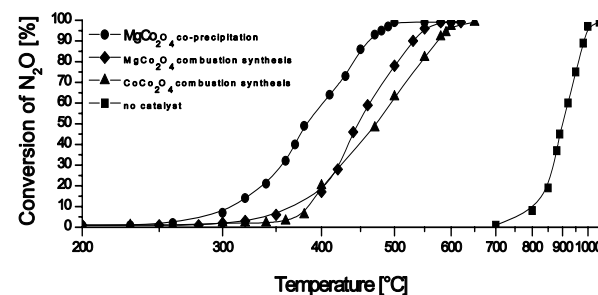| Catalyst	BET [m^2/g]	T$_{50}$ no O$_2$ [°C]	T$_{50}$ 5% O$_2$ [°C]	TPD O$_2$ desorption [µmol/g]
no catalyst	-	905	990	-
CoCo$_2$O$_4$	7.8	475	510	11.1
MgCo$_2$O$_4$ combustion synthesis	52.3	440	470	60.9
MgCo$_2$O$_4$ co-precipitation	143.8	380	415	1330.5

Figure 1. N$_2$O conversion to N$_2$ and O$_2$: 5000 ppm N$_2$O, He=balance.

References

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