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## EFFECTS OF ADDITIONAL GASES ON THE CATALYTIC DECOMPOSITION OF N<sub>2</sub>O OVER Cu-ZSM-5

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### Abstract

N<sub>2</sub>O decomposition into N<sub>2</sub> and O<sub>2</sub> was investigated in the presence of O<sub>2</sub>, NO, CO<sub>2</sub>, CO, CH<sub>4</sub>, SO<sub>2</sub> and water vapor. Activity inhibition was observed in the presence of water vapor and oxidant gases, whilst the reductant gases, enhanced the catalytic activity, in the temperature range of 350-550°C.

*Keywords:* Nitrous oxide, Cu-ZSM-5, decomposition, reduction, inhibition

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## INTRODUCTION

Nitrous oxide (N<sub>2</sub>O) is a greenhouse gas and contributes to destructing the ozone layer. The N<sub>2</sub>O concentration in the atmosphere is increasing at an annual rate of 0.2-0.3% and the estimated human contribution corresponds to 40% of the total emission. A reduction of 70-80% in the antropogenic emissions is necessary in order to stabilize the concentration of atmospheric N<sub>2</sub>O at the present level [1-3].

In the main effluent streams, N<sub>2</sub>O is emitted with additional gases such as O<sub>2</sub>, NO, CO<sub>2</sub>, CO, CH<sub>4</sub>, SO<sub>2</sub> and water vapor. These gases may affect the catalytic activity, either competing or enhancing the N<sub>2</sub>O decomposition [4-6]. Some of the main industrial sources of nitrous oxide are the production of adipic and nitric acids, combustion processes and the automotive emissions [4].

The aim of this work was to investigate N<sub>2</sub>O decomposition in the presence of additional gases (O<sub>2</sub>, NO, CO<sub>2</sub>, CO, CH<sub>4</sub>, SO<sub>2</sub> and water vapor) over Cu-ZSM-5 catalysts with different copper loadings.

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## EXPERIMENTAL

The Cu-ZSM-5 (CZX) samples were prepared using the method proposed by Iwamoto *et al.* [7]. Copper ions were exchanged with Na-ZSM-5 (1 g zeolite/67 mL solution) with copper nitrate solution (0.004-0.01 mol L<sup>-1</sup>). The suspension was stirred for 24 h and diluted ammonia was added dropwise up to pH = 7.0. The suspension was further stirred for 1 h before filtering, washing and vacuum drying. The samples obtained were calcined at 500°C, for 3 h, under flowing dry air.

Chemical compositions were determined using an ARL ICP-AES, model 3410. Surface area for the zeolitic material was determined by N<sub>2</sub>-BET. Powder X-ray patterns were collected on a Shimadzu, XD-3A diffractometer. TPR experiments were carried out in 5%H<sub>2</sub>/N<sub>2</sub> (flow rate = 30mL min<sup>-1</sup>), starting from 24 to 600°C, with a heating rate of 8°C min<sup>-1</sup>. A thermal conductivity detector was used to monitor the H<sub>2</sub> effluent. Prior to measurements the samples (50 mg) were dried and degassed under flowing dry air, at 500°C, for 1 h.

Reaction experiments were carried out using a continuous flow microreactor operated at ambient pressure. Before testing, the catalyst samples (100 mg) were pretreated for 3 h in flowing helium, at 500°C. Activity tests were performed using a total flow of 150 cm<sup>3</sup> min<sup>-1</sup> of the feed gas (GHSV= 45000h<sup>-1</sup>), at a temperature range of 300-550°C. Feed and product gases were analyzed by gas-chromatography, using a TCD, a 5A Molecular Sieve and a Porapak Q columns. The standard feed composition used for the testes was 0.5% N<sub>2</sub>O in He. The additional gases (7% O<sub>2</sub>, 0.5% NO, 5% CO<sub>2</sub>, 1% CO, 1% CH<sub>4</sub>, 75 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O) were supplied to the reactor, using He as carrier. For reaction runs involving addition of water vapor to the feed, a glass saturator containing deionized water kept at 20°C was used to saturate the feed gas with 10% water vapor.

## RESULTS AND DISCUSSION

Chemical compositions and the surface area for the zeolite catalysts are shown in Table 1. The surface area decrease for CZ2 suggested that some pore blocking might have occurred during the preparation of the over-exchanged Cu-ZSM-5. However, the XRD pattern collected for CZ2 did not show the formation of detectable crystallites of CuO or Cu<sub>2</sub>O. If copper oxides were formed, they might be smaller than 4 nm and well dispersed in the zeolite framework.

The reduction profiles and quantitative analyses of the Cu-ZSM-5 are shown in Fig. 1. For CZ1 (CE<100%), isolated Cu<sup>2+</sup> ions in charge compensation positions corresponded to nearly 68% of the exchanged copper. In opposition,

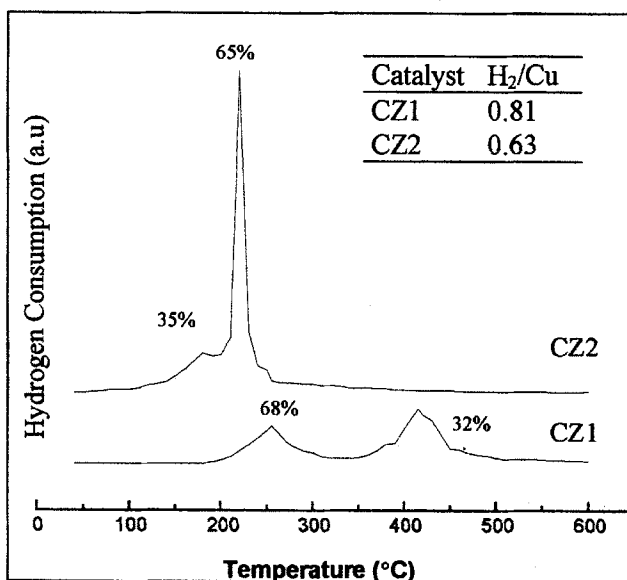
for CZ2 (CE>100%), cationic copper species, bearing an extra-lattice oxygen ( $\text{Cu-O-Cu}^{2+}$ )<sub>n</sub> seemed to be more likely exchanged with the zeolite. Furthermore, the  $\text{H}_2/\text{Cu}$  molar ratio suggested that  $\text{Cu}^+$  is better stabilized in the over-exchanged Cu-ZSM-5 [8].

**Table 1**  
Compositions and surface area of the Cu-ZSM-5 catalysts

Catalyst	%Cu (nominal)	%Cu <sup>a</sup> (experimental)	Si/Al	Cu/Al	%C.E. <sup>b</sup>	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )
Na-ZSM-5	-	-	21	-	-	310
CZ1	1.5	1.75	22	0.40	80	284
CZ2	4.0	3.97	22	0.93	186	239

<sup>a</sup> Determined by ICP-AES.

<sup>b</sup> Calculated considering  $\text{Cu/Al} = 0.5 = 100\%$



**Fig. 1.** TPR profiles and quantitative analyses for the Cu-ZSM-5 catalysts

The steady-state activities of 0.5%  $N_2O$ , in the presence of additional gases and as a function of the reaction temperature, are shown in Fig. 2, a and b, respectively, for CZ1 and CZ2.

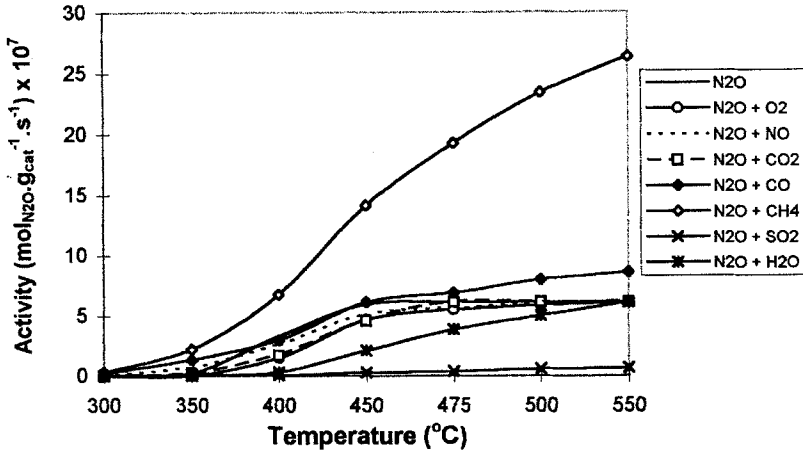


Fig. 2a. Steady-state activity of  $N_2O$  as a function of the temperature, in the presence of additional gases, over CZ1 (Cu-ZSM-5, CE=80%)

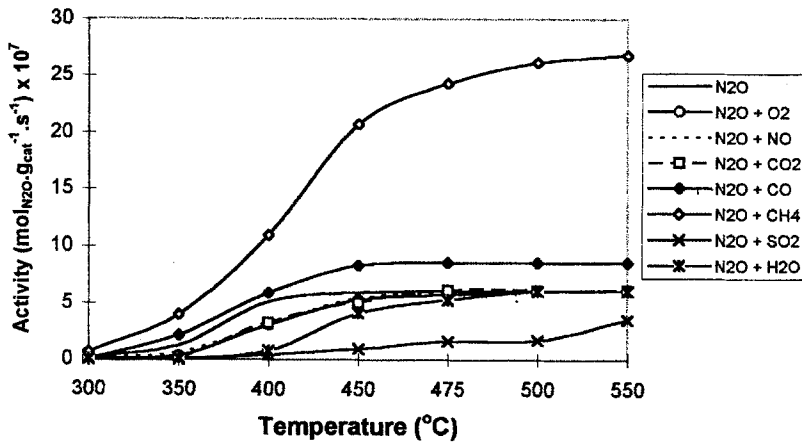


Fig. 2b. Steady-state activity of  $N_2O$  as a function of the temperature, in the presence of additional gases, over CZ2 (Cu-ZSM-5, CE=186%)

The decomposition activity increased with increasing the cation exchange level but different effects were observed in the presence of O<sub>2</sub>, H<sub>2</sub>O, NO, CO<sub>2</sub> and SO<sub>2</sub>, ranging from inhibition due to competitive adsorption up to deactivation due to poisoning. These effects were more significant at lower temperatures, namely ≤ 450°C, and seemed to depend on the nature and distribution of the copper species in the zeolite and on the nature of the additional gas.

The simplest reaction mechanism [4],  $N_2O + * \rightarrow N_2 + O^*$  (\* is a surface active center), is usually envisaged as a charge donation from the catalysts into the antibonding orbitals of N<sub>2</sub>O. At higher temperatures, the oxygen desorption is thermodynamically favored and the subsequent mechanism step,  $2O^* \rightarrow O_2 + 2*$ , no longer limits the reaction. As oxygen, water inhibited the reaction due to competitive adsorption but hydrothermal deactivation may occur after longer runs. Furthermore, the formation of stable intermediates such as carbonates and sulfates might affect the catalytic activity to different extents. SO<sub>2</sub> deactivated the Cu-ZSM-5 catalysts, whereas CO<sub>2</sub> partially inhibited the reaction only at temperatures ≤ 400°C. NO competed with N<sub>2</sub>O for the decomposition sites on the catalysts but the formation of nitrates or nitrites was not observed [8]. Neither SO<sub>3</sub> nor NO<sub>2</sub> was appreciably formed under the reaction conditions, although SO<sub>3</sub> formation seemed to be favored over CZ1 (CE<100%).

On the other hand, reductant gases such as CO and CH<sub>4</sub> enhanced the N<sub>2</sub>O decomposition activity over the Cu-ZSM-5 catalysts, since they can remove adsorbed oxygen according to  $CO + O^* \rightarrow CO_2 + *$ . Both methane combustion and nitrous oxide decomposition were favored over CZ2 (CE>100%). The release of surface oxygen was envisaged as a means of improving the catalytic activity, regenerating the reduced active sites. Methane was gradually converted to CO<sub>2</sub> up to 550°C over Cu-ZSM-5, using either surface bonded oxygen, originating from N<sub>2</sub>O decomposition, or extra-lattice oxygen, provided by the cationic copper oligomers in over-exchanged Cu-ZSM-5 catalysts, as previously determined by TPR.

Thus, the data presented above indicated that over-exchanged Cu-ZSM-5 were more active and less sensitive to the presence of additional gases in the feed than Cu-ZSM-5 bearing CE<100%. Oxidant gases inhibited the catalytic activity due to competitive adsorption or deactivated the catalyst by poisoning or dealumination. Reductant gases enhanced the N<sub>2</sub>O decomposition activity, removing oxygen from the catalysts surface.

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