Decomposition of nitrous oxide in excess oxygen over Co- and Cu-exchanged MFI zeolites

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Received 7 August 1995; accepted 12 December 1995

The decomposition of nitrous oxide on several Co- and Cu-ZSM-5 zeolite catalysts was studied in the absence and presence of excess oxygen. Also, the effect of methane addition, as well as catalyst steaming in dry and wet feeds is reported. N_2O decomposition with no oxygen in the feed was proportional to metal loading on both catalysts. Co-ZSM-5 was much more resistant than Cu-ZSM-5 in excess oxygen. The tolerance of Co-ZSM-5 catalysts to excessive amounts of oxygen is high when Co^{2+} is stabilized in the zeolite framework and depends on the catalyst method of preparation. The presence of methane with no oxygen in the feed enhanced N_2O decomposition while the addition of both methane and oxygen to the feed decreased N_2O conversion on all catalysts tested. Co^{2+} ions stabilized by ZSM-5 framework have high hydrothermal stability in comparison to Cu^{2+}-exchanged ZSM-5.

Keywords: nitrous oxide; decomposition; methane combustion; Co-ZSM-5; Cu-ZSM-5; emission control; metal exchange; ZSM-5; zeolite

1. Introduction

Nitrous oxide is a strong, long-lived absorber of infrared radiation and as such contributes to enhancement of the greenhouse effect. The contribution of nitrous oxide to the greenhouse effect has been rising steadily and was about 6% in the 1980's [1]. Nitrous oxide also acts as a nitric oxide precursor in the stratosphere and in this way plays an important role in the depletion of the ozone layer [2]. A doubling in the atmospheric N_2O concentration could result in a 12% decrease in the total stratospheric ozone [2].

Nitrous oxide enhancement in the atmosphere is mainly due to anthropogenic sources such as burning fossil fuels in mobile and stationary sources. However, the largest amounts of N_2O released into the atmosphere by human activities come from land cultivation and are associated mainly with the use of fertilizers. Biomass burning, nitric acid production and the manufacture of adipic acid (used in nylon production) complete the inventory of known sources [1].

The atmospheric lifetime of nitrous oxide is about 150–160 years [4]. Any reduction in its amount now will not bring about any improvement until after many decades. It has been estimated that in order to stabilize N_2O atmospheric concentration at the current level, a 70–80% reduction in human-made emission of this gas is required [4]. Therefore, there is a need to develop catalytic methods to avoid emission of nitrous oxide into the atmosphere.

Li and Armor [5] have shown that Cu- and Co-ion-exchanged ZSM-5 zeolites are highly active catalysts for the decomposition of N_2O under milder conditions than on previous reported catalysts. Furthermore, the same authors reported [6] the effect of low oxygen concentrations and/or methane addition on nitrous oxide decomposition over Co-ZSM-5. The aim of the present work is to compare the activities of various Co- and Cu-ion-exchanged ZSM-5 zeolites for nitrous oxide decomposition in the absence and presence of excessive amounts of oxygen. Furthermore, the effect of methane addition, as well as catalyst steaming with and without oxygen in the feed under dry and wet conditions was studied over these catalysts.

2. Experimental

2.1. Catalyst preparation

Cu- and Co-ZSM-5 zeolites were prepared by exchanging Cu^{2+} or Co^{2+} into Na-ZSM-5 samples in aqueous solutions. The parent Na-ZSM-5 sample was prepared in our lab via a template-free method [7]. Dilute aqueous solutions (0.05 or 0.1 M) of acetate or nitrate metal salts were used for the exchange. Aliquots (1 g) of parent Na-ZSM-5 were added to 100 ml solution with vigorous stirring using a magnetic stirrer. Various procedures were used for the exchange as specified by numbers in parentheses in table 1. After exchange the sample was exhaustively washed with deionized water, filtered and dried at 100°C. The metal-exchanged zeolite samples were analyzed for Si, Al, Na and the exchanged metal by atomic absorption spectroscopy. The compositions are listed in table 1.

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Table 1
Catalyst compositions

Catalyst[a]	Si/Al atomic ratio	Metal/Al atomic ratio	Metal (wt%)	Na/Al atomic ratio
Na-ZSM-5	14	0.80	1.62	0.80
Cu-ZSM-5(1)	14	0.47	2.80	0.06
Cu-ZSM-5(2)	14	4.12	17.50	0.05
Cu-ZSM-5(3)	14	1.38	6.84	0.13
Co-ZSM-5(1)	14	0.17	0.88	0.44
Co-ZSM-5(2)	14	0.43[b]	1.99	0.39
Co-ZSM-5(2)	14	0.47[b]	2.24	0.39

[a] (1) Co^{2+}or Cu^{2+} from 0.05 M nitrate salt was exchanged once into Na-ZSM-5 zeolite at 80°C, 24 h. (2) Co^{2+}or Cu^{2+} from 0.1 M acetate salt was exchanged into Na-ZSM-5 zeolite at 94°C for 3 h. The procedure was repeated three times. (3) Cu^{2+} from 0.1 M acetate salt was exchanged into Na-ZSM-5 zeolite at 80°C, 24 h. The procedure was repeated three times.

[b] Co/Al ratios are too high for theoretical stoichiometric exchange. Probably localized high pH in zeolite precipitated some Co^{2+} in zeolite channels.

2.2. *Reaction studies*

The catalytic activities were measured at atmospheric pressure in a SS-316 reactor (1/4″ o.d.), in a steady-state plugged-flow mode. The catalyst was pelletized, crushed and then sieved to 50–70 mesh before use. Typically 0.1 g of sample was packed into a 1 cm long bed held between plugs of quartz wool at the center of an electrical furnace. The temperature was monitored by a J-type thermocouple placed externally adjacent to the center of the catalyst bed. The catalysts were given a standard pretreatment. Samples were dehydrated in flowing helium at 500°C for 3 h. The usual temperature ramping was 5°C/min. The flow rate of the feed was 100 cm^3/min (GHSV = 30 000). The concentration of N_2O was 1% in helium. When methane was added its flow was adjusted to obtain 1% methane in the mixture. The same procedure was followed with oxygen addition to obtain 2.6, 17, 35 and 50% oxygen in the mixture. For reaction runs involving steamed catalysts and/or addition of water vapor to the feed, helium was saturated with deionized H_2O contained in a sealed glass bubbler with a medium-pore frit surrounded by a heating tape. The bubbler temperature was kept constant to have 10% water in the feed. An ice-cooled condenser was incorporated right after the reactor to protect the GC column from excessive H_2O. The feed and effluent gases were sampled and analyzed by an on-line gas chromatograph (Varian Star 3400) with a thermal conductivity detector (TCD). Two parallel columns at 40°C could be selected through automatic switching valves. A 5A molecular sieve column (1/8″ × 3 ft stainless steel) was used for the separation of N_2, O_2, and CH_4. A Porapak Q column (1/8″ × 3 ft stainless steel) separated CO, air, N_2O, and CO_2. Nitrous oxide and methane conversions were calculated based on disappearance of nitrous oxide and methane respectively.

3. Results and discussion

3.1. *Extent of Cu^{2+} and Co^{2+} ion exchange*

As indicated in table 1, cation exchange into Na-ZSM-5 zeolite samples using 0.05 M copper nitrate aqueous solution, for 24 h at 80°C, led to 94% Cu^{2+} exchange but only 34% Co^{2+} exchange with 0.05 M cobalt nitrate. Using another source of Cu^{2+} and Co^{2+} cations, such as the corresponding acetate salts in 0.1 M aqueous solutions, over-exchanged Cu-ZSM-5 (276% theoretical exchange) was obtained after three exchanges of 3 h at 94°C, compared to 86–94% theoretical Co^{2+} exchange under identical preparation conditions. It seems that Cu^{2+} is more readily exchanged than Co^{2+} into Na-ZSM-5 zeolite. However, in the latter case the Na/Al ratio is too high when compared to the Co/Al ratio. The high Na/Al ratio is probably due to localized precipitation of $Co(OH)_2$ in zeolite channels during Co^{2+} exchange. The real amount of exchanged Co^{2+} ions are probably represented by the amount of Na ion removed. Therefore, labeled Co-ZSM-5(2) samples may sinter easily as could be concluded from the catalytic tests shown below.

3.2. *Reaction studies*

The catalytic activities of Cu-ZSM-5 and Co-ZSM-5 for 1% N_2O decomposition were measured in the absence and presence of oxygen on various catalysts with different copper or cobalt exchange levels but with the same Si/Al ratio, 14. The temperature range was 100–500°C. However, no conversion was observed under 300°C. It has been shown [9] that thermal decomposition of N_2O requires temperatures higher than 330°C, because molecular oxygen produced in the reaction is tightly bound to the catalyst surface below these temperatures. The conversions on these catalysts in the range 300–500°C are shown in figs. 1 and 2, respectively.

Without oxygen in the feed N_2O conversions increased with the level of copper exchanged and leveled off at approximately 500°C on Cu-ZSM-5 catalysts (see fig. 1). Interestingly, the improvement observed in the conversion of nitrous oxide on "excessively ion-exchanged Cu-ZSM-5" is not significative compared to the almost stoichiometrically exchanged catalyst (2.8 wt% Cu-ZSM-5). It has been considered [10] that in "excessively Cu-ion-exchanged ZSM-5" the excess copper easily migrates and fills in the micropore of the catalyst, because the excess copper is not electrically stabilized on the ion exchange site of the zeolite. The addition of 2.6% O_2 to the feed mixture did not affect conversion at temperatures above 500°C. At lower temperatures, conversion modestly decreased with decreasing metal loading. Addition of excessive amounts of O_2 (50%), completely eliminated the activity on a 6.84 wt% Cu-ZSM-5 catalyst. The decomposition of NO and N_2O

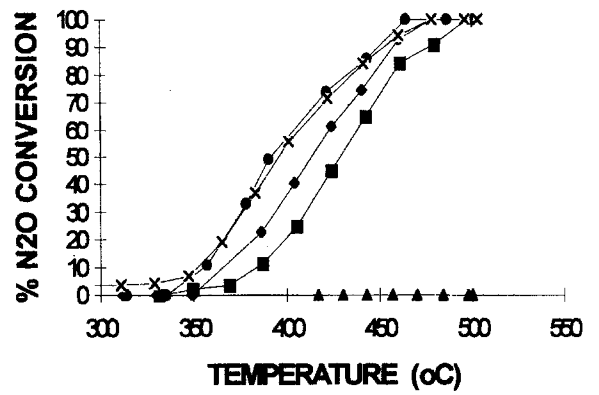

Fig. 1. N_2O decomposition activities of various *copper*-loaded ZSM-5 zeolites, in the presence and absence of oxygen, as function of temperature. The reactions were run on a 0.1 g sample. Total flow rate 100 cm^3/min and $[N_2O]$ = 1% in He. (◆) 2.8 wt% Cu, no O_2; (■) 2.8 wt% Cu, $[O_2]$ = 2.6; (●) 17.5 wt%, no O_2; (×) 17.5 wt% Cu, $[O_2]$ = 2.6%; (▲) 6.8 wt% Cu, $[O_2]$ = 50.0%.

has been described by redox mechanisms on Cu-ZSM-5 and on various metallic oxides [11]. In these cases, the reactant has been considered to be the oxidizing agent and the reduction step of the catalytic cycle has been supposed to occur through the desorption of O_2. These results suggest [11] that the desorption of O_2 plays an important part in these reactions and should lead to an inverse dependence of the decomposition rate on oxygen pressure. As observed in fig. 1, N_2O decomposition activity of 6.8 wt% Cu-ZSM-5 was inhibited by the presence of 50% oxygen in the feed.

In agreement with previous reports [5], fig. 2 shows that conversions on Co-ZSM-5 catalysts with no oxygen in the feed also increase with the level of cobalt exchanged. When O_2 was added to the feed, N_2O decomposition activity of Co-ZSM-5 catalysts varied depending on the amount of O_2 and on the method of catalyst preparation. Similar to the results for Fe(III)-Y reported by Fu and coworkers [12] and for Fe(III)-mordenite reported by Leglise and co-workers [13], the decomposition of N_2O was not inhibited by oxygen on Co-ZSM-5 (0.88 wt% Co) prepared by method (1). Increasing amounts of oxygen (2.6 and 35%) in the feed led to increasing conversions at lower temperatures as compared to no oxygen addition. However, addition of excessive amounts of O_2 (50%) decreased conversion on Co-ZSM-5 (1.99 wt% Co) prepared by method (2). As pointed out, this catalyst may have some Co^{2+}, probably as cobalt oxide, which are not stabilized in the ZSM-5 framework after high temperature treatment. It has been reported [14–16] that oxygen has a strong inhibition effect on N_2O decomposition over metal oxides and perovskites.

N_2O decomposition and methane combustion activities over Cu- and Co-ion-exchanged ZSM-5 materials with feeds consisting of a mixture of 1% N_2O and 1% CH_4 with and without the addition of oxygen are shown in figs. 3–6 respectively. In the absence of oxygen, methane enhanced N_2O conversion on all tested catalysts. Since the reaction products only contained a small amount of O_2 and the fraction of converted methane was mainly CO_2 it seems that nitrous oxide supplies catalyst bound oxygen atoms via its dissociation and these highly reactive oxygen atoms interact with methane which acts to regenerate the active sites by removing surface oxygen. When both nitrous oxide and oxygen were added, nitrous oxide decomposition decreased and methane combustion increased.

As illustrated in fig. 3, N_2O decomposition activity in the presence of methane on Cu-ZSM-5 catalysts increases with increasing metal loading below 470°C and levels off at higher temperatures. Correspondingly, methane combustion is low and a very mild difference is observed with Cu level (see fig. 4). Even though the addition of both methane and oxygen to the feed decreased the N_2O decomposition activity, there is a proportional relation between conversion and metal loading on the

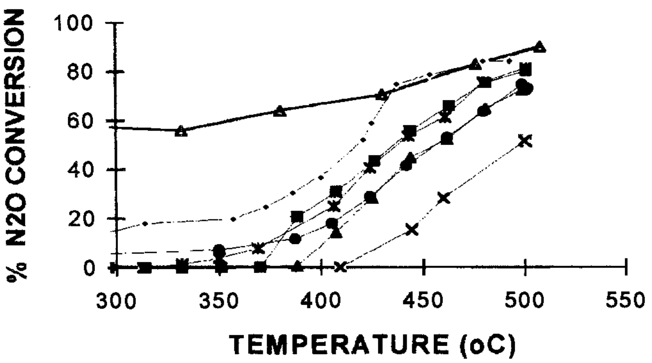

Fig. 2. N_2O decomposition activities of various *cobalt*-loaded ZSM-5 zeolites, in the presence and absence of oxygen, as function of temperature. The reactions were run on a 0.1 g sample. Total flow rate 100 cm^3/min and $[N_2O]$ = 1% in He. (▲) 0.88 wt% Co, no O_2; (●) 0.88 wt% Co, $[O_2]$ = 2.6%; (◆) 2.24 wt% Co, no O_2; (×) 2.24 wt% Co, $[O_2]$ = 50%; (∗) 1.99 wt% Co, no O_2; (■) 1.99 wt% Co, $[O_2]$ = 2.6%; (△) 0.88 wt% Co, $[O_2]$ = 35%.

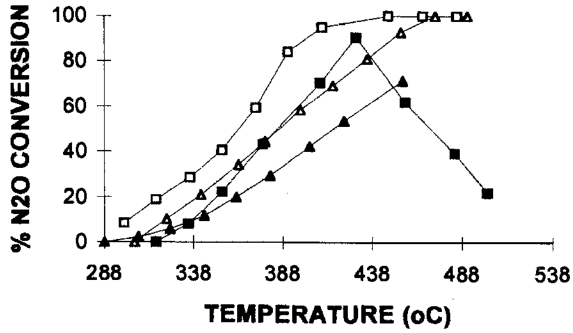

Fig. 3. N_2O decomposition activities of various *copper*-loaded ZSM-5 zeolites, in the presence of methane with and without oxygen in the feed, as function of temperature. The reactions were run on a 0.1 g sample. Total flow rate 100 cm^3/min and $[N_2O]$ = $[CH_4]$ = 1% in He. (△) 2.8 wt% Cu, no CO_2; (▲) 2.8 wt% Cu, $[O_2]$ = 2.6%; (□) 17.5 wt% Cu, no O_2; (■) 17.5 wt% Cu, $[O_2]$ = 2.6%.

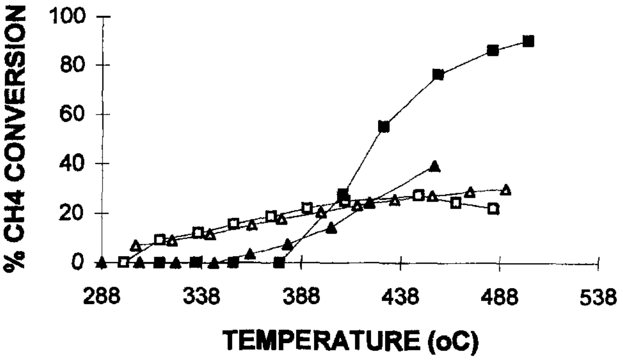

Fig. 4. Methane combustion activities of various *copper*-loaded ZSM-5 zeolites, in the presence of nitrous oxide with and without oxygen in the feed, as function of temperature. The reactions were run on a 0.1 g sample. Total flow rate 100 cm^3/min and $[CH_4] = [N_2O] = 1\%$ in He. (△) 2.8 wt% Cu, no O_2; (▲) 2.8 wt% Cu, $[O_2] = 2.6\%$; (□) 17.5 wt% Cu, no O_2; (■) 17.5 wt% Cu, $[O_2] = 2.6\%$.

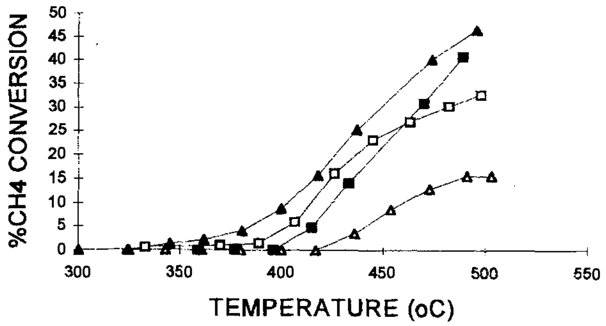

Fig. 6. Methane combustion activities of various *cobalt*-loaded ZSM-5 zeolites, in the presence of nitrous oxide with and without oxygen in the feed, as function of temperature. The reactions were run on a 0.1 g sample. Total flow rate 100 cm^3/min and $[CH_4] = [N_2O] = 1\%$ in He. (△) 0.88 wt% Co, no O_2; (▲) 0.88 wt% Co, $[O_2] = 2.6\%$; (□) 1.99 wt% Co, no O_2; (■) 1.99 wt% Co, $[O_2] = 2.6\%$.

Cu-ZSM-5 catalysts tested (see fig. 3). Under the same conditions, methane combustion also increased with increasing metal loading. The addition of both O_2 and methane led to an abrupt loss of nitrous oxide decomposition activity on the excessively exchanged sample at temperatures higher than 430°C with a corresponding increase in methane combustion.

On Co-ZSM-5 catalysts (see fig. 5), N_2O decomposition activities in the presence of methane differ with metal loading at temperatures under 400°C. The activity of Co-ZSM-5, 0.88 wt% Co, becomes similar and even higher than the activity of 1.99 wt% Co-ZSM-5 at higher temperatures. As shown in fig. 6, methane combustion increases with Co loading. In the presence of both oxygen and methane, N_2O decomposition decreased and methane combustion increased. Again the oxygen inhibition effect for N_2O decomposition was observed on Co-ZSM-5 (1.99 wt% Co) as compared to Co-ZSM-5 (0.88 wt% Co).

The activity for methane combustion under dry conditions on Cu- and Co-ZSM-5 catalysts was tested using excessive amounts of oxygen. As illustrated in fig. 7 Cu-loaded catalysts show more activity than Co-loaded catalysts and the activity increases as the partial pressure of oxygen increases. The activity of Cu-ZSM-5 (6.84 wt% Cu) in a feed containing $O_2/CH_4 = 100$ is much higher than the activity of Cu-ZSM-5 (17.5 wt% Cu) in a feed containing $O_2/CH_4 = 17$. It appears that the increase in partial pressure of oxygen is more effective for methane combustion than copper overloading on ZSM-5. Interestingly, from figs. 6 and 7 it is observed that on Co-ZSM-5 catalysts, methane conversions are higher in presence of monomolecular oxygen via N_2O decomposition than in presence of gaseous O_2 and the activity is proportional to metal loading.

In order to investigate the effect of steaming on the activity of Co- and Cu-ZSM-5 for nitrous oxide decomposition, selected catalyst samples were treated on a 10% water vapor stream for 16 h at 500°C before reaction (figs. 8 and 9). When no water was added to the feed no activity loss is shown on steamed Co-ZSM-5 (0.88 wt% Co) below 500°C (fig. 8). Several minutes after reaching this temperature the activity decreased and remained at

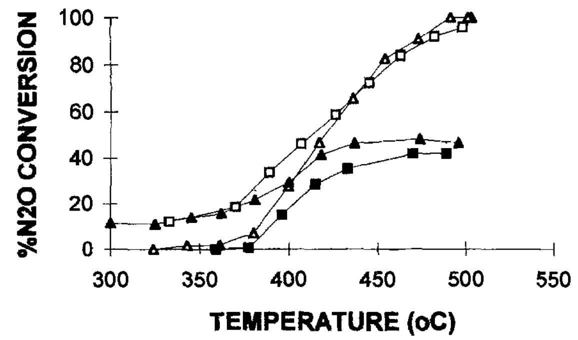

Fig. 5. N_2O decomposition activities of various *cobalt*-loaded ZSM-5 zeolites, in the presence of methane with and without oxygen in the feed, as function of temperature. The reactions were run on a 0.1 g sample. Total flow rate 100 cm^3/min and $[N_2O] = [CH_4] = 1\%$ in He. (△) 0.88 wt% Co, no O_2; (▲) 0.88 wt% Co, $[O_2] = 2.6\%$; (□) 1.99 wt% Co, no O_2; (■) 1.99 wt% Co, $[O_2] = 2.6\%$.

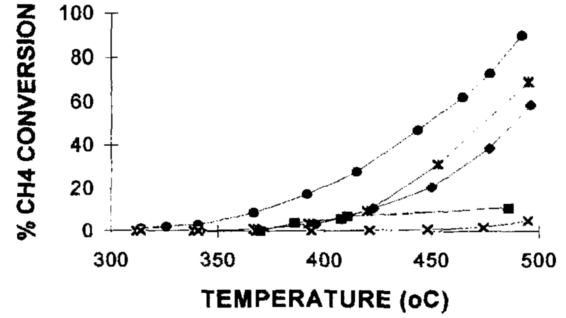

Fig. 7. Methane combustion activities of various *copper*- and *cobalt*-loaded ZSM-5 zeolites as function of temperature. The reactions were run on a 0.1 g sample. Total flow rate 83 cm^3/min. (●) 6.84 wt% Cu, $[CH_4] = 0.5\%$, $[O_2] = 50\%$; (∗) 17.5 wt% Cu, $[CH_4] = 1.0\%$, $[O_2] = 17\%$; (◆) 2.8 wt% Cu, $[CH_4] = 1.0\%$, $[O_2] = 17\%$; (×) 2.24 wt% Co, $[CH_4] = 1.0\%$, $[O_2] = 17\%$; (■) 1.99 wt% Co, $[CH_4] = 0.5\%$, $[O_2] = 50\%$.

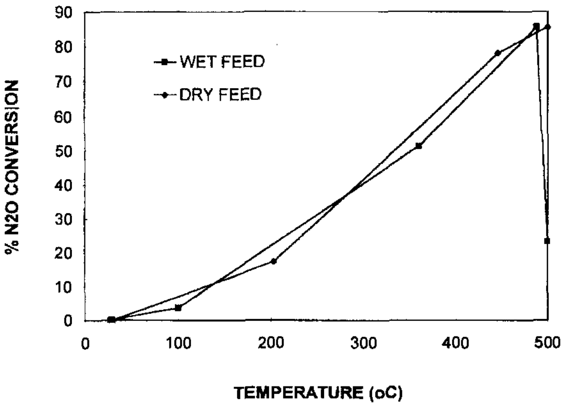

Fig. 8. Effect of water addition on the N_2O conversion over steamed Co-ZSM-5 (0.88 wt% Co) as a function of reaction temperature. GHSV = 30000, $[N_2O] = 1\%$, $[O_2] = 2\%$. For the wet feed $[H_2O] = 10\%$.

approximately 72% conversion (fig. 10). When the temperature was raised to 550 and 600°C the activity was stable at 90 and 95% conversion respectively (fig. 10) suggesting no deactivation by steaming. The addition of 10% water vapor to the feed appeared to increase activity at lower temperatures reaching almost 90% conversion near 500°C (fig. 8). After the catalyst bed reached this temperature the activity decreased to about 23% (fig. 10) showing kinetic inhibition by water. In contrast, Co-ZSM-5 (1.99 wt% Co) lost most of its activity for N_2O decomposition as a result of steaming (not shown). In presence of 2% O_2 and a dry feed, the steamed catalyst showed N_2O conversions between 10 and 20% below 500°C but completely lost its activity in a wet feed. The deactivation of this catalyst may be caused by Co sintering during steaming. On the other hand, Cu-ZSM-5 (2.8 wt% Cu) was not deactivated by steaming. In a dry feed, steamed Cu-ZSM-5 shows increasing N_2O decomposition activity with temperature (fig. 9) and it was stable at 500°C for about 300 min (fig. 11). However, kinetic inhibition by 10% water in the feed is observed in figs. 9 and 11.

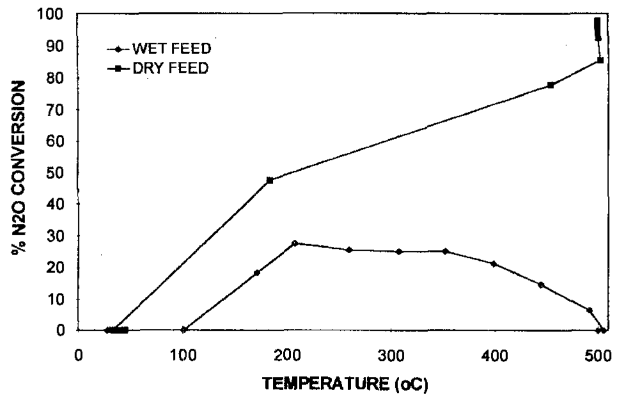

Fig. 9. Effect of water addition on the N_2O conversion over steamed Cu-ZSM-5 (2.8 wt% Cu). GHSV = 30000, $[N_2O] = 1\%$, $[O_2] = 2\%$. For the wet feed $[H_2O] = 10\%$.

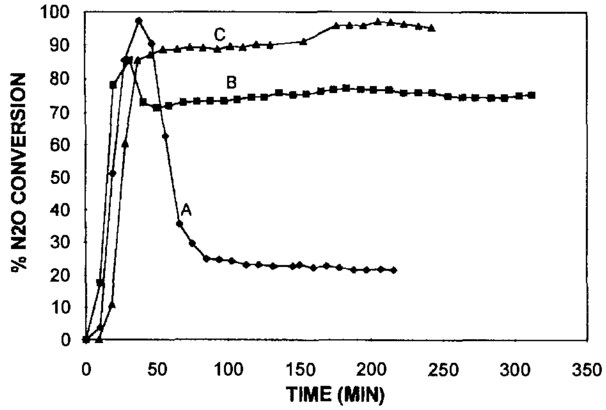

Fig. 10. N_2O conversion vs. time over steamed Co-ZSM-5 (0.88 wt% Co). GHSV = 30000, $[N_2O] = 1\%$, $[O_2] = 2\%$. The reaction was run first adding 10% water to the feed (line A) at 500°C for 2 h. Then, no water was added and the reaction was run at 500°C for 5 h (line B). Finally, the reaction was run again on the same catalyst and the temperature was 550°C for 2 h and 600°C for 1 h.

4. Concluding remarks

(1) The preparation procedure for Co- and Cu-ZSM-5 catalysts is extremely important to obtain Cu^{2+} and Co^{2+} which can be stabilized by the zeolite framework.

(2) Co-ZSM-5 is much more resistant than Cu-ZSM-5 for nitrous oxide decomposition in oxygen-rich atmospheres. Although excessive amounts of Cu in ZSM-5 appear to tolerate moderate concentrations of oxygen, the contribution of such large amount of copper is neither significative for nitrous oxide decomposition nor for methane combustion. Besides, in presence of both oxygen and methane the N_2O decomposition activity on this excessively exchanged Cu-ZSM-5 is almost lost at high temperatures.

(3) Addition of methane with no oxygen in the feed has a positive effect on nitrous oxide decomposition on the tested catalysts. It seems that nitrous oxide decomposition followed by surface reaction of methane with

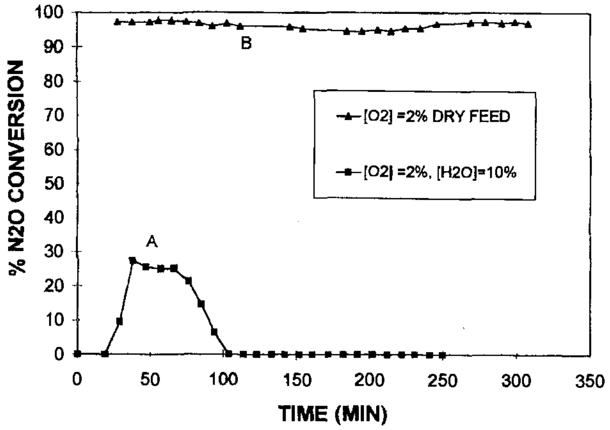

Fig. 11. N_2O conversion vs. time over steamed Cu-ZSM-5 (2.8 wt% Cu). GHSV = 30000, $[N_2O] = 1\%$. The reaction was run at 5°C/min, then 3 h at 500°C (line A). Line B corresponds to a reaction run at 500°C during 300 min.

the product oxygen is the predominant mechanism. Addition of both methane and oxygen decreases nitrous oxide decomposition activity and increases methane combustion on the tested catalysts.

(4) Under dry conditions, Cu-ZSM-5 catalysts are more active than Co-ZSM-5 ones for methane combustion with O_2. However, methane is more efficiently combusted on Co-ZSM-5, using nitrous oxide as an oxygen source instead of O_2.

(5) Co^{2+} positioned in ZSM-5 framework is much more tolerant than Cu-ZSM-5 to wet exhaust streams containing N_2O and oxygen.

Acknowledgement

We are grateful to COLCIENCIAS and Universidad de Antioquia for sponsoring this work.

References

[1] M.A. Wójtowicz, J.R. Pels and J.A. Moulijn, Fuel Process. Technol. 34 (1993) 1.
[2] P.J. Crutzen, in: B. Bolin and R.B. Cook, eds. (Wiley, New York, 1983) pp. 67–112.
[3] J.W. Elkins and R. Rossen, Summary Report 1988: Geophysical monitoring for climatic change, NOAA ERL, Boulder (1989).
[4] J.T. Houghton, G.J. Jenkins and J.J. Ephraums, eds., *Climate Change, The IPCC Scientific Assessment* (Press Syndicate of the University of Cambridge, London, 1990).
[5] Y. Li and J.N. Armor, Appl. Catal. B 1 (1992) L21.
[6] Y. Li and J.N. Armor, Appl. Catal. B 3 (1993) 55.
[7] V.P. Shiralkar and A. Clearfield, Zeolites 9 (1983) 363.
[8] Y. Li and J.N. Armor, Appl. Catal. B 2 (1993) 239.
[9] G.I. Panov, V.Y. Sovolev and A.S. Kharitonov, J. Mol. Catal. 61 (1990) 85.
[10] T. Tabata, M. Kokitsu, O. Okada, T. Nakayama, Y. Yasumatsu and H. Sakane, in: *Catalyst Deactivation*, Stud. Surf. Sci. Catal., Vol. 84, eds. B. Delmon and G.F. Froment (Elsevier, Amsterdam, 1994) p. 410.
[11] J. Valyon and K. Hall, J. Catal. 143 (1993) 520.
[12] C.M. Fu, V.N. Korchak and W.K. Hall, J. Catal. 68 (1981) 166.
[13] J. Leglise, J.O. Petunchi and W.K. Hall, J. Catal. 86 (1984) 392.
[14] E.R.S. Winter, J. Catal. 15 (1969) 144.
[15] E.R.S. Winter, J. Catal. 19 (1970) 32.
[16] G.M. Dhar and V. Srinivasan, Int. J. Chem. Kinet. 14 (1982) 415.