

# Catalytic reduction of N<sub>2</sub>O over steam-activated FeZSM-5 zeolite Comparison of CH<sub>4</sub>, CO, and their mixtures as reductants with or without excess O<sub>2</sub>

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## Abstract

The catalytic reduction of N<sub>2</sub>O by CH<sub>4</sub>, CO, and their mixtures has been comparatively investigated over steam-activated FeZSM-5 zeolite. The influence of the molar feed ratio between N<sub>2</sub>O and the reducing agents, the gas-hourly space velocity, and the presence of O<sub>2</sub> on the catalytic performance were studied in the temperature range of 475–850 K. The CH<sub>4</sub> is more efficient than CO for N<sub>2</sub>O reduction, achieving the same degree of conversion at significantly lower temperatures. The apparent activation energy for N<sub>2</sub>O reduction by CH<sub>4</sub> was very similar to that of direct N<sub>2</sub>O decomposition (140 kJ mol<sup>-1</sup>), being much lower for the N<sub>2</sub>O reduction by CO (60 kJ mol<sup>-1</sup>). This suggests that the reactions have a markedly different mechanism. Addition of CO using equimolar mixtures in the ternary N<sub>2</sub>O + CH<sub>4</sub> + CO system did not affect the N<sub>2</sub>O conversion with respect to the binary N<sub>2</sub>O + CH<sub>4</sub> system, indicating that CO does not interfere in the low-temperature reduction of N<sub>2</sub>O by CH<sub>4</sub>. In the ternary system, CO contributed to N<sub>2</sub>O reduction when methane was the limiting reactant. The conversion and selectivity of the reactions of N<sub>2</sub>O with CH<sub>4</sub>, CO, and their mixtures were not altered upon adding excess O<sub>2</sub> in the feed.

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## 1. Introduction

Nitrous oxide is a powerful greenhouse gas with 310 and 15 times the global warming potential of carbon dioxide and methane, respectively, and was included in the six-gas basket defined by the United Nations Framework Convention on Climate Change in Kyoto (1997) [1]. The harmful effect of N<sub>2</sub>O in our environment is further aggravated by its indirect contribution to the ozone layer depletion as the main precursor of stratospheric NO<sub>x</sub> [2,3]. Due to the anthropogenic action, the atmospheric concentration of N<sub>2</sub>O experiences an annual growth rate of 0.3% (currently 310 ppb) [4], and strategies to control emission of this gas are being intensively explored and in some cases, developed and implemented.

N<sub>2</sub>O emissions that can be reduced in the short term are associated with chemical production and the energy industry

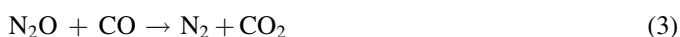
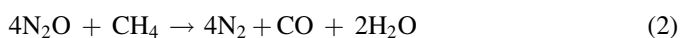
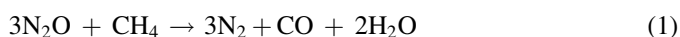
[5,6]. In these sources, catalytic decomposition of N<sub>2</sub>O into N<sub>2</sub> and O<sub>2</sub> is a cost-effective alternative to mitigate this harmful gas, and the identification of promising systems has involved substantial research efforts in the last decade [5,7–10]. A common denominator of N<sub>2</sub>O-containing tail-gases is the coexistence of other components (O<sub>2</sub>, CO<sub>2</sub>, NO<sub>x</sub>, H<sub>2</sub>O, SO<sub>2</sub>, etc.), which often causes adverse effects on the catalyst due to inhibition or poisoning effects, thus limiting its practical application. Iron-containing zeolites are attractive catalysts for N<sub>2</sub>O abatement, exhibiting a unique behavior when these components are present. This includes the insensitivity to O<sub>2</sub>, the positive effect of NO and SO<sub>2</sub> on the rate of N<sub>2</sub>O conversion, and a remarkable resistance towards deactivation by H<sub>2</sub>O [6,11]. Besides, the addition of reducing agents decreases the operation temperature over iron-containing zeolites by selective catalytic reduction (SCR) [12–14]. The latter aspect is of consideration in order to achieve high conversions in low-temperature tail-gases.

Related to this, Delahay et al. [15] showed that CO was a more effective reductant for N<sub>2</sub>O over Fe-beta zeolite (BEA

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structure) in the presence of excess oxygen than propene, *n*-decane, ammonia, and hydrogen. Within light hydrocarbons, Kögel et al. [16] concluded that propane presented higher activities than methane and propene for the simultaneous reduction of NO and N<sub>2</sub>O over FeZSM-5 (MFI structure) in the presence of O<sub>2</sub>. In support of this, van den Brink et al. [17] also showed that propane is a more effective N<sub>2</sub>O reductant than methane over FeZSM-5 in mixtures simulating tail-gases from nitric acid plants, i.e., containing NO<sub>x</sub>, O<sub>2</sub>, and H<sub>2</sub>O besides N<sub>2</sub>O. Contrarily, Kunimori et al. [18] have recently reported that CH<sub>4</sub> reduces N<sub>2</sub>O at lower temperatures than C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> in the presence of O<sub>2</sub> over an ion-exchanged FeZSM-5 catalyst. In addition, this work also claimed that CH<sub>4</sub> is a more efficient reducing agent for N<sub>2</sub>O than CO, although no explanation of this catalytic behavior was provided. The comparison between methane and carbon monoxide in Ref. [18] was made using mixtures with 950–1000 ppm N<sub>2</sub>O and different concentration of reductants (1000 ppm of CO and 500 ppm of CH<sub>4</sub>) and in the absence of O<sub>2</sub>. The stoichiometric amount of CH<sub>4</sub> required to reduce 1 mol of N<sub>2</sub>O is, depending on the selectivity to CO and CO<sub>2</sub> (Eqs. (1) and (2)), 3–4 times lower than that of CO (Eq. (3)). In view of the different reducing power of CH<sub>4</sub> and CO and the excess of methane used in Ref. [18], a fair comparison between both reductants was not established:



In the present work, we have systematically investigated the performance of steam-activated FeZSM-5 in N<sub>2</sub>O + CH<sub>4</sub> and N<sub>2</sub>O + CH<sub>4</sub> + CO mixtures, comparing it with the previously reported N<sub>2</sub>O + CO system over the same catalyst [19,20]. To this end, the reactions were investigated in a broad temperature range using different feed compositions and space velocities. The influence of adding O<sub>2</sub> in the feed mixtures was also studied.

## 2. Experimental

### 2.1. Catalyst preparation

Details on the hydrothermal synthesis of isomorphously substituted FeZSM-5 have been described elsewhere [21–23]. The as-synthesized sample was calcined in air at 823 K for 10 h and converted into the H-form by three consecutive exchanges with an NH<sub>4</sub>NO<sub>3</sub> solution (0.1 M) for 12 h and subsequent air calcination. Finally the zeolite was activated in a flow of nitrogen and steam at 1 bar, using a partial steam pressure of 300 mbar and 30 ml STP N<sub>2</sub> min<sup>-1</sup> at 873 K for 5 h. Detailed characterization studies of the steam-activated FeZSM-5 (Si/Al = 31.3 and 0.67 wt.% Fe) identified various forms of extra framework species, including isolated iron ions and oligonuclear iron species in the zeolite pores, co-existing with iron oxide nanoparticles of 1–2 nm at the external surface of the zeolite crystal [22,23].

### 2.2. Activity tests

Activity measurements were carried out in a fixed-bed quartz reactor (4 mm i.d.) at atmospheric pressure, using 50 mg of catalyst (sieve fraction 125–200 μm, bed height 9 mm), and a gas-hourly space velocity (GHSV) of 10,000 or 90,000 h<sup>-1</sup>. The effect of the feed composition was studied isothermally in gas mixtures with different partial pressures of N<sub>2</sub>O (1.5 mbar), CH<sub>4</sub> (0.2 or 1.5 mbar), CO (0.2, 0.6, or 1.5 mbar), and O<sub>2</sub> (0 or 20 mbar) in He. Before reaction, the catalyst was pre-treated in He at 723 K for 2 h and cooled in that gas flow to the initial reaction temperature. The temperature was increased at intervals of 25 K in the range 475–850 K. This procedure was followed by a stepwise decrease of temperature in 25 K intervals. In this temperature range, deactivation of the catalyst was absent and up- and down-cycles lead to very similar activity curves. Generally, 1 h after a change of conditions (temperature and feed composition), the conversion levels were constant and considered as the steady state. Reactant and product gases were analyzed with a gas chromatograph (HP 6890) equipped with a thermal conductivity detector, using a Porapak Q column (for CH<sub>4</sub>, N<sub>2</sub>O, and CO<sub>2</sub> separation) and a Molsieve 13X column (for N<sub>2</sub>, O<sub>2</sub>, and CO separation).

Along the manuscript, feed mixtures are typically expressed using the ratio of partial pressures. For example, N<sub>2</sub>O/CH<sub>4</sub> = 1.5/1.5 denotes a binary reactant mixture containing 1.5 mbar of each gas with He as balance. Following this example, the molar ratio between reactants is indistinctively denoted as N<sub>2</sub>O/CH<sub>4</sub> = 1.

## 3. Results and discussion

### 3.1. CH<sub>4</sub> versus CO as reductant for N<sub>2</sub>O

Fig. 1 shows the N<sub>2</sub>O conversion versus temperature over steam-activated FeZSM-5 in different feed mixtures. In the absence of reductant, i.e., direct N<sub>2</sub>O decomposition, the catalyst displays a significant N<sub>2</sub>O conversion above 700 K and a complete conversion at 825 K. In the presence of equimolar amounts of methane or carbon monoxide, i.e., N<sub>2</sub>O/CH<sub>4</sub> = 1.5/1.5 or N<sub>2</sub>O/CO = 1.5/1.5 (Fig. 1a), the conversion of nitrous oxide shifts to lower temperatures (up to 150 K with methane). Both reducing agents start to display activity at the similar temperature (above 550 K). However, the slope of the conversion profile with CH<sub>4</sub> is much steeper than with CO. Accordingly, it can be stated that methane is more efficient in the low-temperature N<sub>2</sub>O reduction than carbon monoxide. In this particular experiment, the required temperature for 100% N<sub>2</sub>O conversion is ca. 75 K higher for CO (750 K) than for CH<sub>4</sub> (670 K). The superior low-temperature activity of methane for reduction of nitrous oxide is in agreement with recent work by Kunimori et al. [18].

Table 1 shows the apparent activation energies ( $E_a^{\text{app}}$ ) for N<sub>2</sub>O conversion in N<sub>2</sub>O, N<sub>2</sub>O + CH<sub>4</sub>, and N<sub>2</sub>O + CO mixtures. These were estimated around the inflection of the X versus T curves by assuming a plug-flow model and first-order reaction in N<sub>2</sub>O. As it can be anticipated from the similar slope of the

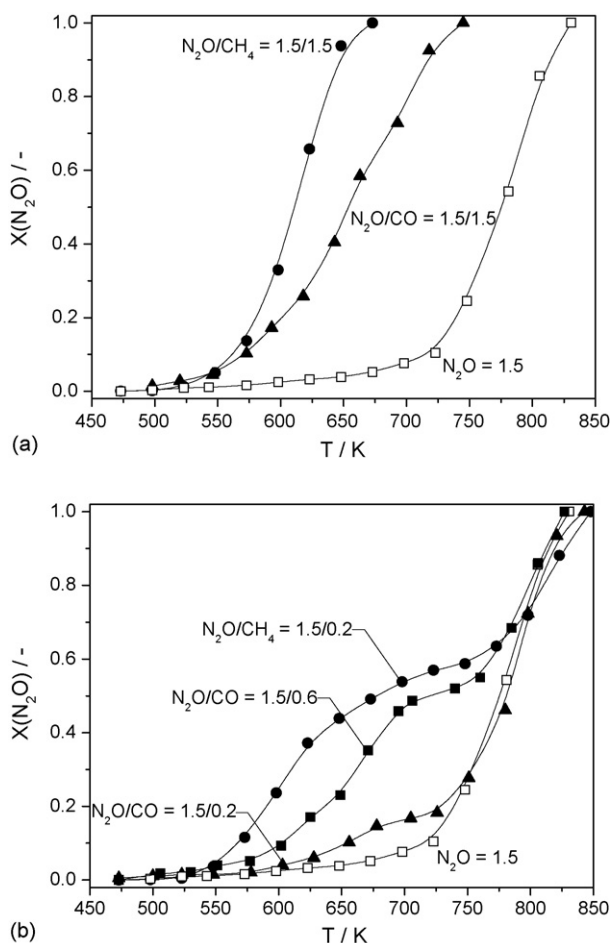


Fig. 1. Conversion of  $\text{N}_2\text{O}$  vs.  $T$  over FeZSM-5 in different feed mixtures of  $\text{N}_2\text{O} + \text{CH}_4$  and  $\text{N}_2\text{O} + \text{CO}$  (labels indicate partial pressures in mbar) at GHSV =  $90,000 \text{ h}^{-1}$  and  $P = 1$  bar. The conversion in direct  $\text{N}_2\text{O}$  decomposition (profile with open symbols) is also included.

conversion profiles, the apparent activation energies in direct decomposition and reduction by  $\text{CH}_4$  are very similar (ca.  $140 \text{ kJ mol}^{-1}$ ). The value of  $E_a^{\text{app}}$  in  $\text{N}_2\text{O} + \text{CO}$  decreases to  $60 \text{ kJ mol}^{-1}$ . These observations are in line with the literature. van den Brink et al. [17] observed that the direct  $\text{N}_2\text{O}$  decomposition and  $\text{N}_2\text{O}$  reduction by  $\text{CH}_4$  and  $\text{C}_3\text{H}_8$  over ion-exchanged FeZSM-5 have very similar apparent activation energies. Kapteijn et al. [24] and Pérez-Ramírez et al. [25] noticed a significant decrease of  $E_a^{\text{app}}$  in  $\text{N}_2\text{O}$  reduction by CO as compared to direct  $\text{N}_2\text{O}$  decomposition using FeZSM-5 and Fe-beta zeolites, respectively, with absolute values in good agreement with those reported here.

Table 1

Apparent activation energies for  $\text{N}_2\text{O}$  conversion in different feed mixtures, using 1.5 mbar of  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and CO, 20 mbar  $\text{O}_2$ , and He as the balance gas

Mixture	$E_a^{\text{app}}$ ( $\text{kJ mol}^{-1}$ )
$\text{N}_2\text{O}$	140
$\text{N}_2\text{O} + \text{CH}_4$	135
$\text{N}_2\text{O} + \text{CO}$	60
$\text{N}_2\text{O} + \text{CH}_4 + \text{CO}$	110
$\text{N}_2\text{O} + \text{CH}_4 + \text{O}_2$	130
$\text{N}_2\text{O} + \text{CH}_4 + \text{CO} + \text{O}_2$	105

The different activation energy for  $\text{N}_2\text{O}$  conversion over steam-activated FeZSM-5 in  $\text{N}_2\text{O} + \text{CH}_4$  and  $\text{N}_2\text{O} + \text{CO}$  is likely related to the different nature of the active iron sites and reaction mechanism associated with the reducing agents. Recent studies using in situ UV/vis spectroscopy [20] and transient isotopic studies in a temporal analysis of products (TAP) reactor [26] have concluded that isolated Fe(III) species in extra framework positions of the zeolite are essential for  $\text{N}_2\text{O}$  reduction by CO, according to their affinity to strongly coordinate carbon monoxide. On the other hand, several authors have concluded in the light of detailed mechanistic studies that oligonuclear iron-oxo clusters are preferred sites in the reduction of  $\text{N}_2\text{O}$  with light hydrocarbons such as  $\text{CH}_4$  [18,27] and  $\text{C}_3\text{H}_8$  [26,28]. Previously, some of us reported that CO is active over isolated iron sites [20], mainly present in the steam-activated Fe-silicalite catalyst used (ca. 70%). This sample proved to be more active for CO oxidation than for  $\text{C}_3\text{H}_8$  oxidation with  $\text{N}_2\text{O}$  [26], which may suggest that oligonuclear iron species are more relevant for propane conversion. We could assume that methane and propane participate in  $\text{N}_2\text{O}$  reduction following a similar mechanism. This can be suggested from the excellent agreement between the work of Kunimori et al. [18] with  $\text{N}_2\text{O} + \text{CH}_4$  and our recent work in the TAP reactor with  $\text{N}_2\text{O} + \text{C}_3\text{H}_8$  [26]. Both studies have concluded the presence of two types of adsorbed atomic oxygen species in the reaction: nascent and thermally accommodated. Furthermore, as mentioned above, Kunimori et al. [18] attributed the activity of the  $\text{N}_2\text{O} + \text{CH}_4$  reaction to binuclear species in FeZSM-5. In good agreement with the above reasoning, the steam-activated FeZSM-5 used in this work, which contains more oligonuclear iron species (ca. 60%) than isolated iron sites (ca. 30%) [20], is more active for  $\text{N}_2\text{O}$  reduction with  $\text{CH}_4$  than with CO. According to this, the reduction of  $\text{N}_2\text{O}$  by  $\text{CH}_4$  over FeZSM-5 seems to occur preferably over oligonuclear iron species, contrarily to the dominant role of isolated sites in the  $\text{N}_2\text{O}$  reduction by CO. Consequently, it is not appropriate to generalize that a certain reducing agent is more efficient than others, since its efficiency

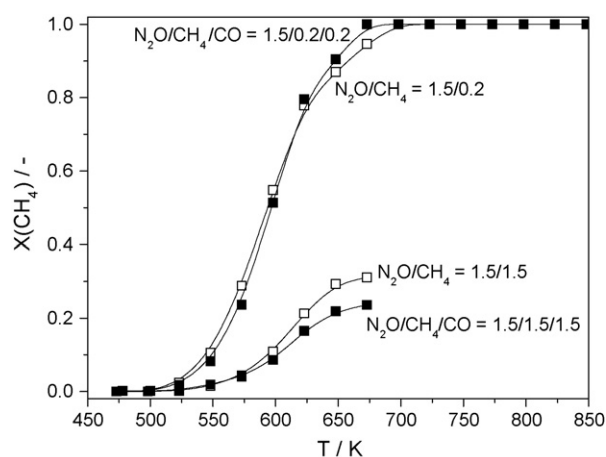


Fig. 2. Conversion of  $\text{CH}_4$  vs.  $T$  over FeZSM-5 in different feed mixtures (labels indicate partial pressures in mbar) at GHSV =  $90,000 \text{ h}^{-1}$  and  $P = 1$  bar.

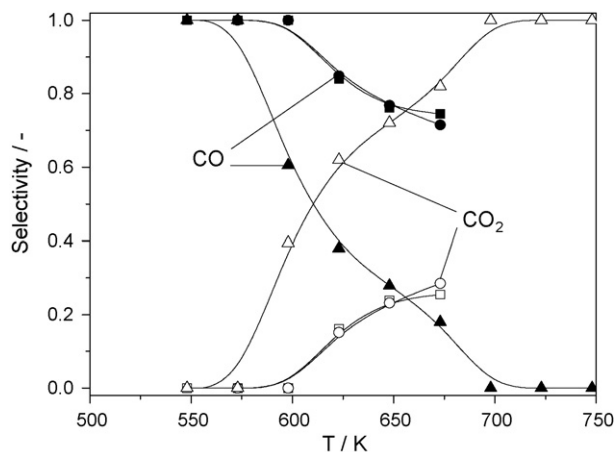


Fig. 3. Selectivity to CO and CO<sub>2</sub> at GHSV = 90,000 h<sup>-1</sup> and  $P = 1$  bar in different mixtures: (●) N<sub>2</sub>O/CH<sub>4</sub> = 1.5/1.5, (▲) N<sub>2</sub>O/CH<sub>4</sub> = 1.5/0.2, and (■) N<sub>2</sub>O/CH<sub>4</sub>/O<sub>2</sub> = 1.5/1.5/20.

will be ultimately determined by the nature of the reductant and the distribution of the iron species in the zeolite.

When the reducing agent was the limiting reactant, i.e., N<sub>2</sub>O/CH<sub>4</sub> or N<sub>2</sub>O/CO = 1.5/0.2, the N<sub>2</sub>O conversion profile experiences a plateau (Fig. 1b) at the temperature at which the reductant is consumed (ca. 725 K for CH<sub>4</sub>, Fig. 2), and the conversion curve

gradually shifts to that of the direct N<sub>2</sub>O decomposition. This plateau is also observed in the CH<sub>4</sub> conversion profile (at 30% conversion, Fig. 2), when N<sub>2</sub>O is totally converted and the latter is the limiting reactant (N<sub>2</sub>O/CH<sub>4</sub> = 1.5/1.5). This was also observed by Kunimori et al. [18] over ion-exchanged FeZSM-5 catalysts. These authors only investigated the N<sub>2</sub>O + CH<sub>4</sub> reaction in excess of reducing agent, so that the conversion of N<sub>2</sub>O reaches 100% before methane was totally converted. In order to establish a proper comparison of CH<sub>4</sub> and CO as N<sub>2</sub>O reductants, the partial feed pressures were adjusted in order to have the same amount of reductant equivalents. This means, attending to the stoichiometry of Eqs. (1)–(3), having a 3–4 times lower CH<sub>4</sub> concentration in the feed mixture compared to CO. To this end, reactions were carried out using mixtures of N<sub>2</sub>O/CH<sub>4</sub> = 1.5/0.2 and N<sub>2</sub>O/CO = 1.5/0.6 (see Fig. 1b). These mixtures exactly have the same reducing power assuming that the selectivity of the N<sub>2</sub>O reduction by CH<sub>4</sub> yields CO with 100% selectivity. As seen in Fig. 3, this is only fulfilled at  $T < 550$  K. Above this temperature, the CO selectivity gradually decreases in favour of CO<sub>2</sub>. However, it is clear that the efficiency of methane for N<sub>2</sub>O reduction is superior to that of carbon monoxide. This can also be concluded by comparing the N<sub>2</sub>O conversion at 625 K in N<sub>2</sub>O/CH<sub>4</sub> = 1.5/0.2 (ca. 40%, solid circles in Fig. 1b) with that at the same temperature in N<sub>2</sub>O/CO = 1.5/1.5 (ca. 25%, solid triangles in Fig. 1a).

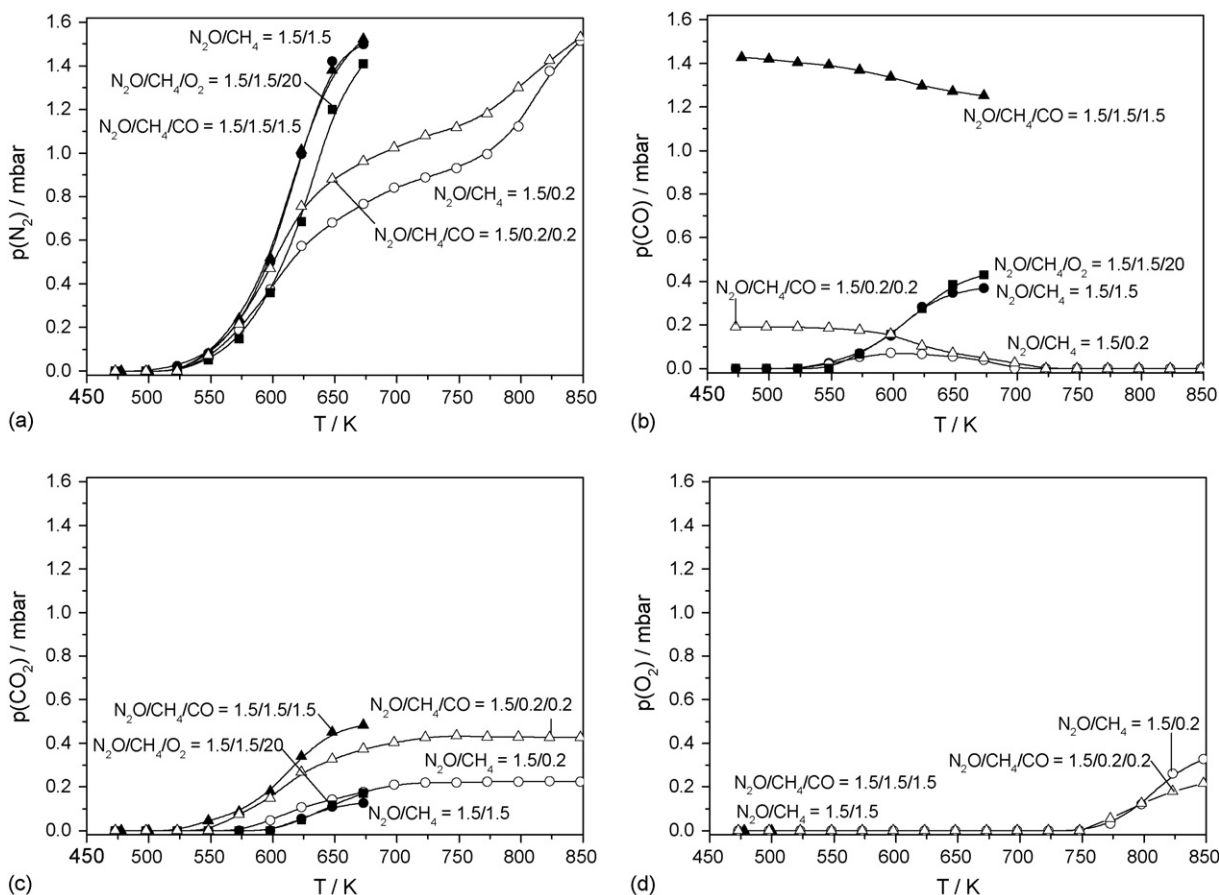


Fig. 4. Partial pressure of N<sub>2</sub>, O<sub>2</sub>, CO, and CO<sub>2</sub> vs.  $T$  over FeZSM-5 in different feed mixtures (labels indicate partial pressures in mbar) at GHSV = 90,000 h<sup>-1</sup> and  $P = 1$  bar.

Fig. 4 shows the partial pressures of reaction products ( $N_2$ ,  $O_2$ ,  $CO$ , and  $CO_2$ ) associated with the experiments in different feed mixtures. As reported in our previous work [19], at molar  $N_2O/CO$  ratios  $\leq 1$  the amount of  $CO_2$  formed equals the amount of  $N_2O$  decomposed and  $N_2$  formed at all temperatures, with no formation of oxygen, in agreement with the stoichiometry of the reaction given in Eq. (3). At molar  $N_2O/CO$  ratios  $> 1$ ,  $O_2$  is produced at temperatures where  $CO$  is consumed, and both direct  $N_2O$  decomposition and  $N_2O$  reduction by  $CO$  take place in the catalyst bed. In the case of  $N_2O$  reduction by methane, at  $N_2O/CH_4 = 1.5/1.5$ , no formation of  $O_2$  was observed and the initial amount of carbon was balanced with that in the effluent, indicating that coke is not formed during the reaction. The selectivity to carbon monoxide ( $S(CO) = 75\%$  at 675 K where  $N_2O$  conversion is complete (solid circles in Fig. 3)) is much higher than that of  $CO_2$ . At  $N_2O/CH_4 = 1.5/0.2$ , the  $N_2$  profile shows a plateau, when  $CH_4$  is totally consumed (similarly to the  $N_2O + CO$  system in Ref. [19]) and the selectivity to  $CO_2$  reaches 100% above 700 K. The production of  $O_2$  starts at 770 K, i.e., when the  $N_2O$  conversion profile shifts to that of direct  $N_2O$  decomposition.

Finally, the influence of the gas-hourly space velocity on the conversion during direct  $N_2O$  decomposition and  $N_2O$  reduction by  $CH_4$  and  $CO$  over steam-activated FeZSM-5 was investigated using equimolar mixtures with 1.5 mbar of each reactive gas. The results in Fig. 5 show that the  $N_2O$  conversion profiles in all these reactions shifted ca. 50 K to lower temperature when the space velocity was reduced from  $90,000 \text{ h}^{-1}$  (open symbols) to  $10,000 \text{ h}^{-1}$  (solid symbols).

### 3.2. $N_2O$ reduction by $CH_4 + CO$ mixtures

Fig. 6 shows the conversion of  $N_2O$  in the binary ( $N_2O + CH_4$  and  $N_2O + CO$ ) and ternary ( $N_2O + CH_4 + CO$ ) systems using different partial pressures of the reducing agents. In the case of mixtures where  $N_2O$  is the limiting reactant (excess of reductant), i.e.,  $N_2O/CH_4/CO = 1.5/1.5/1.5$ , the addition of  $CO$  to the  $N_2O + CH_4$  mixture does not affect the  $N_2O$  conversion profile. The  $CH_4$  conversion slightly decreased from 30% to 20% in the presence of  $CO$  (Fig. 2). An increased  $CO_2$  partial pressure was obtained when adding  $CO$  (Fig. 4c), indicating a higher  $CO_2$  selectivity in the  $N_2O + CH_4 + CO$  mixture as compared to the  $N_2O + CH_4$  mixture.

When the reducing agent was the limiting reactant, as exemplified by the mixture of  $N_2O/CH_4/CO = 1.5/0.2/0.2$ , the  $N_2O$  conversion profile shows a plateau at temperatures at which  $CH_4$  and  $CO$  are consumed, as described earlier for the binary systems (see products distribution in Fig. 4). The  $N_2O$  conversion in  $N_2O/CH_4/CO = 1.5/0.2/0.2$  is significantly higher than in  $N_2O/CH_4 = 1.5/0.2$  due to the contribution of  $CO$  in  $N_2O$  reduction. As shown in Fig. 2, the conversion of  $CH_4$  does not change when adding  $CO$  (0.2 mbar) to the mixture  $N_2O/CH_4 = 1.5/0.2$  (see Fig. 2). The overall  $CO_2$  concentration in Fig. 4c is the sum of the  $CO_2$  coming from  $CH_4$  and  $CO$  conversions. When both  $CH_4$  and  $CO$  are consumed at 725 K,  $O_2$  appears as a product of the direct  $N_2O$  decomposition ( $>750 \text{ K}$ , Fig. 4d).

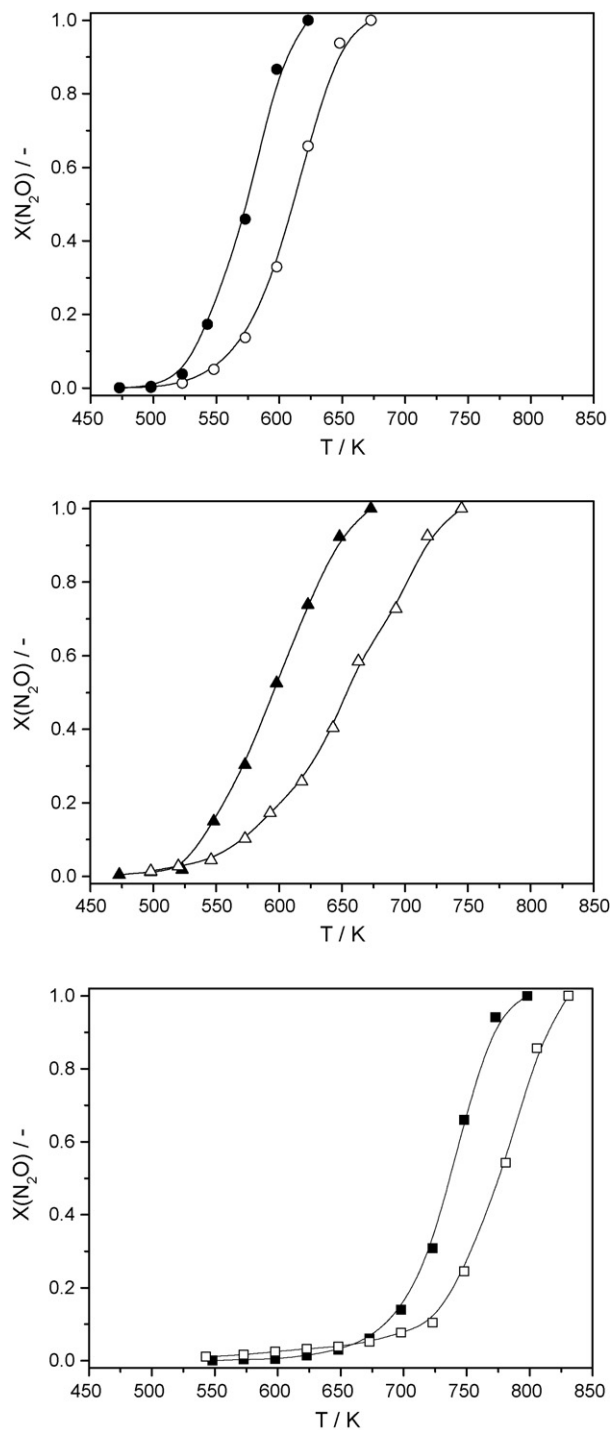


Fig. 5. Effect of the gas-hourly space velocity on the  $N_2O$  conversion vs.  $T$  over FeZSM-5 in equimolar feed mixtures (1.5 mbar of each reactive gas) of  $N_2O + CH_4$  (circles),  $N_2O + CO$  (triangles), and  $N_2O$  (squares). GHSV =  $90,000 \text{ h}^{-1}$  (open symbols) and  $10,000 \text{ h}^{-1}$  (solid symbols).

### 3.3. Influence of $O_2$

The experiments of  $N_2O$  reduction presented so far were carried out in the absence of oxygen. Since relatively high concentrations of oxygen are often present in  $N_2O$ -containing tail-gases, it is important to investigate the catalytic performing upon adding excess  $O_2$  in the feed. Fig. 7 shows the activity of

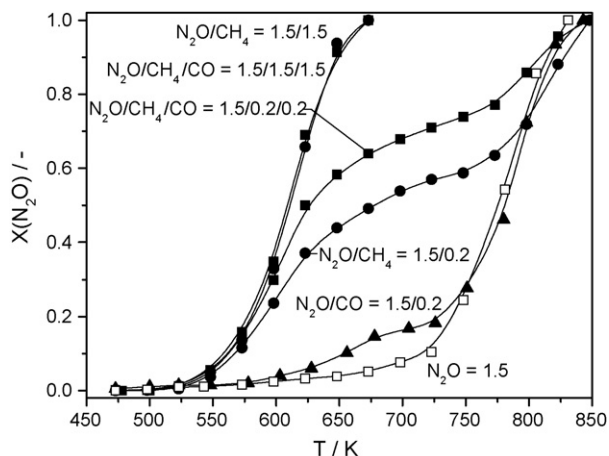


Fig. 6. Conversion of  $N_2O$  vs.  $T$  over FeZSM-5 in different feed mixtures (labels indicate partial pressures in mbar) at GHSV = 90,000  $h^{-1}$  and  $P = 1$  bar.

FeZSM-5 in an equimolar  $N_2O + CH_4 + CO$  mixture (1.5 mbar of each reactive gas) with or without the addition of excess  $O_2$  (20 mbar). The conversions of  $N_2O$  and the reducing agents were not affected by the presence of  $O_2$  in the temperature range investigated. In a similar way, the binary  $N_2O + CO$  and  $N_2O + CH_4$  systems were not affected by  $O_2$  (not shown), confirming the selectivity of the reducing agents for  $N_2O$  on our particular catalytic system. As expected, the apparent activation energies for  $N_2O$  conversion do not change in the absence or presence of oxygen (see Table 1). The selectivity to CO and  $CO_2$  upon methane conversion in the reaction of  $N_2O$  and  $CH_4$  was not changed upon oxygen addition either (Fig. 3). Differently, the work of Kunimori et al. [18] concluded that the  $N_2O$  conversion over an ion-exchanged FeZSM-5 zeolite is shifted to higher temperature when 10 vol.%  $O_2$  is present in the  $N_2O + CH_4$  mixture. Curiously, this result was not elaborated or even mentioned by the authors. Besides, the selectivity to  $CO_2$  increased with oxygen in the feed. At this stage, we do not have a clear explanation for this distinct behavior over these catalysts. However, it should be stressed that the different iron

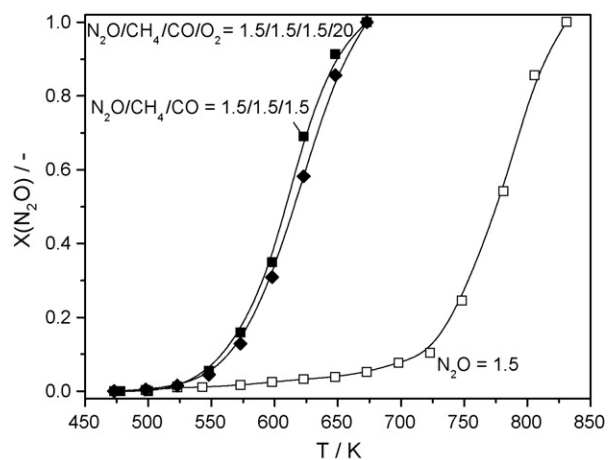


Fig. 7. Effect of  $O_2$  on the conversion of  $N_2O$  vs.  $T$  over FeZSM-5 in an equimolar feed mixture of  $N_2O + CH_4 + CO$  at GHSV = 90,000  $h^{-1}$  and  $P = 1$  bar.

constitution in the materials, principally determined by the preparation approach applied, may directly explain the different catalytic performance. It is well known that the liquid ion-exchanged method of preparation (similar to that in Ref. [18,27]) differs to the steam-activation of isomorphously substituted FeZSM-5 applied here in nature and distribution of iron species as well as catalytic performance [11]. In addition, the oxygen concentration in Ref. [27] was 5 times higher than in this study.

#### 4. Conclusions

Our comparative study of the selective catalytic reduction of  $N_2O$  by  $CH_4$  or  $CO$ , and their corresponding mixtures over steam-activated FeZSM-5 has concluded that  $CH_4$  is a more efficient reducing agent for  $N_2O$  reduction than  $CO$ . For example, complete  $N_2O$  conversion was achieved with methane at a temperature 80 K lower (670 K) than with carbon monoxide (750 K) at a molar  $N_2O/X$  ratio = 1 ( $X = CH_4$  or  $CO$ ). The apparent activation energy in the direct  $N_2O$  decomposition and  $N_2O$  reduction by  $CH_4$  was very similar (140  $kJ mol^{-1}$ ), being significantly lower in  $N_2O$  reduction by  $CO$  (60  $kJ mol^{-1}$ ). The addition of  $CO$  to the  $N_2O + CH_4$  system does not affect the  $N_2O$  conversion when methane is in excess with respect to nitrous oxide. At low partial  $CH_4$  pressures, the  $N_2O$  reduction is shifted to higher temperatures, motivating the contribution of  $CO$  to the  $N_2O$  conversion. Our observations suggest that the reduction of  $N_2O$  by  $CH_4$  and  $CO$  proceed via a markedly different reaction mechanism and might occur over different iron sites of the zeolite. The degree of conversion of the reactants and products selectivity in the binary and ternary systems investigated was not affected by the presence of oxygen in the feed.

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