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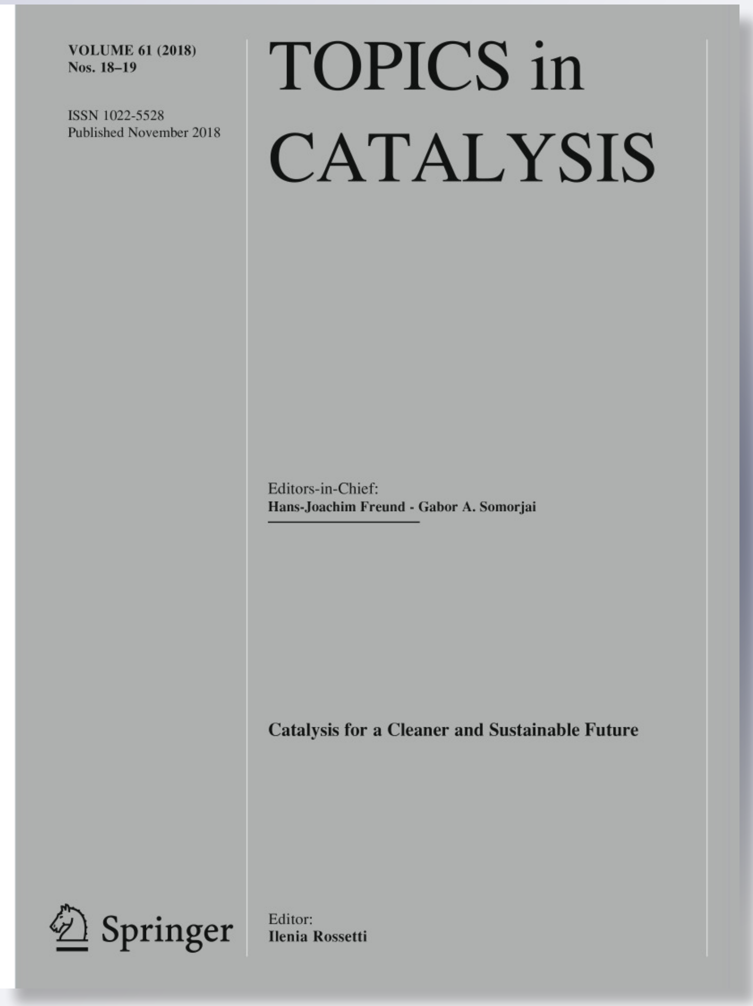

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ORIGINAL PAPER

The Effect of CH_4 on NH_3-SCR Over Metal-Promoted Zeolite Catalysts for Lean-Burn Natural Gas Vehicles

Roberta Villamaina[1] · **Isabella Nova**[1] · **Enrico Tronconi**[1] · **Teuvo Maunula**[2] · **Matthew Keenan**[3]

Abstract

We present a systematic investigation of the deNO$_x$ activity of two commercial metal exchanged zeolite NH_3-SCR catalysts, a Cu-SAPO and a Fe-BEA, in view of their application to the exhaust after-treatment systems of lean-burn natural gas vehicles. The catalytic activity data collected under realistic operating conditions, representative of the after-treatment system of lean-burn vehicles, were compared to those obtained adding methane to the gas feed stream in order to assess the impact of this hydrocarbon, which is usually emitted from natural gas engines, on the NH_3-SCR catalytic chemistry. Our results indicate a negligible impact of methane on the SCR activity at all conditions, but in the presence of a large excess of NO_2 at $T > 400$ °C due to methane oxidation by NO_2. The data collected over the two individual metal-promoted zeolites were also compared with those obtained combining both catalysts in sequential arrangements, in order to take advantage of their complementary high activities in different temperature ranges. The Fe-zeolite + Cu-zeolite sequence outperformed the two individual components in terms of both overall deNOx efficiency and N_2O selectivity, and was equally insensitive to methane.

Keywords NH_3 SCR · Natural gas vehicles · Metal zeolite catalysts · Methane oxidation

1 Introduction

Currently, the abatement of gaseous polluting emissions from combustion processes has become one of the main challenges in the automotive field. The main pollutants in exhaust gases from vehicle engines include carbon dioxide, carbon monoxide, hydrocarbons, nitrogen oxides (NO$_x$), sulfur dioxide and particulates. The use of natural gas (NG), in engines operating in lean conditions, or its blend with diesel can be a good way to produce lower emission compared to those produced by using regular diesel fuel. Indeed, lean operating natural gas fuelled engines have the potential to deliver low CO_2 transportation solutions compared to diesel and dual fuel applications. Operating solely on natural gas provides the emissions control solution with its own unique set of challenges and opportunities. Simultaneous control of methane and oxides of nitrogen is required. In order to comply with the stricter and stricter emission standard limitations (e.g. Euro VI), the development of more advanced exhaust after-treatment technologies plays a key role. In order to purify the exhaust gases emitted by lean-burn natural gas vehicles and meet the current emission limitations, the typical after-treatment system has to comprise two main sections: the first one is dedicated to the oxidation of unburned methane over a dedicated catalyst (MOC—methane oxidation catalyst). The second one is devoted to the abatement of NO$_x$ emissions (SCR—selective catalytic reduction) [1] followed by an ammonia slip catalyst (ASC) which prevents the NH_3 release caused by the limited SCR activity at low temperatures and during rapid changes in engine operation. Understanding the synergies and interactions of these catalyst systems is key to delivering highly efficient and durable after-treatment systems. Moreover, due to the nature of methane combustion and the fuel itself

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not containing carbon–carbon bonds, an exhaust particle filter is not required.

The main challenges are controlling methane, in a lean exhaust which is generally cool and determining the impact of any methane slip on the downstream SCR system. The lean operating natural gas engine operates at exhaust temperatures higher than a diesel but lower than a stoichiometric gasoline. Hence, selection of the most appropriate SCR catalyst is key to meeting the emissions requirements, durability targets and minimising N_2O emissions, which are known to occur over SCR systems. Previous investigations have not studied the impact of methane on zeolite and vanadia based SCR systems as currently there are no dedicated natural gas lean burn engines on the market. Current, natural gas engines operate under stoichiometric conditions. Hence, the focus of this paper is NO_x abatement for a dedicated natural gas engine operating under lean conditions. NH_3/urea SCR is worldwide recognized as the most effective technology for the abatement of NO_x emission form heavy-duty diesel vehicles, with the growing introduction of the same technology for light duty applications [2]. In the SCR technology applied to the after-treatment system of lean-burn engines, nitrogen oxides present in the flue gases can be reduced to harmless N_2 and H_2O through the injection of NH_3/urea over iron- or copper-exchanged zeolite catalysts on monolithic substrates [3–8] or on Vanadia-based catalysts [3, 9, 10]. The SCR process is based on the following three main reactions:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad \text{Standard SCR} \tag{1}$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \qquad \text{Fast SCR} \tag{2}$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \qquad NO_2\ \text{SCR} \tag{3}$$

The MOC upstream of the SCR converter in the exhaust line ensures the presence of NO_2 in the feed stream to the SCR converter, thus enabling improved deNO$_x$ efficiency in the low temperature region where the Fast SCR reaction (2) is by far more active [2, 11–13] than the Standard SCR reaction (1).

As mentioned before, one of the main issues related to the typical after-treatment system for lean-burn NG vehicles concerns the MOC. The long-term use of natural gas (< 10 ppm S content) as fuel in lean-burn engines can cause sulfur poisoning of the after-treatment system and the excess oxygen in the combustion chamber under lean operations leads to lower exhaust gas temperatures [14]. The result is an incomplete conversion of methane in the exhaust, which would thus be present in the exhaust gases downstream of the MOC unit. In general terms, it is well known that the hydrocarbon slip can affect negatively the activity of the SCR catalysts [15–17]. Focusing on short chain hydrocarbons, only C_3H_6 seems to be able to modify the NH_3-SCR catalytic activity. Heo et al. [17] showed how this hydrocarbon affects the SCR-deNO$_x$ activity of V_2O_5/TiO_2, Cu-ZSM-5 and Fe-ZSM-5 based catalysts: at low temperatures, NH_3 and C_3H_6 compete in the adsorption over catalyst surface, while at high temperatures NH_3 is consumed by side reactions, which involve the hydrocarbon. On the other hand, it also known that light hydrocarbons can behave as reducing agents like ammonia and thus contribute to the NO_x removal (Hydrocarbon SCR) [18–23].

Very limited specific information is available about the two possible mechanisms through which CH_4 can interact with NH_3-SCR catalysts at the typical conditions of the after-treatment systems of lean-burn natural gas vehicles. To fill this gap, therefore, the present work aims to investigate the effect of CH_4 on the activity of state-of-the-art NH_3-SCR catalysts. To this end, a systematic catalytic activity study under typical NH_3-SCR conditions both in presence and in absence of methane was performed over state-of-the-art Fe- and Cu-zeolite catalysts, focusing on the main reactions of the SCR system (Standard SCR, Fast SCR and NO_2-SCR).

2 Experimental

SCR runs were performed over two different NH_3-SCR monolith catalysts (thermally stable Cu-SAPO and Fe-BEA), supplied by Dinex Ecocat [24]. A small amount (< 15 wt% of the coating) of binder was mixed to the zeolites in coated catalysts. The Fe-BEA catalyst consisted of a cylindrical rolled metallic substrate whose flat and corrugated metal foils were coated with the catalyst layer (length = 20 mm, diameter = 12.5 mm, volume = 2453 mm^3, coating = 0.42 g). Instead, the Cu-SAPO catalyst was tested in the form of a coated ceramic honeycomb (length: 41.8 mm; height: 7.7 mm; width: 7.7 mm, volume = 2478 mm^3, coating = 0.283 g). The combined systems were realized putting both catalysts in series, so that the total catalyst volume was composed by 50% of the Cu-sample and 50% of the Fe-sample. The catalysts were hydrothermally (HT) aged at 700 °C for 20 h in air flow with 10% of water [24].

Before being loaded in a stainless-steel reactor tube, the samples were wrapped with a tape of inert quartz in order to avoid by-pass of gases. For the same reason, the hole in the center of the cylindrical metallic Fe-BEA catalyst was also plugged with inert quartz wool. The catalysts were topped with quartz spheres, and by a quartz wool layer, in order to increase the turbulence and thus ensure a good mixing of the reactants. The reactor tube (405 mm in length, 15 mm i.d.), containing the catalyst sample, was inserted in a cylindrical electric oven, whose temperature (up to 550 °C) was remotely controlled by a PID controller (Eurotherm model 2132). The reactor was equipped with three K-type thermocouples: one was used to monitor the inlet gas temperature and two were placed in contact with the top and the bottom of the catalyst.

Before starting the tests, the catalysts were subjected to the conditioning pre-treatment by heating them up to 500 °C with a ramp of 15 °C min^{-1} and holding the maximum temperature for 1 h in a continuous flow of 5% (v/v) O_2 with nitrogen balance (75,000 h^{-1} GHSV). Steady state runs were carried out in order to investigate the catalytic activities, using defined reactant feed concentrations and temperature steps. The feed concentrations were chosen as similar as possible to those of real after treatment system: $NH_3 = 500$ ppm, $NO_x = 500$ ppm ($NO_2/NO_x = 0$–1), $O_2 = 5\%$ (v/v), $H_2O = 5\%$ (v/v) and balance N_2. In the specific experiments that aim to the investigation of the hydrocarbon effect on the deNO_x activity 1000 ppm of CH_4 were also fed.

H_2O was metered by a volumetric piston pump (Gilson model 305): the feed rate was around 0.025 mL min^{-1} ±0.0001 for GHSV = 75,000 h^{-1}. Afterwards, the liquid feed was vaporized in a hot pipeline kept at 190 °C, and then mixed with the other gaseous species and fed to the reactor.

A wide range of temperature (150–550 °C) was investigated for each adopted experimental condition and all the experimental runs were realized using the GHSV of 75,000 h^{-1}. The GHSV was calculated as the flow rate divided by the overall volume of the monolith catalysts.

All the gaseous species (except N_2) were continuously monitored at the reactor outlet by a FT-IR gas analyzer (Bruker MATRIX MG5).

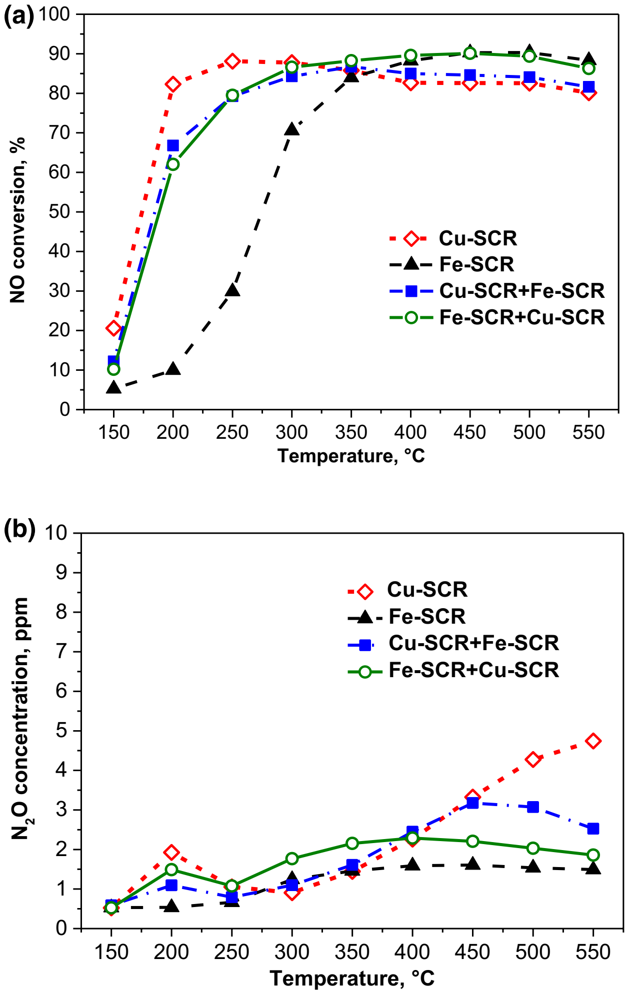

Fig. 1 Steady-state NO conversions (**a**) and N_2O concentrations (**b**) obtained in the Standard SCR reaction over Cu-zeolite, Fe-zeolite, Fe- + Cu-zeolite and Cu- + Fe-zeolite sequential systems. GHSV = 75,000 h^{-1}, $NH_3 = 500$ ppm, NO = 500 ppm, $O_2 = 5\%$ (v/v), $H_2O = 5\%$ (v/v), $T_{range} = 150$–550 °C

3 Results and Discussion

3.1 Standard SCR

SCR reactivity of the NH_3–NO–O_2 mixture was studied at steady state conditions over the 150–550 °C temperature range for all tested catalysts. For this purpose, 500 ppm of NO and 500 ppm of NH_3 were continuously fed to the reactor in presence of 5% (v/v) of O_2 and 5% (v/v) of H_2O and balance nitrogen. In order to do compare the deNO_x activities of the investigated catalysts, we show NO conversions and N_2O productions in Fig. 1. In the supporting information we provide as well NH_3 conversions and N_2O selectivities, computed according to [$2 \times N_2O$ production/(NH_3 + NO) consumption]. Since N_2O is the only side product of the SCR process, the N_2 selectivity is then just the complement of the N_2O selectivity. Looking at NO conversions and N_2O productions obtained over the Fe- and the Cu-zeolite catalysts, shown in Fig. 1a, b, some considerations can be done. Cu-zeolite data showed a much greater deNO_x activity at low temperature with respect to the Fe-zeolite, as well known [13]. Beyond 250 °C, where the maximum deNO_x efficiency was achieved, NO conversion started to decrease over the copper catalyst. This slight decrease was attributed to the oxidation of the reductant NH_3, which approached complete conversion already at 250 °C (Fig. S1), according to the following reactions

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad (4)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (5)$$

At temperature higher than 350 °C the Fe-zeolite catalyst showed better deNO_x efficiency, reaching 90% of NO conversion at 450–500 °C. Also in this case, however, NO conversion never reached 100% because of the NH_3 oxidation side reactions (4) and (5), which consumes NH_3 (Fig. S1). Literature studies confirm that Cu-zeolites suffer from a greater NH_3 oxidation activity than Fe-zeolite catalysts [13, 25]. Moreover, the copper-based catalyst exhibited worse performance in terms of N_2O production compared to the Fe-zeolite, over which this undesired reaction can be considered negligible.

Hence, the collected data over these two different catalysts indicate that Cu-zeolites are more active at low temperature (< 350 °C) (Fig. 1), while Fe-zeolites are more selective at higher temperatures (> 400 °C) (Fig. S2), in agreement with the literature [25–27]. Since these two catalysts showed their best performance in different temperature regions, a catalytic system comprising both Fe- and Cu-zeolites was tested to exploit potential synergies, as already proposed in previous works [3, 6, 27, 28].

Two sequential arrangements were examined, namely the series with the Cu-zeolite monolith followed by a Fe-zeolite monolith and the reverse configuration. In fact, Fig. 1a contains not only the comparison among the NO conversions obtained at Standard SCR conditions over Cu-zeolite, over Fe-zeolite but also those reached over these two sequential catalyst combinations. The first sequential configuration (Cu-zeolite followed by Fe-zeolite) exhibited a behaviour similar to that of the Cu-zeolite catalyst: a very high NO_x conversion at temperatures below 350 °C, with a maximum NO conversion of about 85% at that temperature, and a decreasing conversion at high temperature, very close to those reached over the Cu-zeolite catalyst only. These data indicate that in the whole investigated temperature region most of the reactants were consumed in the upstream Cu-zeolite section, while the Fe-zeolite was hardly utilized. This is clearly visible at high temperatures: although the Standard SCR reaction over the Fe-zeolite results in higher conversions, NO conversions are equal to those reached over the individual Cu-catalyst which confirms that the NO reduction occurs almost totally over the first section, namely the Cu-zeolite. When the catalyst sequence was reversed, the overall $deNO_x$ performance was improved. At low temperatures, NO_x conversions measured over the two configurations are very similar and they approached those obtained over the copper-zeolite, but at high temperatures the configuration with the Fe-zeolite positioned in front of Cu-zeolite enabled NO_x conversions equal to those of the Fe-zeolite, that again means that the second section of the combined system was not involved in the NO reduction. Since the Fe-zeolite catalyst outperformed the Cu-zeolite in this temperature range, the sequential arrangement in which the Fe-zeolite comes first can be considered the best configuration in order to obtain an overall NO_x conversion at a high level at all the investigated temperatures, in agreement with literature results [27, 28]. Concerning N_2O formation, both sequential configurations allowed to produce about the same amount of N_2O produced over the individual catalysts but lower than that produced over the Cu-zeolite catalyst both in the low and in the high temperature ranges (Fig. 1b). In terms of N_2O selectivity, the two sequential configurations grant better overall performances compared to those of the individual catalysts (Fig. S2). Anyway, due to all the considerations made, we focused the investigation of the other reacting systems and the effect of methane only on the two individual Me-zeolite catalysts and on the sequential arrangement in which the Fe-zeolite is placed before the Cu-one.

As mentioned in Sect. 1 , the main goal of this work is the evaluation of how methane, which is usually contained into exhausts of lean-burn natural gas or duel-fuel engines, interacts with the $deNO_x$ activity of the tested SCR catalysts. Therefore, the SCR catalytic activity runs were replicated with the addition of a fixed concentration of methane to the gaseous feed mixture. Specifically, the Standard SCR reaction was repeated including 1000 ppm of CH_4 in the previous reacting system, varying the temperature between 150 and 550 °C and adopting the same space velocity (75,000 h^{-1}) to the end to compare NO conversions and N_2O productions of the two cases. Hence, Fig. 2 compares NO conversions and N_2O productions in Standard SCR conditions in absence of methane with those obtained including CH_4 in the reacting system (the comparison between the corresponding NH_3 conversions is shown in Fig. S3). It is clearly apparent that, within experimental error (~ ± 5%), the Standard SCR activity in presence of methane shows exactly the same behavior observed without CH_4. Moreover, CH_4 started to be converted at temperatures above 450 °C with the corresponding formation of CO_x only (not shown), as confirmed by the carbon balance which remains equal to 1000 ppm in all the investigated temperature range.

3.2 Fast SCR

NO_x reduction is promoted by the presence of NO_2 in the gas stream, especially at low temperatures, both over Cu- and Fe-zeolite catalysts, although the activity increment is much more dramatic for Fe-zeolites [25, 27, 29]. The effect of NO_2 on the $deNO_x$ activity of the tested Cu-zeolite, the Fe-zeolite and Fe- + Cu-zeolite sequential system was evaluated varying the NO_2/NO_x feed ratio in the NH_3–NO–NO_2 reacting system. Specifically, three levels of NO_2/NO_x were adopted: 0 (which corresponds to the Standard SCR conditions previously presented), 0.5 and 1.

Using a NO_2/NO_x feed ratio equal to 0.5 the $deNO_x$ efficiency was studied under Fast SCR conditions. Hence, the runs were firstly performed feeding to the reactor 500 ppm of NH_3, 250 ppm of NO_2 and 250 ppm of NO ($NO_2/NO = 1$), 5% (v/v) of O_2 and 5% (v/v) of H_2O, with balance nitrogen, and then they were replicated with the addition of 1000 ppm of CH_4. Figure 3a, b shows the results of the

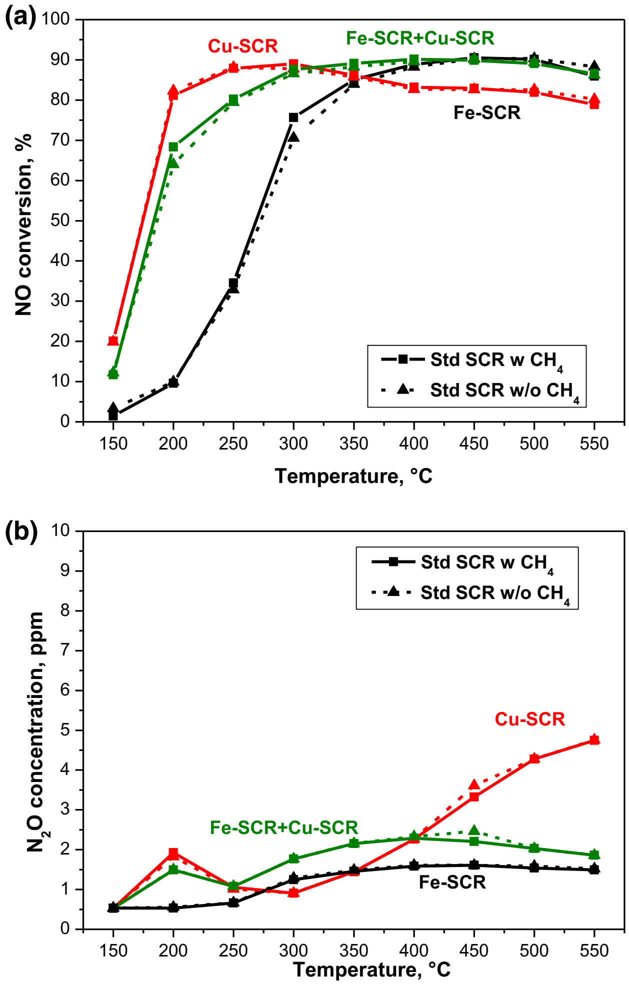

Fig. 2 CH_4 effect on Standard SCR over Cu-zeolite, Fe-zeolite and Fe- + Cu-zeolites sequential system: steady-state NO conversions (**a**) and N_2O concentrations (**b**). GHSV = 75,000 h^{-1}, NH_3 = 500 ppm, NO = 500 ppm, CH_4 = 0–1000 ppm, O_2 = 5% (v/v), H_2O = 5% (v/v), T_{range} = 150–550 °C

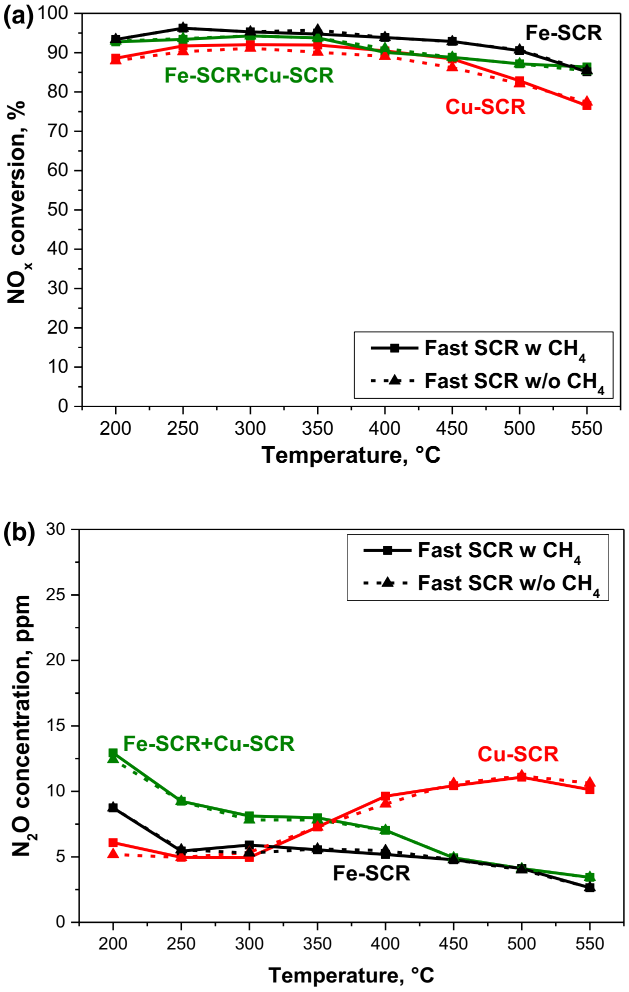

Fig. 3 CH_4 effect on Fast SCR over Cu-zeolite, Fe-zeolite and Fe- + Cu-zeolites sequential system: steady-state NO conversions (**a**) and N_2O concentrations (**b**). GHSV = 75,000 h^{-1}, NH_3 = 500 ppm, NO = 250 ppm, NO_2 = 250 ppm, CH_4 = 0–1000 ppm, O_2 = 5% (v/v), H_2O = 5% (v/v), T_{range} = 200–550 °C

tests in terms of comparison between NO_x conversions and N_2O concentrations when the hydrocarbon is present and absent in the gaseous mixture, measured at steady state in the 200–550 °C T-range over all the tested catalysts. Looking at dotted lines, representative of the results of the reference conditions, namely Fast SCR in absence of CH_4, it is clearly visible that through the occurrence of this reaction boosted deNO_x performances can be obtained in the whole temperature range and over all the investigated catalytic systems with respect to those reached only with the Standard SCR reaction. Specifically, The highest deNO_x activity was reached over Fe-zeolite, with NO_x conversions always above the 85% (Fig. 3a). Cu-zeolite showed a similar trend but with conversions slightly lower than the Fe-zeolite in the whole temperature range. Concerning the NH_3 emissions, Fast SCR conditions enabled to achieve 100% NH_3 conversion almost over the whole investigated temperature range (Fig. S4). As seen for the Standard SCR, also for the Fast SCR the sequence of Fe- and Cu-zeolite catalysts enabled NO_x conversion curves placed between those of the individual catalyst components. At high temperature NO_x conversions decreased over all catalysts due to the occurrence of NH_3 oxidation reaction, which became important above 400 °C reducing the ammonia available for the Fast SCR reaction. However, our data confirm that the Fast SCR reaction is associated with the highest deNO_x activity in the 200–300 °C T-range for all the catalytic systems, as shown in the literature [30, 31].

Concerning N_2O formation (Fig. 3b), again, Fe-zeolite produced the smallest amount of this undesired species in the whole temperature range. In fact, higher N_2O concentrations were detected over the other two systems, in particular the Cu-zeolite showed a maximum of about 10 ppm at 500 °C while the Fe- + Cu-zeolite combination was associated with a maximum of 12 ppm at 200 °C. The corresponding N_2O selectivity data are shown in Fig. S5.

Concerning the impact of methane, negligible changes of the NO_x removal efficiency in the $NO–NO_2–NH_3/O_2$ reacting system were observed upon addition of 1000 ppm of CH_4. Again, under these operating conditions the only reaction which involved methane was its oxidation to CO_x above 450 °C, confirmed by the closure of carbon balance to 1000 ppm (not shown).

3.3 NO_2 SCR

To complete the investigation of the possible impact that methane can have on the NH_3-SCR application, we had examined the case of $NO_2/NO_x = 1$, i.e. at conditions corresponding to the NO_2-SCR reaction. Steady state results were collected in the 200–550 °C T-range both feeding to the reactor 500 ppm of NH_3, 500 ppm of NO_2, O_2 (5%, v/v), H_2O (5%, v/v), and adding 1000 ppm of CH_4 to the same gaseous mixture. In Fig. 4a, c, e the NO_2 and NH_3 conversions were plotted, comparing the base case (0 ppm of methane) and that with the addition of the hydrocarbon over all tested catalysts; instead, in Fig. 4b, d, f the NO and N_2O produced under these operating conditions are shown, again as comparison between the two cases.

Starting from the base case, under NO_2-SCR conditions a catalytic activity was already visible below 250 °C corresponding to a 1/1 NO_2/NH_3 molar consumption ratio, in line with the stoichiometry of ammonium nitrate formation, reaction (6) [9]

$$2NH_3 + 2NO_2 \rightarrow N_2 + NH_4NO_3 + H_2O \quad (6)$$

The Fe-zeolite catalyst showed a higher low-temperature activity with respect to the Cu-zeolite. Such a behavior could be ascribed to the different zeolite structures of the two catalysts, being the BEA zeolite characterized by higher formation of ammonium nitrate due to its larger pores [32]. This can also explain the greater production of N_2O observed below 250 °C, over the Fe-zeolite catalyst, associated with the thermal decomposition of ammonium nitrate according to reaction (7)

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \quad (7)$$

In their study of NH_3-SCR over parent and Cu-promoted zeolites with different frameworks (BEA, CHA, SAPO), Ruggeri et al. [32] proposed that the zeolite pore size is determining for the NH_4NO_3 formation and its subsequent decomposition to N_2O. Our data show in fact a lower production of N_2O over the Cu-SAPO catalyst, which is characterized by a zeolite structure with smaller pores than Fe-BEA [24].

Concerning the sequence of Fe- and Cu-zeolite catalysts, NO_x conversions were in between those measured over the individual Fe- and Cu-zeolite catalysts, thus enabling better deNO_x performances than over the Cu-zeolite, and very similar to the optimal Fe-zeolite catalyst. Unfortunately, however, the N_2O production over the Fe-zeolite + Cu-zeolite sequence was also in between the two individual catalysts below 300 °C, where the Fe-zeolite plays a more important role. Negligible differences were noted instead at higher temperatures (the direct comparison of the three catalytic systems in terms of N_2O selectivity is shown in Fig. S6).

Contrary to Standard and Fast SCR, the NO_2 SCR runs replicated with the addition of 1000 ppm of CH_4 exhibited some differences from those without methane, as apparent from the inspection of Fig. 4. Looking at NO_2 and NH_3 (Fig. 4a, c, e), we can conclude that the presence of CH_4 did not affect the reactivity of all systems up to 400 °C, as the light-off curves are more or less overlapped. Above this temperature, where the ammonia conversion was already complete, the presence of the hydrocarbon resulted in converting more NO_2, specifically in the case of the Cu-zeolite catalyst. At the same time, the production of N_2O remained more or less the same despite the presence of methane, while the NO production above 400 °C was higher when methane was present in the reacting mixture. Moreover, CH_4 was consumed (up about 20% conversion) by oxidation reactions, which produced CO_x species (Fig. 5). These changes in the NO_2 SCR reactivity when methane is present can be rationalized assuming that NO_2 was involved in methane oxidation reactions above 400 °C. The participation of NO_2 to the methane oxidation was supported by a greater conversion of NO_2 at high temperatures when CH_4 was contained in the gaseous mixture, with a corresponding greater production of NO. This strongly suggests the onset of a reactivity between CH_4 and NO_2 at high temperatures over all the investigated catalyst systems.

This last important result needs to be further investigated in more details in a dedicated study in order to clarify the potential of NO_2 in the oxidation of CH_4 and the related effect of the reaction conditions.

4 Conclusions

We have first systematically studied the NH_3-SCR deNO_x activity of Fe-BEA, of Cu-SAPO and of a sequential arrangement of these two commercial metal-exchanged zeolite catalysts at typical operating conditions of after treatment systems for lean-burn engines. Under Standard SCR conditions, the Cu-zeolite is associated with the highest deNO_x efficiency below 350 °C, while in the

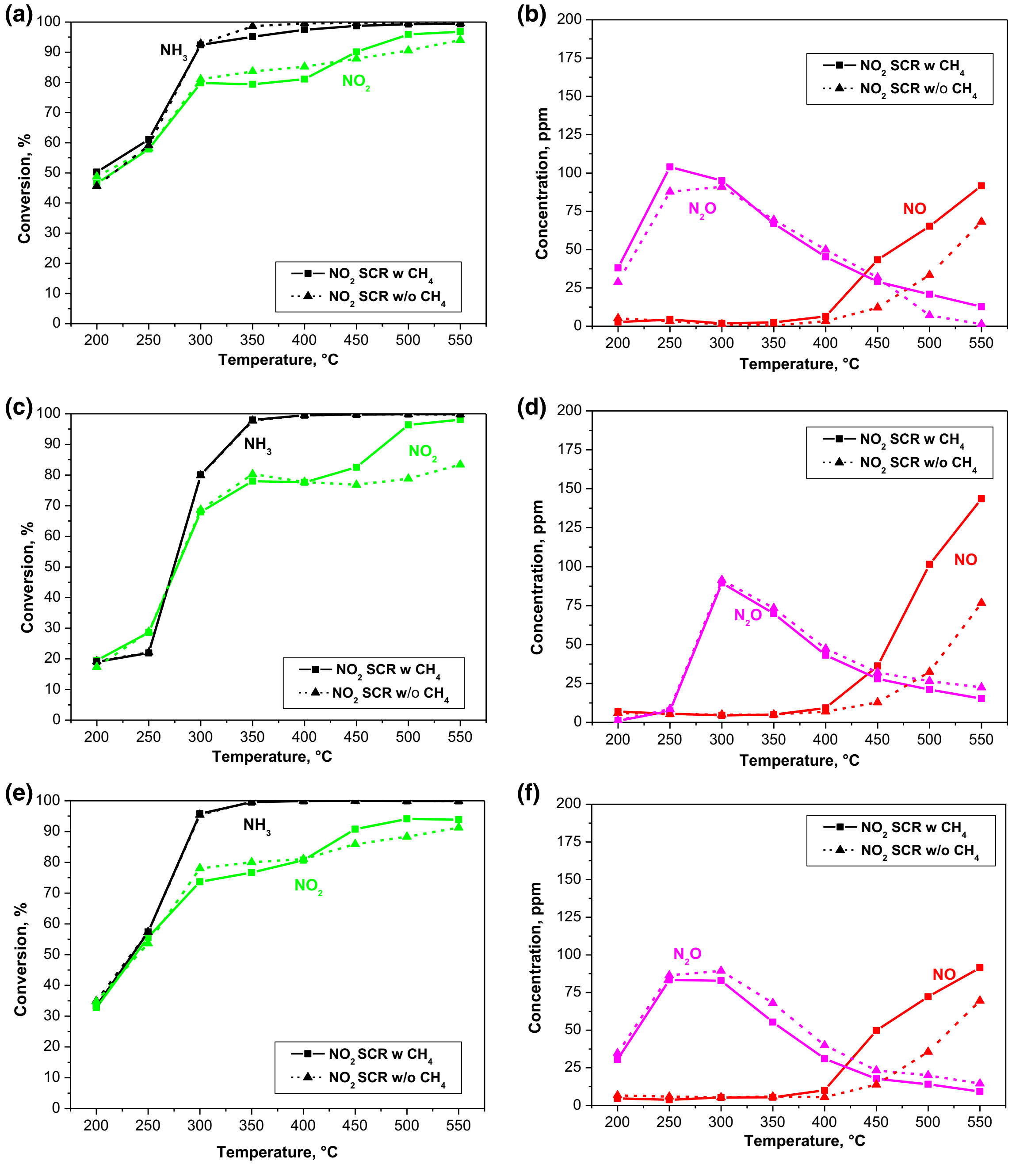

Fig. 4 CH_4 effect on NO_2 SCR: NO_2 and NH_3 steady state conversions over Fe-zeolite (**a**), Cu-zeolite (**c**) and Fe-+Cu-zeolite sequential system (**e**); N_2O and NO steady-state concentrations over Fe-zeolite (**b**), Cu-zeolite (**d**) and Fe-+Cu-zeolite sequential system (**f**). GHSV = 75,000 h^{-1}, $NH_3 = 500$ ppm, $NO_2 = 500$ ppm, $CH_4 = 0/1000$ ppm, $O_2 = 5\%$ (v/v), $H_2O = 5\%$ (v/v), $T_{range} = 200–550$ °C

high temperature range the highest NO_x conversions and N_2 selectivities are achieved over the Fe-zeolite catalyst. Accordingly, the sequential arrangement of the two zeolites (Fe-BEA followed by Cu-SAPO) has demonstrated a good synergy between the two systems, with high deNO_x efficiencies across the whole temperature range, while ensuring also a low N_2O production.

The main goal of this study was to assess the impact of the presence of methane in the exhausts (as typical of ATS for lean-burn NG engines) on the deNO_x activity of the tested SCR catalyst systems. Our data clearly indicate that methane does not interfere with the chemistry and the kinetics of the Standard SCR and Fast SCR reactions. Under NO_2-SCR conditions, on the other hand, we have observed

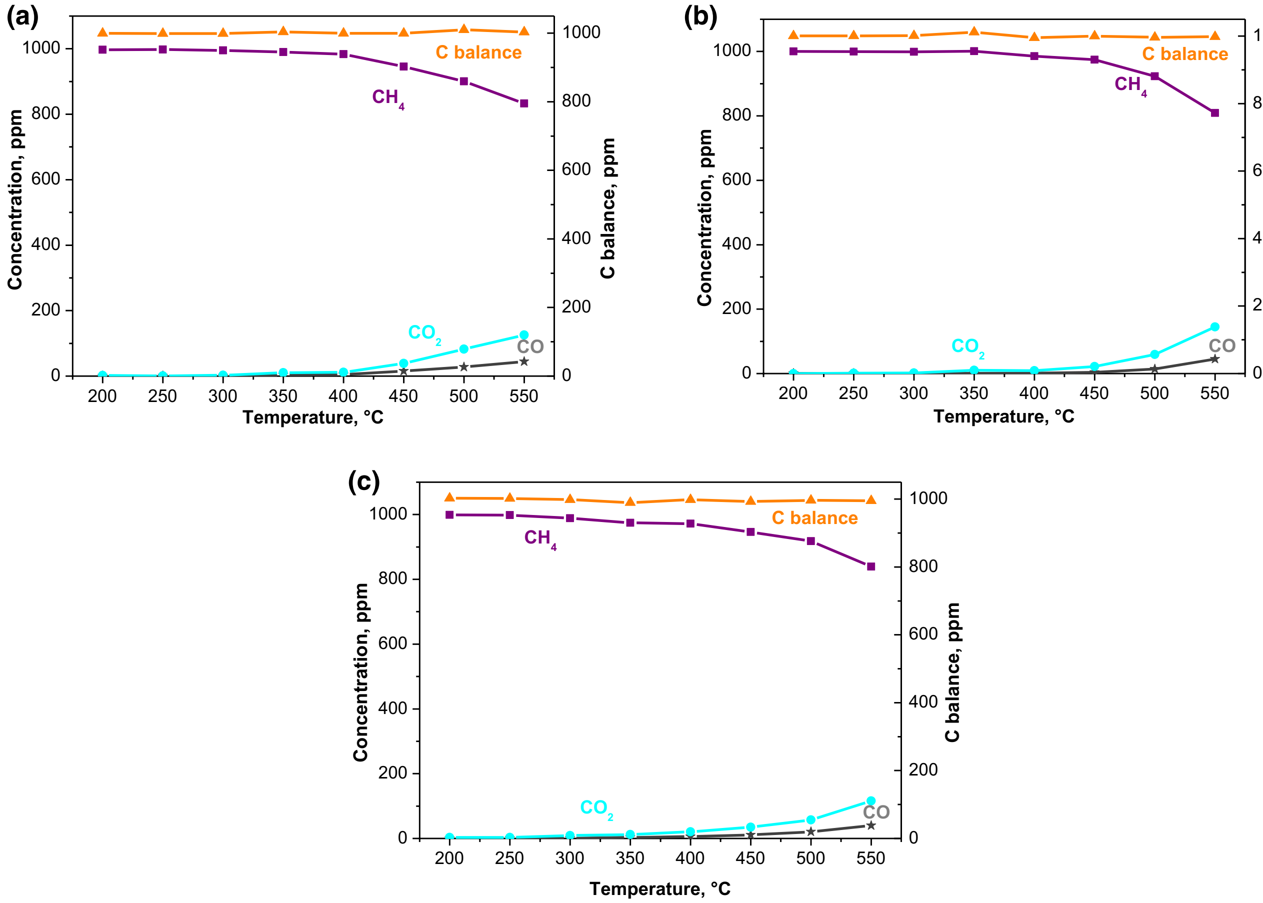

Fig. 5 CH_4 effect on NO_2 SCR: CH_4, CO, CO_2 steady state concentrations and carbon balances over Fe-zeolite (**a**), Cu-zeolite (**b**) and Fe-+Cu-zeolite sequential system (**c**). GHSV = 75,000 h^{-1}, $NH_3 = 500$ ppm, $NO_2 = 500$ ppm, $CH_4 = 1000$ ppm, $O_2 = 5\%$ (v/v), $H_2O = 5\%$ (v/v), $T_{range} = 200–550$ °C

an effective oxidation of methane to CO_x above 400 °C over all the tested catalyst systems. While such oxidation reactions did not affect the overall $deNO_x$ process to a large extent in our conditions, they suggest however a significant reactivity between NO_2 and CH_4 already at relatively low temperatures over metal-exchanged zeolite catalysts. We will further study such a reactivity, so far unreported, in future dedicated work.

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