ORIGINAL PAPER

Experimental Study of the NO Oxidation to NO₂ Over Metal Promoted Zeolites Aimed at the Identification of the Standard SCR Rate Determining Step

Maria Pia Ruggeri · Isabella Nova · Enrico Tronconi

Abstract Steady state and transient kinetic runs devoted to the comparative analysis of NO oxidation and standard SCR reactions over commercial Cu- and Fe-promoted zeolite catalysts are herein presented with the aim to clarify whether NO oxidation to NO₂ is the rate determining step (rds) of the standard SCR reaction. It is found that this statement seems questionable in the light both of the herein collected experimental results and of scattered evidence from the literature.
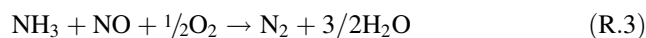
Keywords NH₃-SCR · Cu zeolite · Fe zeolite · Standard SCR mechanism · NO oxidation · H₂O inhibiting effect

1 Introduction

The NH₃-SCR technology is currently applied worldwide for NOx control in the exhausts of stationary power plants and is nowadays also considered as one of the best solutions to comply with regulations of NO_x emissions in the exhausts of lean-engine vehicles [1, 2].

Since NO_x in the exhaust gases is primarily constituted of NO, the standard SCR reaction (R.3), in which NO is reduced by ammonia in the presence of oxygen, contributes most significantly to the deNOₓ activity. Over metal (Fe, Cu) promoted zeolites NO oxidation to NO₂ (R.1) is reported to take place, as well [3–5], and many authors in the literature [6–8] propose this reaction to be the rate determining step in the standard SCR mechanism. Indeed,

under this assumption the STD SCR reaction should proceed via the following pathway:

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 + \tag{R.1}$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O = \tag{R.2}$$

$$NH_3 + NO + \tfrac{1}{2}O_2 \rightarrow N_2 + 3/2H_2O \tag{R.3}$$

wherein NO is oxidized (R.1) to NO₂, which then reacts with more NO and ammonia according to the Fast SCR reaction (R.2): by adding the stoichiometry of these two reactions, in fact, the aforementioned standard SCR reaction (R.3) is obtained. Moreover, since the (R.2) step is by far faster than NO oxidation, the latter becomes the rate determining step in the standard SCR reaction mechanism.

The present proposal, however, is not universally accepted in the literature due to some experimental evidence which cannot be fully explained by this scheme. It has been reported for instance that the rate of NO oxidation is much less than the one associated with the standard SCR reaction under identical operating conditions [9]. Furthermore, several studies report a different effect of water on the two reaction rates over metal promoted zeolites [9, 10]. In the present work we analyze comparatively standard SCR and NO oxidation over both Cu- and Fe- zeolite catalysts, accounting also for temperature and H₂O effects, in order to collect evidence concerning the relationship between the kinetics and mechanisms of the two reactions.

2 Methods

The catalysts employed in this study were commercial Cu and Fe zeolites. A 390 CPSI honeycomb Cu zeolite washcoated monolith was used both in the form of powder and

M. P. Ruggeri · I. Nova · E. Tronconi (✉)
LCCP, Dipartimento di Energia, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milan, Italy
e-mail: enrico.tronconi@polimi.it

of small core monoliths for experiments at two different scales. In microflow reactor runs, 80 mg of the crushed monolith, sieved to 90 μm average particle size, were diluted with cordierite up to 160 mg, and then loaded in a quartz reactor (6 mm ID) placed in an electric furnace. NO, NH$_3$, NO$_2$ outlet concentrations were continuously measured by a UV analyzer (ABB LIMAS 11HW), whereas a quadrupole mass spectrometer (BALZERS QMS 200) could also detect N$_2$ and N$_2$O. A detailed description of the laboratory rig used for these tests can be found in [10, 11]. NO oxidation and standard SCR reaction were investigated in the 150–550 °C range, using 0–500 ppm of NO and 500 ppm of NH$_3$ in a Helium carrier gas with 8 % O$_2$ (GHSV around 918,000 cm^3*g$_{ap}^{-1}$*min^{-1} STP). The effect of water has been addressed cofeeding 0–8 % H$_2$O.

Small core monolith samples (5 cm^3) both of the Cu zeolite catalyst and of a 400 CPSI honeycomb Fe zeolite wash-coated catalyst were also tested in a different rig at T = 180 °C, feeding 0–500 ppm of NH$_3$, 500 ppm of NO in a N$_2$ flow (GHSV = 35,000 h^{-1}), either in absence or in presence of 8–10 % water. NO, NH$_3$, NO$_2$ outlet concentrations were detected by an UV analyzer (ABB LIMAS 11HW), whereas N$_2$O was detected by a IR analyzer (ABB URAS-14). The monolith rig is extensively described in [12].

3 Results and Discussion

3.1 Powdered Catalyst Runs

3.1.1 NO Oxidation

Figure 1 shows the results of NO oxidation runs over the powdered Cu zeolite catalyst both in the absence (dashed lines) and in the presence of 8 % water (solid lines), together with the NO/NO$_2$ equilibrium concentration profiles (dotted lines). 500 ppm of NO were fed to the reactor with 8 % of oxygen in helium flow at 150 °C and then a temperature ramp with an heating rate of 2 °C min^{-1} was performed up to 550 °C.

Concerning the runs carried out under dry conditions (dashed lines), NO consumption was observed starting from 200 °C and, at the same time, an equal amount of NO$_2$ was produced. The NO conversion increased with temperature and then reached a maximum of about 20 % around 350 °C. Above this temperature the conversion was thermodynamically limited (dotted lines) and hence, NO conversion decreased.

The outlet concentration profiles were thus in line with the NO oxidation reaction (R.1) which, as extensively reported in literature, exhibits a poor activity over Cu zeolites [10].
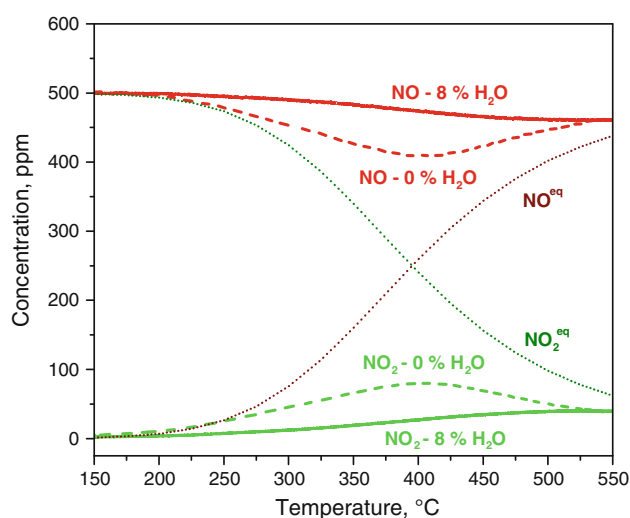

Fig. 1 Powdered catalyst, NO oxidation reaction. Effect of water: NO = 500 ppm, H$_2$O = 0–8 %, O$_2$ = 8 %, T = 150–550 °C, GHSV = 918,750 cm^3/(h*g$_{ap}$) STP. Dry conditions *dashed lines*; wet conditions *solid lines*; thermodynamic equilibrium *dotted lines*

When water was added to the feed stream (Fig. 1, solid lines), keeping the other experimental conditions unchanged, NO was again converted to NO$_2$, starting at 200 °C as well, but then proceeding very slowly: a maximum conversion of only about 10 % was indeed reached only at T = 490 °C.

Comparing the NO profiles obtained in the two cases (0 % H$_2$O = dashed lines; 8 % H$_2$O = solid lines), it clearly appears that water has a dramatic inhibiting effect on the NO oxidation to NO$_2$. This effect is well known and extensively reported in the literature [6, 10, 13, 14] for several catalytic systems: our results further confirm these observations over a Cu zeolite catalyst under typical SCR operating conditions.

3.1.2 Standard SCR

After the study of NO oxidation, the focus of our work shifted to the investigation of the NH$_3$–NO–O$_2$ reacting system under identical experimental conditions.

Figure 2 shows the outlet concentration profiles of reactants and products versus temperature measured in steady state runs wherein 500 ppm of NO and NH$_3$ each were co-fed to the microreactor in presence of 8 % of oxygen in helium flow, both under dry (dashed lines) and wet (solid lines) conditions.

As regards to the experiment performed in the absence of water, it can be noticed that NO and NH$_3$ were consumed in a molar ratio close to 1:1, starting from 150 °C. The reactants conversion increased steeply with growing temperature up to 250 °C at which almost complete conversion was reached. At the same time, N$_2$ was the only
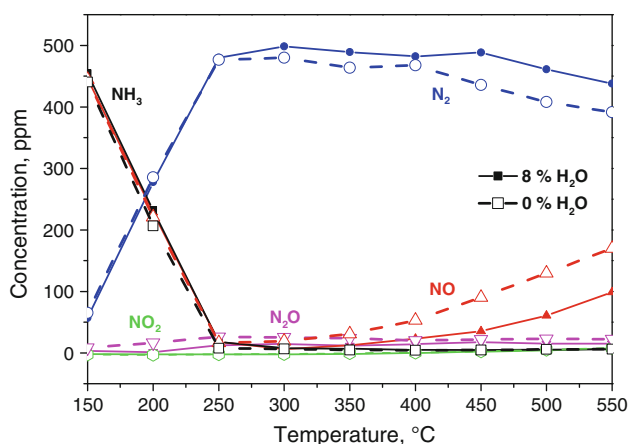
Fig. 2 Powdered catalyst, standard SCR reaction. Effect of water: NO = NH$_3$ = 500 ppm, H$_2$O = 0–8 %, O$_2$ = 8 %, T = 150–550 °C, GHSV = 918,750 cm^3/(h*g$_{ap}$) STP. Dry conditions *dashed lines* and *open symbols*; wet conditions *solid lines* and *solid symbols*

product, as neither N$_2$O nor NO$_2$ were detected in significant amounts at any investigated temperature. The reactants consumption and products formation are in line with the standard SCR stoichiometry (R.3). The overconsumption of NH$_3$ with respect to NO observed at higher temperatures (350 °C) is indeed ascribed to NH$_3$ oxidation [4, 10].

Comparing the NH$_3$–NO–O$_2$ results with what observed previously for the NO–O$_2$ reacting system, we can point out that the performance of NO oxidation (Fig. 1) were quite low between 150 and 250 °C, with NO conversion in the range 0–10 %, whereas the NO conversion for the standard SCR reaction was between 10 and 98 % in the same T-range. Moreover, on increasing the temperature the NO conversion in NO oxidation continued to increase very slowly, reaching its maximum of 20 % at 350 °C, while the standard SCR showed complete conversion already at 250 °C. Above 350 °C, NH$_3$ conversion was still complete but the NO conversion decreased due to the ammonia oxidation, as already pointed out. Accordingly, it seems that not only the reaction rates, but also the temperature dependences of the rates for standard SCR and for NO oxidation, its alleged rate determining step, are different.

When adding water to the NO–NH$_3$–O$_2$ reacting system (Fig. 2 squares, solid lines), the same behavior described in the case of dry conditions (Fig. 2 squares, dashed lines) can be observed. Indeed, water only slightly affected the catalyst performances in the low temperature region and prevented the ammonia oxidation observed at very high temperature [4].

Comparing the results obtained in wet conditions for the standard SCR reaction (Fig. 2, solid lines), with those discussed for NO oxidation under the same operating conditions (Fig. 1, solid lines), it is evident that the

reaction rates were very different in this case too, being the NO oxidation activity even much lower than the standard SCR activity. This clearly indicates that the inhibiting effect of water is much more evident on NO oxidation, whereas it is almost negligible for standard SCR. This piece of evidence seems also in contrast with the idea that NO oxidation might be the rate determining step of the standard SCR reaction.

3.2 Monolith Catalyst Runs

3.2.1 Cu Zeolite

Figure 3 shows the results of a couple of dynamic runs carried out over the Cu zeolite core monolith sample. These experiments have been performed at a constant temperature of 180 °C, feeding in subsequent steps 500 ppm of NO, NO + 8 % O$_2$, and NO + 8 % O$_2$ + 500 ppm NH$_3$, in the absence (Fig. 3a) and in the presence of 8 % H$_2$O (Fig. 3b).

Results in Fig. 3a show that upon adding 8 % O$_2$ to 500 ppm of NO (t = 7,500 s), 25 ppm of NO$_2$ are formed, corresponding to a NO conversion of 5 %. However, when NH$_3$ is added (t = 10,500 s), all the other reaction conditions being unchanged, no NO$_2$ could be detected and a much higher NO conversion, 80 %, was achieved. This is in line with previous observations reported for the powdered catalyst. The same dynamic experiment carried out in presence of 10 % H$_2$O showed no significant NO conversion for NO oxidation versus a conversion of 70 % for the standard SCR reaction.

3.2.2 Fe Zeolite

The same experiment was replicated on small core monolith samples of a commercial Fe zeolite catalyst. Looking first at Fig. 4a, reporting the experiment under dry conditions, it is evident that adding 8 % oxygen to 500 ppm of NO (t = 7,000 s) resulted in the consumption of roughly 80 ppm of the reactant and in a corresponding production of NO$_2$ in line with the NO–NO$_2$ oxidation reaction. When also NH$_3$ was added (at t = 8,600 s), a transient evolution of the NO concentration profile can be noticed, in line with literature evidence for Fe zeolite catalysts [4]. At first the NO conversion was increased, and in parallel, the NO$_2$ outlet concentration dropped. When the catalyst started to be saturated by ammonia, the NO concentration increased and stabilized around a steady state value of 450 ppm that was close to that of ammonia (430 ppm), while NO$_2$ was not detected anymore.

The lower conversion of NO measured in this part of the experiment, associated with the standard SCR reaction, with respect to that observed when feeding only NO–O$_2$,
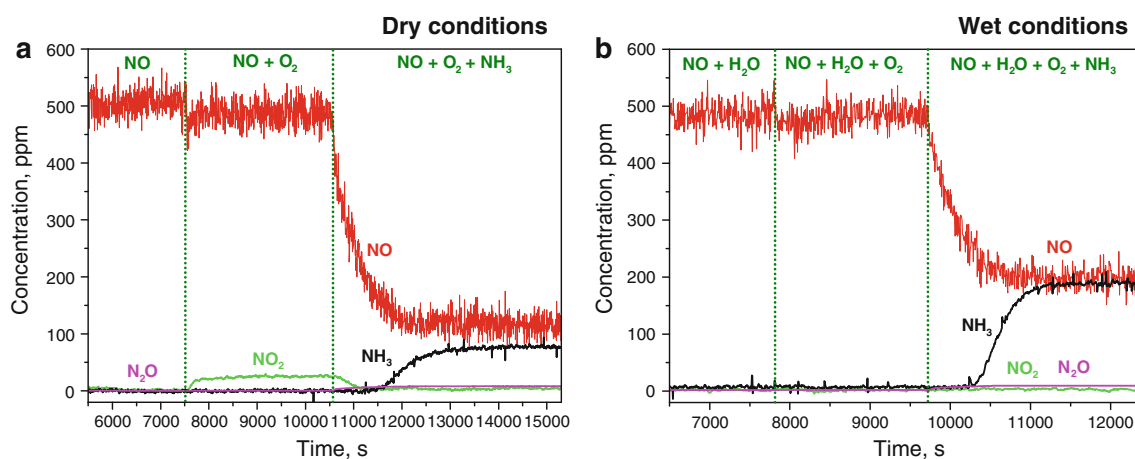
Fig. 3 Cu zeolite monolith catalyst, dynamic tests: NO = 500 ppm; NH_3 = 0–500 ppm; O_2 = 8 %, T = 180 °C, GHSV = 35,000 h^{-1}. **a** 0 % H_2O; **b** 10 % H_2O

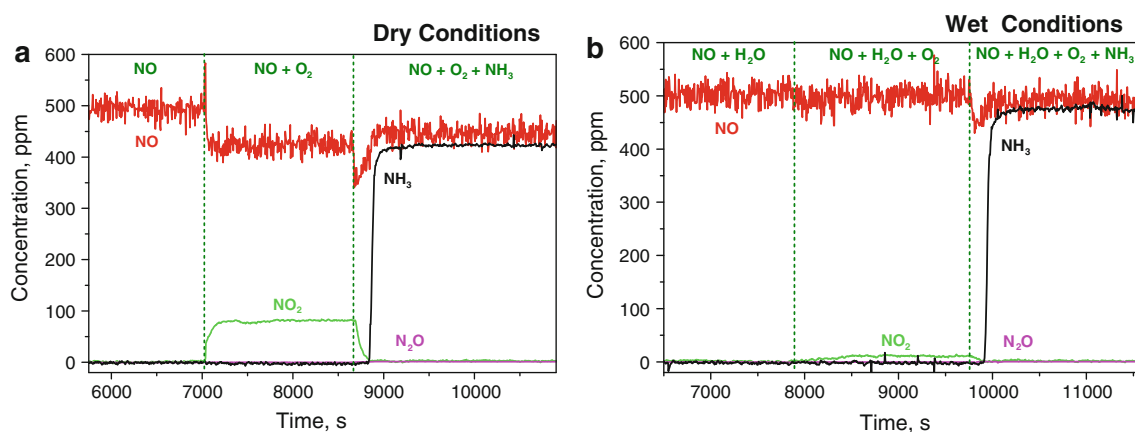**Fig. 4** Fe zeolite monolith catalyst, dynamic tests: NO = 500 ppm; NH_3 = 0–500 ppm; O_2 = 8 %, T = 180 °C, GHSV = 35,000 h^{-1}. **a** 0 % H_2O; **b** 8 % H_2O

and associated with the NO oxidation to NO_2, is not surprising, since it is reported in the literature that Fe zeolites are more active in NO oxidation than in standard SCR in the 150–250 °C temperature region [3]. This piece of evidence could support the hypothesis that the standard SCR is rate limited by NO oxidation to NO_2. However, following this assumption, NO_2 formed by NO oxidation in the second phase of the experiment, should react with ammonia and NO in the third phase according to the Fast SCR reaction (R.2). Accordingly, in this phase, as no NO_2 is detected, the overall NO converted should be 160 ppm (80 ppm of NO to NO_2 and another 80 ppm of NO consumption in the Fast SCR): however, these calculations are in contrast with the measured NO variation, which was as low as 50 ppm.

The same experiment was then repeated in the presence of water (Fig. 3b): water almost completely suppressed NO oxidation while it had only a modest effect on the standard SCR activity, in line with what found on the Cu zeolite

powdered and monolith catalysts. Furthermore, the NO oxidation activity was in this case lower than that of the standard SCR reaction.

4 Conclusions

The NO oxidation to NO_2 and standard SCR reactions have been comparatively studied in order to clarify if the former could be the rate determining step of the latter one.

Data collected over a Cu zeolite powdered catalyst pointed out great differences both in the NO conversion activity and in the inhibiting effect of water for the two reactions.

Similar differences were also observed when running transient experiments over both a Cu- and a Fe zeolite catalyst in the form of wash-coated monoliths. Furthermore, the analysis of the steady state concentrations of the reactants measured during such experiments showed that

they are not quantitatively consistent with a pathway wherein the standard SCR reaction proceeds according to NO oxidation to NO_2 followed by a Fast SCR step.

In summary, then, the overall evidence collected in the present work is clearly at variance with the popular hypothesis that NO oxidation to NO_2 represents the rate determining step in the standard SCR mechanism.

An alternative mechanism, involving two different rate determining steps for the two reactions, can be envisaged, wherein both reactions require formation of oxidized intermediates (HONO, nitrites/nitrates species) in the presence of NO and O_2 [15, 16]. Surface nitrites can then decompose to gaseous NO_2: this can be identified as the slow step in the case of NO oxidation to NO_2 [17]. Indeed, the HONO—Nitrites/nitrates equilibrium is strongly affected by water, which may explain the strong H_2O inhibiting effect on NO oxidation [18]. When ammonia is present, on the other hand, HONO/nitrites species quickly react instead with ammonia to form N_2: in this case re-oxidation of the metal active sites by O_2 then represents the standard SCR rate determining step.

Different rate determining steps for NO oxidation to NO_2 and standard SCR explain why the rates of the two reactions are so different. Moreover, different stabilities of nitrites/nitrates adspecies, depending on their interaction with the metal sites, explain the differences noted between Cu and Fe zeolite activities in NO oxidation.

Further investigations are ongoing in order to conclusively assess the mechanistic relationship between NO oxidation and standard SCR chemistries.

References

1. Forzatti P, Lietti L, Tronconi E (2002) Nitrogen oxides removal—industrial. Wiley, New York
2. Johnson T.V., SAE Technical Paper 2008-01-0069
3. Colombo C, Nova I, Tronconi E (2010) Catal Today 151:223–230
4. Grossale A, Nova I, Tronconi E (2008) Catal Today 136:18–27
5. Devadas M, Krocher O, Elsener M, Wokaun A, Soger N, Pfeifer M, Demel Y, Mussmann L (2006) Appl Catal B 67:187–196
6. Metkar PS, Balakotaiah V, Harold MP (2011) Chem Eng Sci 66:5192–5203
7. Iwasaki M, Shinjoh H (2010) Appl Catal A 390:71–77
8. Sjovall H, Blint RJ (2009) Olsson. Appl Catal B 92:138–153
9. Schwidder M, Heikens S, De Toni A, Geisler S, Berndt M, Brückner A, Grűnert J (2008) Catalyst 259:96–103
10. Tronconi E, Nova I, Ciardelli C, Chatterjee D, Bandl-Konrad B, Burkhardt T (2005) Catal Today 105:529–536
11. Ciardelli C, Nova I, Tronconi E, Bandl-Konrad B, Chatterjee D, Ecke K, Weibel M (2004) Chem Eng Sci 59:5301–5309
12. Forzatti P, Nova I, Tronconi E, Kustov A, Thøgersen JR (2012) Catal Today 184:153–159
13. Metkar PS, Salazar N, Muncrief R, Balakotaiah V, Harold MP (2011) Appl Catal B 104:110–126
14. Colombo M, Nova I, Tronconi E, Schmeisser V, Bandl-Konrad B, Zimmermann L (2012) Appl Catal B 111–112:106–118
15. Ruggeri MP, Grossale A, Nova I, Tronconi E, Jirglova H, Sobalik Z (2012) Catal Today 184:107–114
16. Kefirov R, Ivanova E, Hadjiivanov K, Dzwigaj S, Che M (2008) Catal Lett 125:209–214
17. Delahay G, Valade D, Guzman-Vargas A, Coq B (2005) Appl Catal B 55:149–155
18. Li M, Yeom Y, Weitz E, Sachtler WMH (2005) J Catal 235:201–208