Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2023, **33**, 696–698

Mendeleev Communications

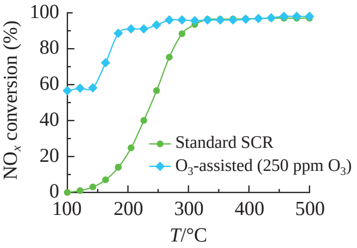
O_3-assisted NH_3-SCR over FeBEA catalyst at low reaction temperature

Dmitriy A. Bokarev, Ivan V. Paramoshin, Sergey A. Kanaev, Galina O. Bragina and Alexander Yu. Stakheev*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: st@ioc.ac.ru

DOI: 10.1016/j.mencom.2023.09.033

The injection of O_3 upstream to the SCR catalyst, FeBEA zeolite, significantly improves its catalytic performance at 100–200 °C. This improvement is due to the oxidation of NO by O_3, which proceeds even at ambient temperature, and to the further reduction of the NO + NO_2 mixture as a result of fast SCR, NO_2-SCR and accumulation of NH_4NO_3 on the catalyst surface.



Keywords: ozone catalytic oxidation, OZCO, zeolites, FeBEA, selective catalytic reduction (SCR), NO_x, air purification.

Currently, one of the important areas of application of ozone is the control of environmental pollution, including the purification of exhaust gases.[1,2] Nitrogen oxides NO and NO_2 (NO_x) are considered among the most dangerous pollutants emitted by heavy diesel engines and power plants. Selective catalytic reduction with ammonia (NH_3-SCR) is widely used to reduce NO_x emissions. However, the catalytic activity of commercial catalysts at temperatures below 250 °C is insufficient due to the low rate of the standard SCR reaction [equation (1)].[3,4] A promising way to increase the efficiency of low-temperature NO_x removal is to pre-oxidize some of the NO to NO_2 to initiate the fast SCR pathway [equation (2)].[5] It should be noted that when the NO_2/NO ratio > 1, NO_x removal occurs not only *via* the fast SCR pathway, but also *via* the NO_2-SCR pathway [equation (3)]. It is remarkable that Iwasaki *et al.* clearly showed that the contributions of the fast SCR and NO_2-SCR strongly depend on the reaction temperature.[6] It has been demonstrated that as the reaction temperature decreases below 150–170 °C, the contribution of the fast SCR rapidly diminishes, and the NO_2-SCR pathway predominates. Thus, at 100–170 °C, the descending sequence of NO_x conversion rates should be: NO_2-SCR > fast SCR > standard SCR.[6]

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \quad (2)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \quad (3)$$

The combination of fast SCR and NO_2-SCR reactions can be considered as the most effective method to boost the SCR activity of the aftertreatment system at low temperature by installing an oxidation catalyst upstream of the SCR catalyst, thus achieving the required NO/NO_2 ratio.[7] Unfortunately, the activity of the oxidation catalyst is usually insufficient at cold start and idle regime due to the low temperature of the exhaust gases. To overcome the limitations imposed by the insufficient activity of oxidation catalysts in the conversion of NO to NO_2, various ‘physical’ methods have been proposed, such as photocatalytic oxidation of NO,[8] non-thermal plasma oxidation[9] and electron beam irradiation.[10] However, these methods are difficult to implement in a vehicle or power plant, and their effect on exhaust gas components can cause a number of undesired side reactions.

Oxidation of nitric oxide NO with ozone can be proposed as a convenient alternative to various ‘physical’ methods. NO has been demonstrated to react with ozone [equation (4)] in the gas phase even at room temperature.[11]

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (4)$$

Therefore, it can be expected that NO can be effectively oxidized by ozone injected into the exhaust gases upstream to a $DeNO_x$ catalyst. This pre-oxidation of a portion of NO to NO_2 would potentially allow the selective catalytic reduction of NO_x to be directed towards fast SCR and/or NO_2-SCR, thereby significantly improving the NO_x abatement efficiency at low temperature (100–150 °C).

This research focused on improving SCR performance of FeBEA zeolite catalyst, which is considered one of the most promising catalysts for SCR systems with high N_2 selectivity and hydrothermal stability.[12] Unfortunately, the activity of the catalyst is insufficient at temperatures below 200 °C, and we have tried to enhance its efficiency in reducing NO_x emissions by injecting O_3 into the exhaust gases, as described above.

The FeBEA catalyst was prepared by ion exchange of the parent BEA (NH_4^+-form, Si/Al = 12.5, S_{BET} = 657 $m^2\,g^{-1}$, Zeolyst) in an aqueous solution of $Fe(NO_3)_3$ followed by drying and calcination. The resulting catalyst was examined by ICP, XRD, scanning electron microscopy (SEM-EDS) and tested in a conventional NH_3-SCR process and an O_3-assisted NH_3-SCR process (for details, see Online Supplementary Materials).

XRD patterns of BEA and FeBEA samples show a broad peak at 2θ around 7–8° and narrower peaks at 2θ 13.4°, 14.6°, 21.4°, 22.4°, 25.3°, 27.0°, 28.7° and 29.6° characteristic of BEA zeolite (Figure 1). A broad peak at 2θ 7.8° with an implicit shoulder on the left (7.3°) indicates that FeBEA consists of two similar (intergrowths) BEA zeolites: polymorph types A and B.[13] Regularly shaped zeolite microcrystals are easily distinguishable in the SEM image with an average size of 0.3–0.5 μm. EDS mapping clearly shows an even distribution of Fe and other elements (Figure 2).

Figure 3 compares NO_x conversions over the FeBEA catalyst in the conventional NH_3-SCR and O_3-assisted NH_3-SCR as a

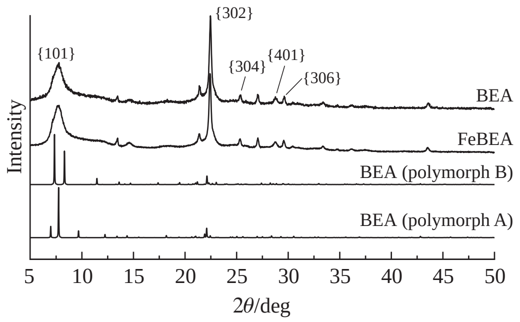


Figure 1 XRD patterns of parent BEA and FeBEA.

function of reaction temperature in the range of 100–500 °C. In the conventional NH_3-SCR process, complete NO_x conversion is only achieved at 310 °C. Below 180 °C, NO_x conversion does not exceed 15% and approaches zero as the reaction temperature decreases to 100 °C, which indicates that at 100 °C the efficiency of the standard SCR is negligible.

O_3 injection significantly improves the NH_3-SCR performance of the FeBEA catalyst at 100–250 °C. The injection of 125 ppm O_3 ($O_3/NO = 0.25$) leads to an increase in NO_x conversion to ~33% at a temperature as low as 100 °C, and 100% conversion is achieved at 265 °C compared to 310 °C in the course of the conventional NH_3-SCR. With an increase in the O_3 concentration to 250 ppm ($O_3/NO = 0.5$), a further increase in the NO_x conversion is observed up to 55% at 100 °C and above 90% at 175 °C. Injection of 400 ppm O_3 further improves NO conversion up to 70% at 100 °C. However, in the temperature range of 200–350 °C, NO conversion tends to decrease.

Catalytic tests at various ozone concentrations (0–400 ppm) were repeated five times. The results of the experiments showed complete reproducibility of the catalytic performance typical for each concentration of O_3. This observation indicates that ozone injections do not change the characteristics of the catalyst.

The data obtained suggest that the improvement of NO_x conversion at 100–250 °C at higher O_3 concentration stems from the increasing contribution of fast SCR and/or NO_2-SCR reactions [see equations (2) and (3)].[6,14,15] Variation in the ozone concentration leads to a change in the NO_2/NO ratio in the inlet stream, which affects the contributions of the standard, fast and NO_2 SCR routes.

It is informative to analyze the distribution of reaction products in the course of standard NH_3-SCR and O_3-assisted NH_3-SCR at different O_3 concentrations (Figure 4). In the absence of ozone, NH_3 and NO are consumed over FeBEA at 150–500 °C in a ratio of ~1/1 [Figure 4(*a*)], which corresponds to the stoichiometry of the standard NH_3-SCR [see equation (1)]. With an NH_3/NO ratio of 1.3, NH_3 slip (100–150 ppm) was observed in this experimental series. The absence of other products indicates that NH_3-SCR over FeBEA proceeds with high selectivity to N_2. This fact is in good agreement with the previously reported data.[16,17]

The injection of 125 ppm ozone leads to a significant improvement in NO conversion up to ~33% even at 100 °C [Figure 4(*b*)]. It is of interest to tentatively estimate the contribution of various reactions to the overall process of NO_x removal at 100 °C. Such an estimation can be made taking into account the following experimental observations. Upon injection of 125 ppm O_3, the inlet flow contains ~125 ppm NO_2 and ~375 ppm NO. After passing through the catalyst, NO_2 completely disappears, and the NO concentration decreases to ~335 ppm, *i.e.* 165 ppm total NO_x ($NO + NO_2$) is removed over the catalyst. The observed changes in $NO_2 + NO$ concentration indicates that the contribution of the fast SCR pathway is minor, as the reaction stoichiometry suggests the removal of equimolar concentrations of NO_2 and NO [see equation (2)], which would result in the disappearance of 250 ppm NO_x and ~50% NO_x conversion. This experimental fact evidences that the SCR process mainly follows the stoichiometry of the NO_2-SCR pathway [see equation (3)].

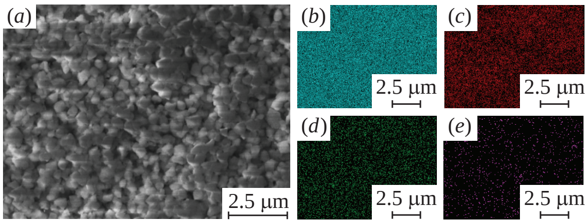


Figure 2 (*a*) FeBEA surface morphology with EDS maps of element distribution: (*b*) Si, (*c*) O (*d*) Al and (*e*) Fe.

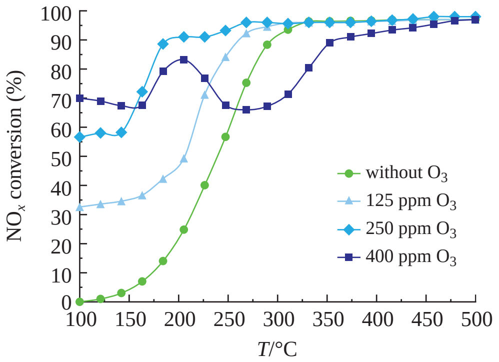


Figure 3 Catalytic performance of FeBEA in conventional NH_3-SCR (0 ppm O_3) and O_3-assisted NH_3-SCR (125–400 ppm O_3).

The injection of 250 ppm O_3 improves the NO_x conversion at 100 °C to ~56%. Comparison of inlet and outlet NO_x concentrations indicates that ~280 ppm total NO_x has been removed from the inlet flow. Taking into account that the inlet flow contains ~250 ppm NO_2, which completely disappears when passing through the catalyst, it can be concluded that the NO_2-SCR remains the predominant pathway and the contribution of the fast SCR is minor, since the stoichiometry of the fast SCR suggests either a complete conversion of the 1 : 1 mixture of $NO + NO_2$, or a

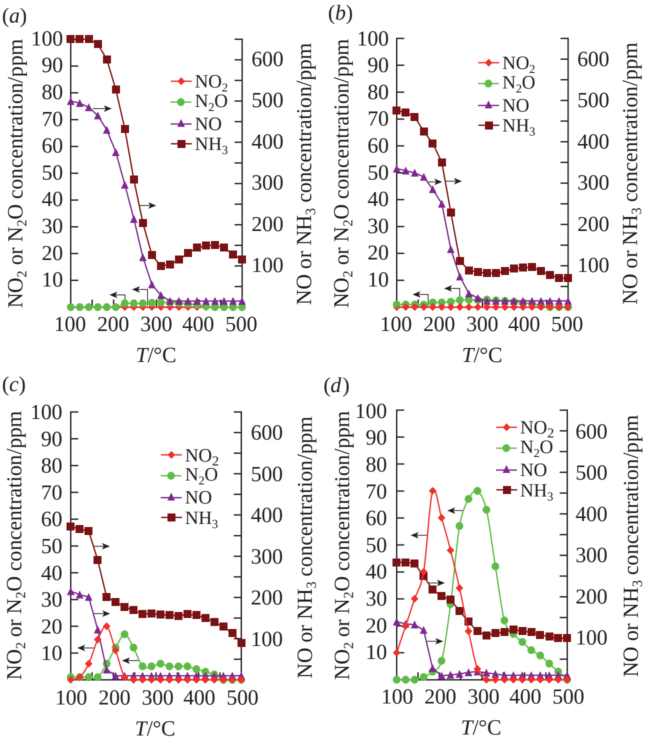


Figure 4 Product distribution during O_3-assisted NH_3-SCR over FeBEA catalyst in the presence of (*a*) 0, (*b*) 125, (*c*) 250 and (*d*) 400 ppm O_3.

breakthrough of equimolar concentrations of NO and NO_2 in case of incomplete conversion.

It should be mentioned that, upon injection of 250 ppm O_3, we observed the appearance of a minor amount of NO_2 and N_2O (~20 ppm) in the reaction products with an increase in the reaction temperature to 150–250 °C [Figure 4(*c*)]. This observation presumably indicates the beginning of the accumulation of ammonium nitrate on the catalyst surface, in accordance with the known data.[16,18,19]

$$2NH_3 + 2NO_2 \rightarrow N_2 + NH_4NO_3 + H_2O \qquad (5)$$

When the reaction temperature rises to 120–130 °C, the reaction between NH_4NO_3 and NO results in the evolution of NO_2 [equation (6)].

$$NH_4NO_3 + NO \rightarrow NO_2 + N_2 + 2H_2O \qquad (6)$$

A further increase in the reaction temperature initiates the decomposition of ammonium nitrate, as evidenced by the release of N_2O [equation (7)].

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

With an increase in temperature to 175–250 °C, an increase in NO_x conversion is associated with the occurrence of a fast SCR reaction [see equation (2)] and the reduction of nitrogen oxides with the participation of ammonium nitrate [equation (8)].[20]

$$NH_4NO_3 + 2NO + 2NH_3 \rightarrow 3N_2 + 5H_2O \qquad (8)$$

These data allow us to conclude that the removal of NO by O_3-assisted SCR at 100–200 °C and high ozone concentration occurs through a combination of three pathways: NO_2-SCR [see equation (3)], fast SCR [see equation (2)] and accumulation of NH_4NO_3 on the catalyst surface [equation (5)] followed by secondary reactions [see equations (6)–(8)].

The experiment with injection of 400 ppm O_3 into the inlet gas mixture revealed an evident increase in the contribution of NH_4NO_3 accumulation on the catalyst surface [see equation (5)], followed by its secondary transformations according to equations (6)–(8), as indicated by a significant increase in NO_2 and N_2O evolution to 70 ppm [Figure 4(*d*)]. It worth noting that, comparing the composition of the reaction products presented in Figure 4(*d*), and the temperature dependence of NO_x conversion obtained upon injection of 400 ppm O_3 (see Figure 3), we can conclude that the apparent decrease in NO_x conversion observed at 200–350 °C stems from the formation of NO_2 and N_2O caused by the intensification of the secondary reactions of NH_4NO_3 decomposition [see equations (6) and (7)].

The obtained data allow us to conclude that O_3-assisted SCR can provide an effective approach to improve the efficiency of NO_x removal at the reaction temperature as low as 100–150 °C. NO_x removal occurs through a combination of several pathways: fast SCR, NO_2-SCR and accumulation of NH_4NO_3 on the catalyst surface followed by its secondary transformations. The contribution of each pathway strongly depends on ozone concentration and reaction temperature, which deserves further study.

This work was supported by the Russian Science Foundation (grant no. 23-13-00214).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.09.033.

References

1 B. Liu, J. Ji, B. Zang, W. Huang, Y. Gan, D. Y. C. Leung and H. Huang, *J. Hazard. Mater.*, 2022, **422**, 126847.
2 A. I. Mytareva, A. S. Gilev, I. S. Mashkovsky, D. A. Bokarev, G. N. Baeva, S. A. Kanaev, A. V. Kazakov and A. Yu. Stakheev, *Kinet. Catal.*, 2022, **63**, 515 (*Kinet. Katal.*, 2022, **63**, 584).
3 P. Balle, B. Geiger, D. Klukowski, M. Pignatelli, S. Wohnrau, M. Menzel, I. Zirkwa, G. Brunklaus and S. Kureti, *Appl. Catal., B*, 2009, **91**, 587.
4 A. I. Mytareva, D. A. Bokarev and A. Yu. Stakheev, *Kinet. Catal.*, 2021, **62**, 1 (*Kinet. Katal.*, 2020, **61**, 751).
5 S. Kasaoka, T. Yamanaka and E. Sasaoka, *J. Fuel Soc. Jpn.*, 1977, **56**, 834.
6 M. Iwasaki and H. Shinjoh, *Appl. Catal., A*, 2010, **390**, 71.
7 G. Madia, M. Koebel, M. Elsener and A. Wokaun, *Ind. Eng. Chem. Res.*, 2002, **41**, 3512.
8 Z. Wu, H. Wang, Y. Liu, B. Jiang and Z. Sheng, *Chem. Eng. J.*, 2008, **144**, 221.
9 A. B. Oskooei, J. Koohsorkhi and M. Mehrpooya, *Chem. Eng. Sci.*, 2019, **197**, 135.
10 A. G. Chmielewski, A. Ostapczuk, Z. Zimek, J. Licki and K. Kubica, *Radiat. Phys. Chem.*, 2002, **63**, 653.
11 Y. S. Mok and E. Y. Yoon, *Ozone: Sci. Eng.*, 2006, **28**, 105.
12 Y. Xin, Q. Li and Z. Zhang, *ChemCatChem*, 2018, **10**, 29.
13 J. M. Newsam, M. M. J. Treacy, W. T. Koetsier and C. B. De Gruyter, *Proc. R. Soc. London, Ser. A*, 1988, **420**, 375.
14 A. Grossale, I. Nova and E. Tronconi, *Catal. Today*, 2008, **136**, 18.
15 M. Iwasaki, K. Yamazaki and H. Shinjoh, *Appl. Catal., A*, 2009, **366**, 84.
16 D. S. Krivoruchenko, A. V. Kucherov, N. S. Telegina, D. A. Bokarev, P. Selvam and A. Yu. Stakheev, *Russ. Chem. Bull.*, 2014, **63**, 389.
17 A. I. Mytareva, D. A. Bokarev, D. S. Krivoruchenko, G. N. Baeva, A. Yu. Belyankin and A. Yu. Stakheev, *Top. Catal.*, 2019, **62**, 86.
18 A. Grossale, I. Nova and E. Tronconi, *J. Catal.*, 2009, **265**, 141.
19 A. Grossale, I. Nova, E. Tronconi, D. Chatterjee and M. Weibel, *J. Catal.*, 2008, **256**, 312.
20 P. Forzatti, I. Nova and E. Tronconi, *Angew. Chem., Int. Ed.*, 2009, **48**, 8366.

Received: 16th May 2023; Com. 23/7172