



Improvement of Low-Temperature Activity of FeBeta Monolith Catalyst in NH₃-SCR of NO_x

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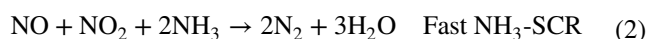
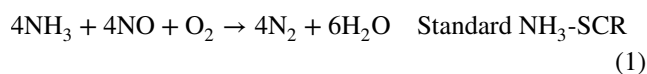
Abstract

FeBeta//Mn–Ce/FeBeta catalyst was prepared by coating cordierite monolith with FeBeta zeolite followed by an impregnation of its downstream part by Mn–Ce solution. The resulting dual-zone catalyst demonstrates improved catalytic performance in the selective catalytic reduction of NO_x by NH₃ (NH₃-SCR) as compared to the parent Fe-Beta. The catalyst exhibits 80–90% NO_x conversion and 100% selectivity to N₂ within wide temperature ranges: 180–500 °C (at GHSV = 18,000 h^{−1}) and 260–500 °C (at GHSV = 54,000 h^{−1}). Moreover, the dual-zone catalyst provides favorable NH₃-slip removal efficiency even at NH₃/NO = 1.60.

Keywords Low-temperature NH₃-SCR · NH₃ oxidation · Honeycomb cordierite · Monolithic catalyst · FeBeta · Mn–Ce/FeBeta

1 Introduction

Anthropogenic nitrogen oxide (NO_x = NO, NO₂) emissions originate mostly from fossil fuel combustion in both stationary and mobile sources [1, 2]. Selective catalytic reduction by ammonia (NH₃-SCR) is one of the most efficient technologies for NO_x abatement [3, 4]. NH₃-SCR is based on chemical reactions of NO and NO₂ with NH₃ to form molecular nitrogen and water:



Today, the main goal of the NH₃-SCR technology is to develop an eco-friendly catalyst possessing high activity and selectivity to N₂ at a relatively low-temperature range (150–400 °C) [5, 6]. Combined (or hybrid) catalytic systems, prepared by mixing oxide component (e.g. MnO_x, Ce_yZr_{1−y}O₂, and etc.) and zeolite (e.g. FeBeta or FeZSM-5)

can be considered as promising candidates [7–11]. It was shown that such systems provide favorable low-temperature NH₃-SCR activity and sufficient N₂-selectivity. It should be mentioned that NO_x conversion over combined catalyst exceeds the sum of conversion obtained over the individual oxide and zeolite indicating strong synergistic effect arose between components. In addition, lower N₂O formation (typical for Mn-containing catalysts) is observed, when they are mixed with zeolites [7, 8]. However, obvious drawbacks of the combined catalysts are the still noticeable N₂O formation and the decrease in NO_x conversion at temperatures above 400–450 °C [8, 10] because of NH₃ overoxidation on the oxide component. Moreover, the uniform coating of such mechanical mixtures on the monolith walls is a complex task, because of the large difference between the bulk densities of the oxide component and zeolite. This fact also limits the practical application of the combined catalysts.

This study was aimed to design FeBeta//Mn–Ce/FeBeta dual-zone monolithic catalyst by loading MnO_x–CeO_y species directly on FeBeta surface. On the one hand, this approach potentially allows us to enhance the synergistic effect between oxide and zeolite components due to intimate contact between MnO_x–CeO_y and FeBeta. On the other hand, it was suggested, that by combining the low-temperature activity of Mn–Ce/FeBeta with the high-temperature activity of FeBeta, it should be possible to obtain a system

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providing efficient NO_x abatement within a broader temperature range. Catalytic tests were performed at different GHSV and various NH_3/NO ratio to mimic real operating conditions.

2 Experimental

2.1 Catalyst Preparation

2.1.1 FeBeta Monolithic Catalysts

Commercial cordierite with a cell density of 400 cpsi was cut to obtain three monoliths with 24 square channels (30 mm length \times 7 mm diameter). In order to improve adherence strength of washcoat layer with the cordierite, highly dispersed boehmite (Disperal P2, Sasol) was used as a binder [12]. A thin layer of alumina was coated by immersing the monoliths in a binder slurry composed of 5 wt% Disperal P2 and 50:50 mixture of distilled water and ethanol for 1 min. The monoliths were dried at room temperature overnight and calcined at 550 °C for 4 h.

Resulted monoliths were coated by the layer of FeBeta (Zeolyst; Si/Al = 12,5; 0.9 wt% Fe). The slurry for coating composed of 20 wt% of a solid phase (80 wt% FeBeta powder, 20 wt% Disperal P2) and 80 wt% of a liquid phase (50:50 mixture of distilled water and ethanol). The monoliths were immersed in the slurry for 1 min, blown by air to remove excess of slurry, dried at 120 °C for 30 min. This procedure was repeated to achieve the desirable zeolite loading (~20 wt% of the total monolith weight). The monoliths were calcined at 550 °C for 4 h. The total washcoat loadings for all three monoliths were almost identical: 104, 104, and 105 g/l. The resulted sample is shown in Fig. 1a.

Mn–Ce/FeBeta monolithic catalyst (12 wt% Mn and 12 wt% Ce) was prepared by incipient wetness co-impregnation of FeBeta monolith with the aqueous solution of manganese(II) nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, Aldrich, 98%) and cerium(III) nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Aldrich, 99%). The resulted catalyst was dried at room temperature overnight and calcined at 550 °C for 4 h (Fig. 1b).

FeBeta||Mn–Ce/FeBeta dual-zone monolithic catalyst (12 wt% Mn and 12 wt% Ce) was prepared using the co-impregnation method described above. However, in this preparation only ~1/2 part of the FeBeta monolith was loaded with Mn and Ce by limiting the solution volume. The resulted dual-zone catalyst was dried at room temperature overnight and calcined at 550 °C for 4 h (Fig. 1c).

2.2 Catalytic Activity Tests

The NH_3 -SCR activity of the monolithic FeBeta, Mn–Ce/FeBeta and the dual-zone catalyst was measured using a

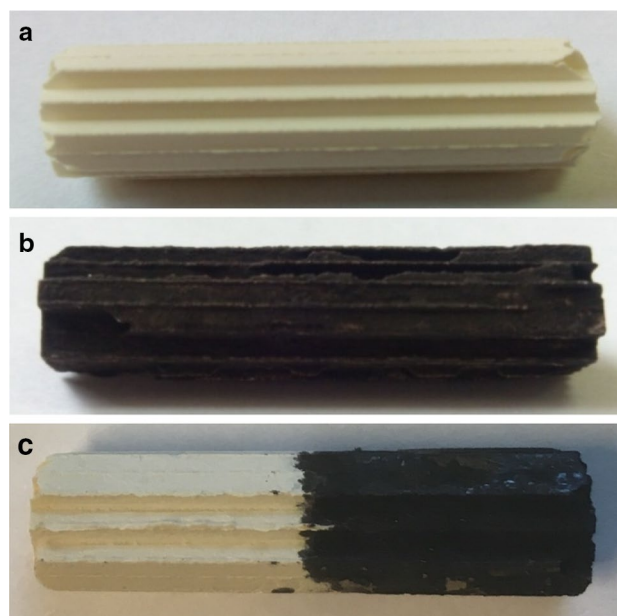


Fig. 1 Different monolithic catalysts prepared for testing in NH_3 -SCR: **a** FeBeta; **b** Mn–Ce/FeBeta; **c** FeBeta||Mn–Ce/FeBeta dual-zone

fixed-bed flow quartz reactor (id = 10 mm) operating at atmospheric pressure. The feed gas mixture consisted of 230–530 ppm NH_3 (depending on the experiment), 330 ppm NO, 10% O_2 , 6% H_2O and a balance of N_2 . The flows of reactant gasses were regulated using thermal mass flow controllers F-201CV (Bronkhorst, The Netherlands) to give the desired reactant compositions, and the total gas flow was varied from 300 to 900 ml min^{-1} (GHSV = 18,000–54,000 h^{-1}). The temperature was ranged from 500 to 100 °C at a cooling rate of 2 °C/min. All reactor lines were heated up to 180 °C in order to prevent water condensation and deposition of ammonium nitrate.

The concentrations of NH_3 , NO, NO_2 , N_2O , H_2O were continuously monitored at the inlet and outlet in real time using an FTIR gas analyzer Gaset DX-4000 (Temet Instruments Oy, Finland). The conversions of NO_x and NH_3 (X_{NO_x} and X_{NH_3}) were calculated using the following equations:

$$X_{\text{NO}_x} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \quad (3)$$

$$X_{\text{NH}_3} = \frac{[\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}}{[\text{NH}_3]_{\text{in}}} \quad (4)$$

where subscripts *in* and *out* referred to the NO_x ($\text{NO} + \text{NO}_2 + 2\text{N}_2\text{O}$) or NH_3 concentration at the reactor inlet and outlet, respectively. In order to make the catalytic data better distinguishable the results are presented as separated data points with a temperature step of ~20 °C calculated by

averaging 10 outlet NO, NO₂, N₂O, and NH₃ readings for each data point.

2.3 Catalyst Characterization

The surface morphology of the dual-zone catalyst was characterized using Hitachi SU8000 (Hitachi High-Technologies Corporation, Japan) field-emission scanning electron microscope (FE-SEM) [13]. Before measurements, the monolith was cut carefully and small parts were mounted on a 25 mm aluminium specimen stub and fixed by conductive graphite adhesive tape. Images were acquired in secondary electron mode with 10 kV accelerating voltage and at working distance 8–10 mm. Qualitative and quantitative analysis of catalyst elements were carried out using energy dispersive X-ray spectroscopy (EDX) on Oxford Instruments X-max (Oxford Instruments, United Kingdom) with 10 kV accelerating voltage and at working distance 9 mm.

Temperature-programmed reduction (H₂-TPR) of the crushed FeBeta and Mn–Ce/FeBeta parts of FeBeta||Mn–Ce/FeBeta dual-zone catalyst was carried out using a homemade setup equipped with a thermal conductivity detector (TCD) interfaced to a computer [14]. In order to remove water formed upon reduction a trap was placed between the

reactor and the TCD. The trap was cooled to $-70\text{ }^{\circ}\text{C}$ with a mixture of dry ice and ethanol.

Prior to the H₂-TPR experiments, the samples (150 mg) were treated with argon at 325 $^{\circ}\text{C}$ for 1 h, then cooled down to room temperature. The reactor temperature was raised to 700 $^{\circ}\text{C}$ at a constant heating rate of 10 $^{\circ}\text{C}/\text{min}$ in H₂ (5 vol%)/Ar with a flow rate of 30 ml/min.

3 Results and Discussions

3.1 FE-SEM-EDX

The morphologies of the FeBeta and Mn–Ce/FeBeta parts of the dual-zone catalyst are shown in Fig. 2a, b, respectively. In both SEM images, one can easily distinguish large zeolite microcrystals of regular shape. No obvious change in the morphology of FeBeta is observed after manganese and cerium loading. However, the surface of Mn–Ce/FeBeta zone is significantly smoother than those of FeBeta zone, indicating that zeolite microcrystals are uniformly embedded in Mn–Ce oxide thin layer.

EDX mapping results for FeBeta and Mn–Ce/FeBeta zones are summarized in Fig. 2c, d, respectively. The presence of O, Al, Si, Mn and Ce is clearly revealed, high

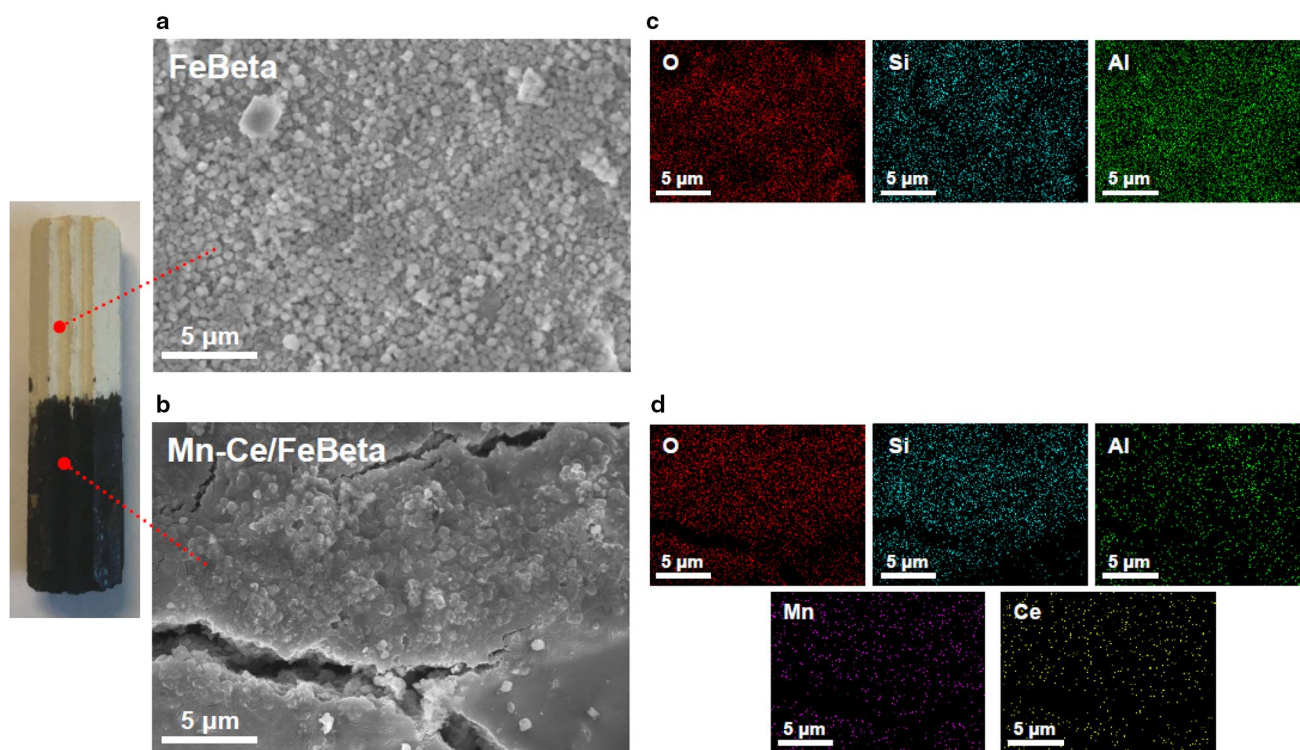


Fig. 2 SEM micrographs and EDX images of FeBeta (a, c) and Mn–Ce/FeBeta (b, d) of FeBeta||Mn–Ce/FeBeta dual-zone catalyst

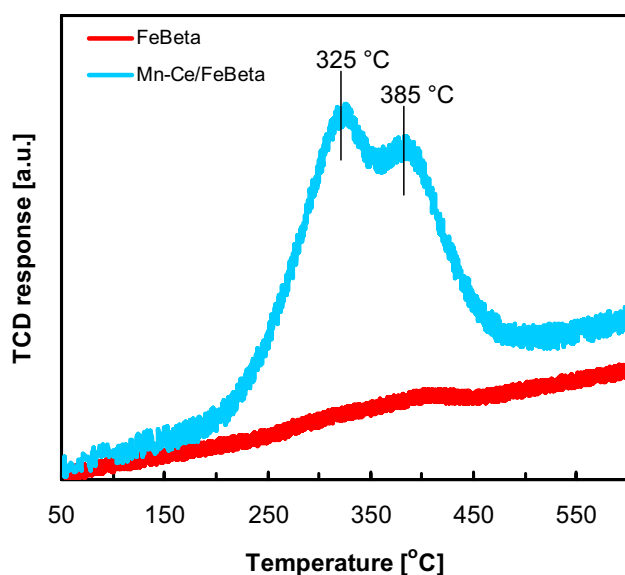


Fig. 3 H_2 -TPR profiles for FeBeta and Mn-Ce/FeBeta parts of FeBeta||Mn-Ce/FeBeta dual-zone catalyst

dispersion and well distribution of all elements are shown, indicating a well-mixed state of the dual-zone catalyst.

3.2 H_2 -TPR

H_2 -TPR profiles of FeBeta and Mn-Ce/FeBeta samples are displayed in Fig. 3. There are two distinguishable peaks at 325 °C and 385 °C in the TPR-profile of Mn-Ce/FeBeta, which is in a good agreement with the results of our previous study on characterization of the similar Mn-Ce/FeBeta powder sample [14]. The peak at lower temperature can be assigned to the reduction of MnO_2 to Mn_2O_3 , while the peak at 385 °C is attributable to the reduction of Mn_2O_3 to MnO, respectively [14, 15]. Relatively low reduction temperatures for MnO_x presumably results from the interaction between manganese and cerium oxides (e.g. due to formation of solid solution with enhanced mobility of oxygen species [16]). These results are in a good agreement with the literature [14, 17].

3.3 NH_3 -SCR Performance

The catalytic performance of FeBeta, Mn-Ce/FeBeta monoliths and FeBeta||Mn-Ce/FeBeta dual-zone catalyst are comparatively studied in NH_3 -SCR (Figs. 4, 5 depict activity and reaction product distribution, respectively). The low-temperature activity of the parent FeBeta catalyst is minor.

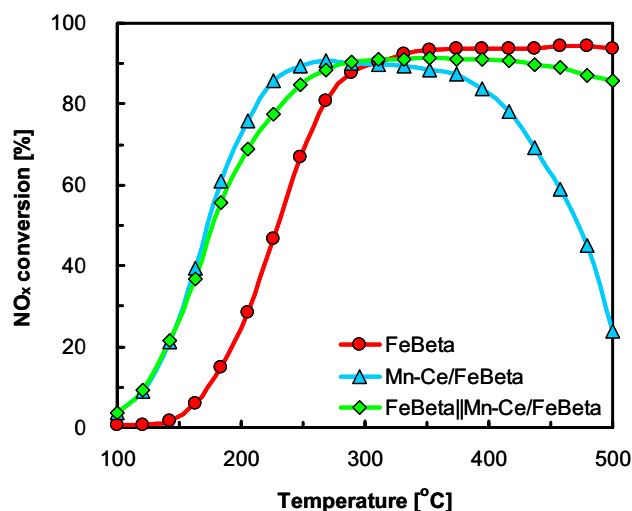


Fig. 4 NH_3 -SCR performances of FeBeta, Mn-Ce/FeBeta monoliths and FeBeta||Mn-Ce/FeBeta dual-zone catalyst. 380 ppm NH_3 , 330 ppm NO, 10% O_2 , 6% H_2O and a balance of N_2 (GHSV = 36,000 h^{-1}). Cooling rate of 2 °C/min

The reaction starts only at 150 °C, and almost complete NO_x conversion is attained at ~300 °C.

The modification of FeBeta monolith by MnO_x - CeO_x results in the significant improvement of the catalytic activity at 150–300 °C. NO_x conversion profile over Mn-Ce/FeBeta catalyst is shifted toward lower temperatures by 50–60 °C as compared to the parent FeBeta monolith. However, at $T_{\text{react.}}$ above 300–400 °C Mn-Ce-based catalyst demonstrates lower NO_x abatement efficiency, which can be explained by a depletion of the reductant due to the high activity of MnO_x - CeO_x in NH_3 oxidation [8].

The dual-zone FeBeta||Mn-Ce/FeBeta catalyst demonstrates pronounced improvement of the catalytic performance as compared to the parent FeBeta or fully impregnated Mn-Ce/FeBeta monoliths exhibiting favorable NO_x conversion within broad temperature window (200–500 °C). This can be explained by the fact that the downstream Mn-Ce/FeBeta zone provides high NH_3 -SCR activity at 150–300 °C, while at temperatures above 300 °C NO_x is converted over upstream FeBeta zone.

It should be noted, that the inverse dual-zone catalyst configuration with Mn-Ce/FeBeta as the upstream part and FeBeta as the downstream part (Mn-Ce/FeBeta||FeBeta) demonstrates NH_3 -SCR performance, which is essentially identical to the performance of the fully impregnated Mn-Ce/FeBeta and does not reveal any noticeable improvement (not shown here).

The reaction product distributions in the course of NH_3 -SCR over FeBeta, Mn-Ce/FeBeta and

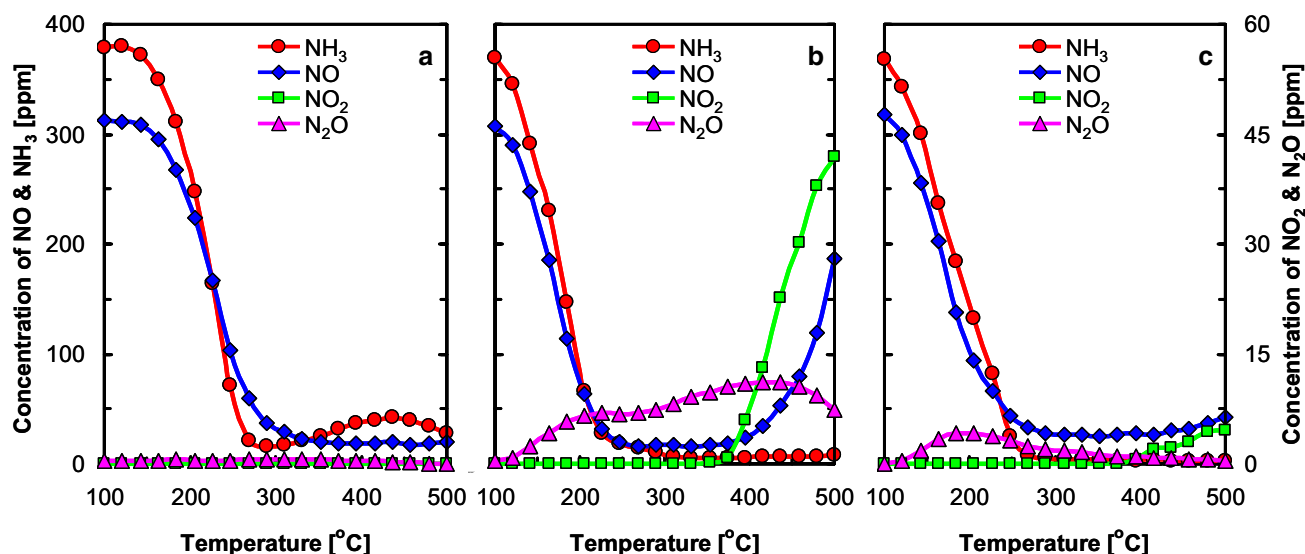


Fig. 5 Product distribution during NH_3 -SCR on **a** FeBeta, **b** Mn–Ce/FeBeta monoliths and **c** FeBeta||Mn–Ce/FeBeta dual-zone catalyst. 380 ppm NH_3 , 330 ppm NO, 10% O_2 , 6% H_2O and a balance of N_2 (GHSV = 36,000 h^{-1}). Cooling rate of 2 $^\circ\text{C}/\text{min}$

FeBeta||Mn–Ce/FeBeta monoliths are compared in Fig. 5. NO_x and NH_3 over FeBeta are consumed at $\approx 1/1$ ratio at 150–500 $^\circ\text{C}$ (Fig. 5a), which corresponds to the stoichiometry of the standard NH_3 -SCR reaction (Eq. 1). Since in this experimental series the NH_3/NO ratio was 1.15, NH_3 slip (≈ 50 ppm) was observed. Other products, except NO and NH_3 , are not detected, indicating that NH_3 -SCR over FeBeta monolith proceeds with high selectivity to N_2 .

Detailed analysis of the reaction products formed on Mn–Ce/FeBeta allows us to conclude that the decrease in NO_x conversion above $T_{\text{react.}} > 350$ $^\circ\text{C}$ stems from NH_3 overoxidation to NO and NO_2 at high temperatures (Fig. 5b). Moreover, the formation of N_2O is observed at 125–500 $^\circ\text{C}$. Such behavior is typical for Mn-based catalysts [18–20].

It is remarkable that the by-product formation over the FeBeta||Mn–Ce/FeBeta dual-zone catalyst is radically reduced, as compared to the Mn–Ce/FeBeta. N_2O and NO_2 concentrations do not exceed 5 ppm (Fig. 5c). Moreover, N_2O is formed within a narrow temperature range (125–300 $^\circ\text{C}$). These data indicate that NH_3 -SCR over the FeBeta||Mn–Ce/FeBeta dual-zone catalyst proceeds with excellent selectivity to N_2 .

3.4 Effect of NH_3/NO

The NH_3/NO ratio must be adjusted carefully to avoid a slip of unreacted ammonia. For the standard NH_3 -SCR

the reaction stoichiometry requires $\text{NH}_3/\text{NO} = 1$ (Eq. 1), but depending on the dynamic operating conditions, higher ratios can be used in order to compensate random NO_x spikes and NH_3 losses in side reactions. For studying an impact of NH_3/NO ratio, NH_3 -SCR performance of FeBeta||Mn–Ce/FeBeta dual-zone catalyst was additionally investigated by varying NH_3/NO in the range of 0.70–1.60 (Fig. 6a).

It was observed, that at $\text{NH}_3/\text{NO} = 0.70$, NO_x conversion does not exceed 65% due to the lack of reductant. The increase in NH_3 concentration significantly improves the efficiency of NO_x removal within 200–500 $^\circ\text{C}$, and the maximum NO_x conversion is achieved at NH_3/NO ratio = 1.15.

It is important to note, that even at NH_3/NO ratio = 1.60, excessive NH_3 is fully converted over dual-zone FeBeta||Mn–Ce/FeBeta at 330–500 $^\circ\text{C}$ (Fig. 6b). Moreover, it was observed, that by-products formation is negligible at stoichiometric and over-stoichiometric NH_3/NO . Thus, emission of NO_2 (Fig. 7a) and N_2O (Fig. 7b) does not exceed 8 and 6 ppm. These data indicate that FeBeta||Mn–Ce/FeBeta is capable to provide effective NH_3 -slip removal within the wide range of NH_3/NO ratios.

3.5 Effect of GHSV

The effect of GHSV on the NH_3 -SCR performance of FeBeta||Mn–Ce/FeBeta dual-zone catalyst is displayed in Fig. 8. Effect of GHSV was studied by changing the total

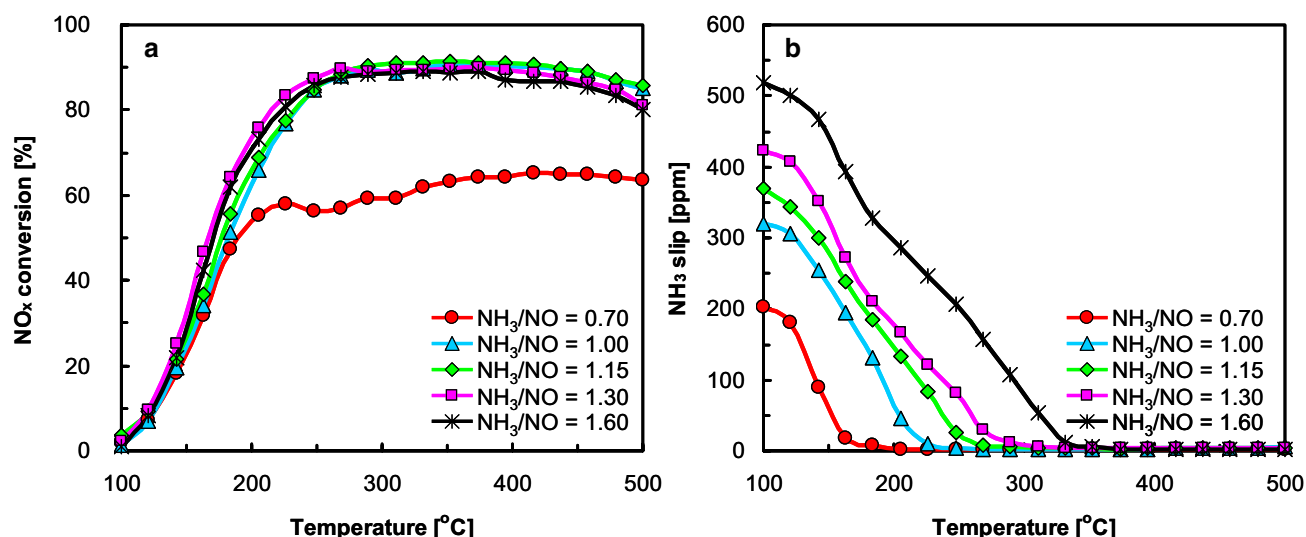
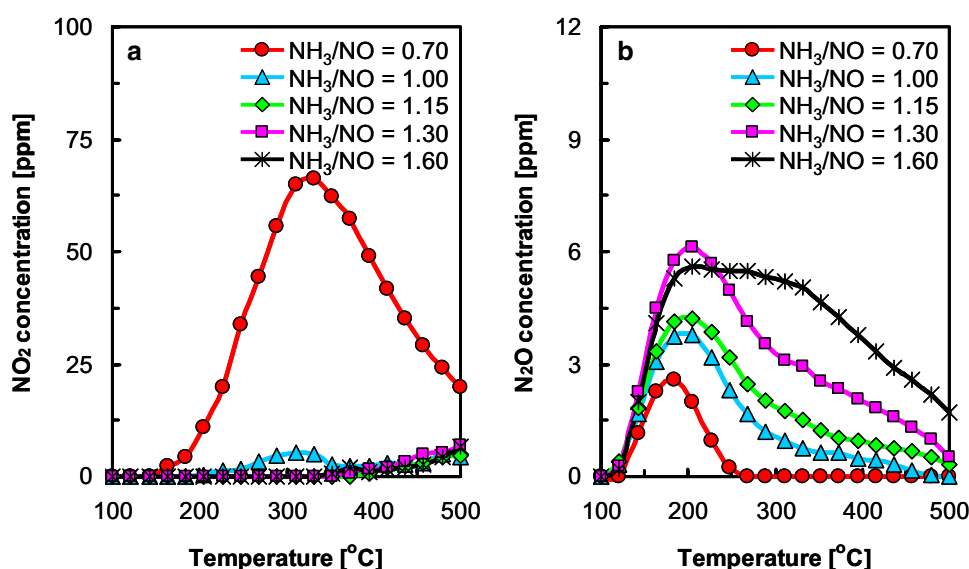


Fig. 6 NO_x conversion (a) and NH₃ slip (b) as a function of temperature at various NH₃/NO ratios in the course of NH₃-SCR. 230–530 ppm NH₃, 330 ppm NO, 10% O₂, 6% H₂O and a balance of N₂ (GHSV = 36,000 h⁻¹). Cooling rate of 2 °C/min

Fig. 7 a NO₂ and b N₂O emission as a function of temperature at various NH₃/NO ratios in the course of NH₃-SCR. 230–530 ppm NH₃, 330 ppm NO, 10% O₂, 6% H₂O and a balance of N₂ (GHSV = 36,000 h⁻¹). Cooling rate of 2 °C/min



flow rate of the feeding gas from 300 to 900 ml/min. The data obtained indicate that the decrease in space velocity from 54,000 to 18,000 h⁻¹ significantly improves NO_x conversion at 100–250 °C, while at the higher temperatures the influence of GHSV becomes negligible. The dual-zone catalyst exhibits 80–90% NO_x conversion at 260–500 °C at GHSV of 54,000 h⁻¹.

It should be mentioned, that the space velocity range of 18,000–54,000 h⁻¹ for the monolithic catalyst is equivalent

to GHSV of 93,000–280,000 h⁻¹ for the corresponding powder Mn–Ce/FeBeta catalyst with a bulk density of 0.600 g/ml, which is about the same range as commonly used in studying NH₃-SCR process (typically 30,000–100,000 h⁻¹ [21]). The data obtained indicate that FeBeta/Mn–Ce/FeBeta dual-zone catalyst is capable to provide favorable NO_x abatement at high space velocity, which is crucial for application in diesel vehicles with limited space on board.

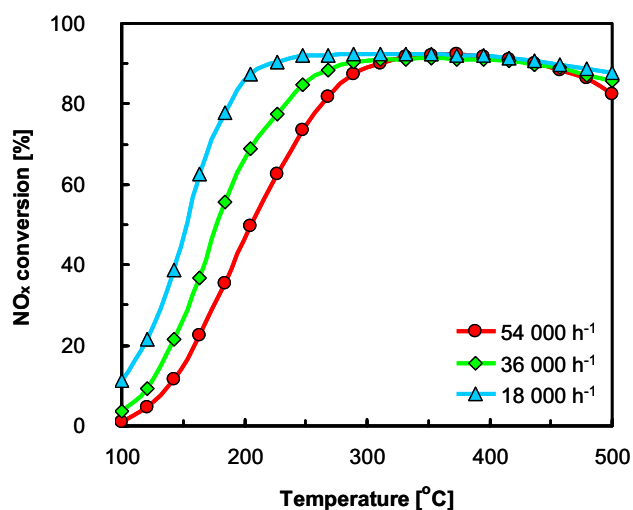


Fig. 8 Effect of GHSV on NH_3 -SCR performance of FeBeta//Mn–Ce/FeBeta dual-zone catalyst. 380 ppm NH_3 , 330 ppm NO, 10% O_2 , 6% H_2O and a balance of N_2 (GHSV = 18,000–54,000 h^{-1}). Cooling rate of 2 $^\circ\text{C}/\text{min}$

4 Conclusions

The NH_3 -SCR performance of the FeBeta//Mn–Ce/FeBeta dual-zone catalyst prepared by Mn and Ce loading on downstream part of monolithic FeBeta was studied in details. It was shown, that such modification results in the significant improvement of catalytic activity and N_2 selectivity within the wide temperature range. Moreover, the dual-zone catalyst is capable to provide effective NH_3 -slip removal even at $\text{NH}_3/\text{NO} = 1.60$.

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References

- Alessandro A, Ana RD (2009) *Energy* 34(3):348–354
- Johnson T (2008) *Platin Met Rev* 52(1):23–37
- Gao F, Tang X, Yi H, Zhao S, Li C, Li J, Shi Y, Meng X (2017) *Catalysts* 7(7):199
- Guan B, Zhan R, Lin H, Huang Z (2014) *Appl Therm Eng* 66(1–2):395–414
- Li JH, Chang H, Ma L, Hao JM, Yang RT (2011) *Catal Today* 175(1):147–156
- Fu M, Li C, Lu P, Qu L, Zhang M, Zhou Y, Yu M, Fang Y (2014) *Catal Sci Technol* 4(1):14–25
- Stakheev AY, Baeva GN, Bragina GO, Teleguina NS, Kustov AL, Grill M, Thøgersen JR (2013) *Top Catal* 56(1–8):427–433
- Salazar M, Becker R, Grünert W (2015) *Appl Catal B* 165:316–327
- Salazar M, Hoffmann S, Tkachenko OP, Becker R, Grünert W (2016) *Appl Catal B* 182:213–219
- Stakheev AY, Mytareva AI, Bokarev DA, Baeva GN, Krivoruchenko DS, Kustov AL, Grill M, Thøgersen JR (2015) *Catal Today* 258(Part I):183–189
- Mytareva AI, Stakheev AY, Baeva GN, Bokarev DA, Kustov AL, Thøgersen JR (2016) *Top Catal* 59(10–12):919–924
- Avila P, Montes M, Miró EE (2005) *Chem Eng J* 109(1–3):11–36
- Kashin AS, Ananikov VP (2011) *Russ Chem Bull Int Ed* 60(12):2602–2607
- Krivoruchenko DS, Telegina NS, Bokarev DA, Stakheev AY (2015) *Kinet Catal* 56(6):741–746
- Sun W, Li X, Mua J, Fan S, Yin Z, Wang X, Qin M, Tadé M, Liu S (2018) *J Colloid Interface Sci* 531:91–97
- Tang X, Li Y, Huang X, Xu Y, Zhu H, Wang J, Shen W (2006) *Appl Catal B* 62(3–4):265–273
- Wu Z, Jin R, Liu Y, Wang H, Catal (2008) *Commun* 9(13):2217–2220
- Kapteijn F, Singoredjo L, Andreini A, Moulijn JA (1994) *Appl Catal B* 3(2–3):173–189
- Casapu M, Kröcher O, Elsener M (2009) *Appl Catal B* 88(3–4):413–419
- Mytareva AI, Bokarev DA, Baeva GN, Krivoruchenko DS, Belyankin AY, Stakheev AY (2016) *Petr Chem* 56(3):228–233
- Kašpar J, Fornasiero P, Hickey N (2003) *Catal Today* 77(4):419–449