HOKKAIDO UNIVERSITY

Title	NH3-SCR by monolithic Cu-ZSM-5 and Cu-AFX catalysts: Kinetic modeling and engine bench tests
Author(s)	Shibata, Gen; Eijima, Wataru; Koiwai, Ryutaro; Shimizu, Ken-ichi; Nakasaka, Yuta; Kobashi, Yoshimitsu; Kubota, Yoshihiro; Ogura, Masaru; Kusaka, Jin
Citation	Catalysis Today, 332, 59-63 https://doi.org/10.1016/j.cattod.2018.06.023
Issue Date	2019-07-15
Doc URL	http://hdl.handle.net/2115/82221
Rights	© 2019. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
Rights(URL)	http://creativecommons.org/licenses/by-nc-nd/4.0/
Type	article (author version)
File Information	2018 Catalysis today.pdf

NH$_3$-SCR by monolithic Cu-ZSM-5 and Cu-AFX catalysts: Kinetic modeling and engine bench tests

Gen Shibata[a,*], Wataru Eijima[a], Ryutaro Koiwai[a], Ken-ichi Shimizu[b,*], Yuta Nakasaka[a], Yoshimitsu Kobashi[a], Yoshihiro Kubota[c], Masaru Ogura[d], Jin Kusaka[e]

[a] Research Faculty of Engineering, Hokkaido University, N-13 W-8, Kita-ku, Sapporo 060-8628, Japan
[b] Institute for Catalysis, Hokkaido University, N-21, W-10, Kita-ku, Sapporo 001-0021, Japan
[c] Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodoagaya-ku, Yokohama 240-8501, Japan
[d] Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
[e] Faculty of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

ARTICLE INFO

ABSTRACT

A simple kinetic model for the standard NH$_3$-SCR reaction by Cu-ZSM-5 catalysts has been developed by assuming three reaction steps: NH$_3$ adsorption (desorption), reactions of adsorbed NH$_3$ with O$_2$ (NH$_3$ oxidation) and NO (NH$_3$-SCR). The model is based on Arrhenius parameters for NH$_3$-SCR and NH$_3$ oxidation by a powder catalyst, combined with models for heat and mass transport and parameters of monolithic catalysts. The model is validated with the experimental results, not included in the estimation of the model, for NH$_3$-SCR by monolithic catalysts with different parameters (catalyst loading and cell density). NOx removal from diesel exhaust, generated by engine bench, was also carried out by using monolithic Cu-ZSM-5 and Cu-AFX catalysts. The results suggest the poisoning effect of hydrocarbons in the exhaust emissions on NOx conversion is more significant for Cu-ZSM-5 than Cu-AFX.

1. Introduction

The introduction of real driving emission measurements has been decided in Europe [1]. So, accurate emission control of ammonia selective catalytic reduction (NH$_3$-SCR) by Cu-zeolite catalysts [2] is becoming a critical issue. Thus, kinetic modeling of NH$_3$-SCR is indispensable for the state-of-the-art diesel NOx emission control. Although previous studies have shown excellent kinetic models of NH$_3$-SCR by zeolite catalysts [3–12], two critical issues remain to be solved. First, some of the models are too complicated to be used in general. Second, there are a limited information on a difference between a model reaction system using a surrogate gas mixture and a practical de-NOx system for engine bench.

Based on these backgrounds, we study herein a simple kinetic model for NH$_3$-SCR and then show a comparison between NH$_3$-SCR for a model gas mixture and real diesel exhaust emissions generated by engine bench. First, we show a simple kinetic model for the standard NH$_3$-SCR on the basis on the activation energy and frequency factor for a powder Cu-ZSM-5 catalyst, which is combined with a model for heat and mass transport in a monolithic catalyst [13,14]. The model is validated by comparison of the simulated NH$_3$-SCR data and NH$_3$-SCR

data obtained by monolithic Cu-ZSM-5 catalysts under steady state conditions. Then, the model gas tests and engine bench tests are conducted for two representative monolithic catalysts: Cu-ZSM-5 (medium pore zeolite) and Cu-AFX (small pore zeolite). The test results suggest the inhibition effect of hydrocarbon emissions on NOx conversions at low temperatures. The results are discussed in terms of the sizes of hydrocarbon molecules and the micropores of ZSM-5 and AFX.

2. Experimental

Cu-ZSM-5 (Cu/Al = 0.635) and Cu-AFX (Cu/Al = 0.32) catalysts, prepared by a standard ion-exchange method, were supplied from the Research Association of Automotive Internal Combustion Engines (AICE), Japan [15]. Powder-coated cordierite monolithic catalysts of Cu-ZSM-5 and Cu-AFX were also supplied by AICE. The powder type catalysts of Cu-ZSM-5 are used to obtain kinetic parameters.

NH$_3$-SCR and NH$_3$ oxidation reactions with powder Cu-ZSM-5 catalyst (Fig. 3) were performed by a flow-type micro-reactor (quartz tube with an inner diameter of 9 mm) equipped with mass flow controllers (MFC) using model gas mixture (0 or 500 ppm NO, 500 ppm NH$_3$, 10% O$_2$, 2% H$_2$O in He, a total flow rate of 100 cm^3/min) and 0.02–0.15 g
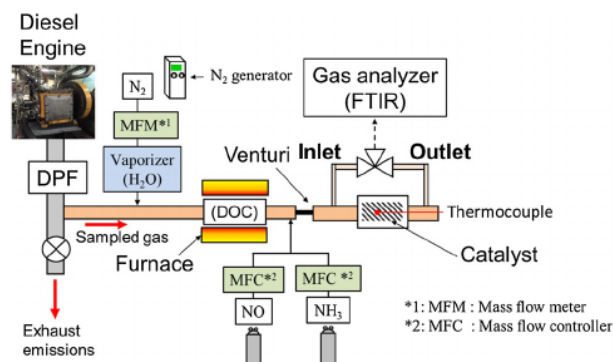
Fig. 1. Outline of the apparatus for mixed gas tests and engine exhaust tests by monolithic catalysts.

catalyst. Steady-state reaction rates were measured under the condition where NO and NH_3 conversions were below 30% by changing catalyst amount. The effluent gas was analyzed by FTIR spectroscopy (JASCO, FTIR-4100) with a heated gas cell (JASCO, LPC-8M-S).

NH_3-SCR by monolithic catalysts (Figs. 4 and 5) were performed by a flow-type reactor (stainless tube of an inner diameter of 27.6 mm). Fig. 1 shows an apparatus for gas feed and catalytic tests. The monolithic Cu-ZSM-5 or Cu-AFX catalyst illustrated in Fig. 2 (a diameter of 25.4 mm, a length of 40 mm, a cell density of 600 or 400 cpsi, a catalyst amount of 100 or 150 g/L) was surrounded by a glass wool to avoid gas slip between the reactor wall and the catalyst. For the reaction with a model gas mixture (Fig. 4), the gas mixture (300 ppm NO, 350 ppm NH_3, 5% O_2, 3% H_2O, in N_2 balance) was fed by MFC at a flow rate of 15 L/min, corresponding to space velocity (SV) of 108,000 h^{-1}. Water was fed into the N_2 stream from a syringe pump with a micro-feeder. After exposure of the catalyst to the mixture at 500 °C for 1 h, NO conversions under steady-state conditions were measured at various temperatures (600 °C to 150 °C). The gas mixture was pre-heated by a furnace before introduction to the catalyst. The catalyst temperature was measured by a K-type thermocouple at the center of the monolith. Inlet and outlet gasses were analyzed using a HORIBA MEXA-4000FTIR analyzer. All tubes and the FTIR gas cell were heated at 113 °C to avoid condensation of water and formation of NH_4NO_3. NO_x conversion was calculated as $(c_{NOx-IN} - c_{NOx-OUT})/c_{NOx-IN}$, where NOx is the sum of NO and NO_2.

De-NOx from the real diesel exhaust (Fig. 5) was carried out using the same apparatus for the above monolithic catalyst tests. We used a single cylinder light-duty direct injection diesel engine (Table S1) with a high pressure common rail fuel injection system, and the fuel used in the experiments is the commercially available #2 Japanese diesel fuel (cetane number 54). The engine operation conditions are shown in Table S2. Under the engine operation conditions with 0.5 MPa BMEP (break mean effective pressure) load condition, the exhaust contains 370 ppm NO, 10 ppm NO_2, 120 ppmC hydrocarbons, 11% O_2, and 4% H_2O. Diesel particulates were removed from the exhaust by diesel particle filter (DPF) without oxidation catalysts. A part of the exhaust gas flow (15 L/min) sampled from the exhaust was heated with a furnace and was mixed with a NH_3 flow from MCF, and the mixture containing 420 ppm NH_3 was fed to the monolithic catalyst. For a control NH_3-SCR reaction with small amounts of hydrocarbons in Fig. 5,
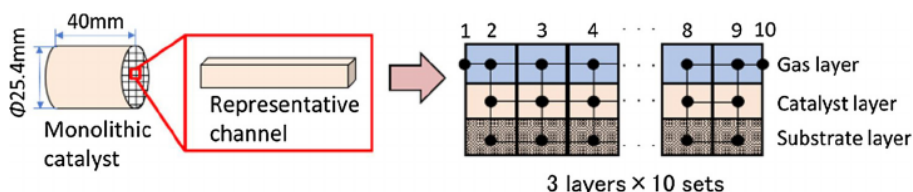
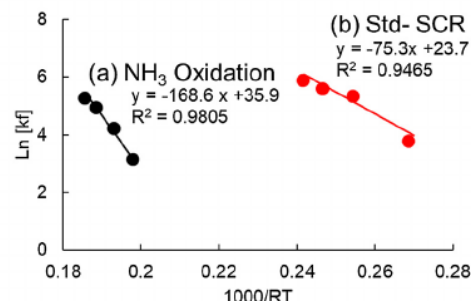| Reaction	Pre-exponential factor [1/s]	Activation energy [kJ/mol]
NH3 oxidation	1.9×10^{17}	168.6
Standard-SCR	1.6×10^{11}	75.3

Fig. 3. Arrhenius plots for (a) NH_3 oxidation and (b) standard SCR by a Cu-ZSM-5 powder catalyst. Conditions: 500 ppm NO, 500 ppm NH_3, 10% O_2, 2% H_2O in N_2 balance.
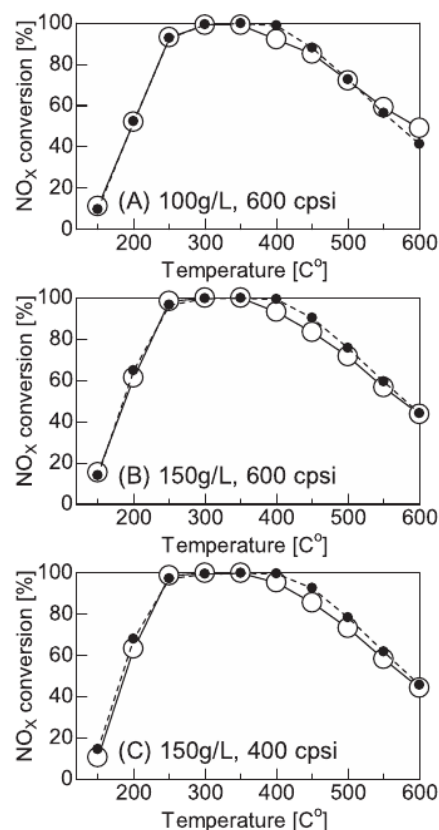

Fig. 4. The measured (○) and calculated (●) NOx conversions for the standard NH_3-SCR by monolithic Cu-ZSM-5 (A)-(C) with different catalyst coating amount (g/L) and cell density (cpsi). Conditions: 300 ppm NO, 350 ppm NH_3, 5% O_2, 3% H_2O in N_2 balance, SV of 108,000 h^{-1}.

Fig. 2. Schematic outline of monolithic catalysts and a model for the channel structure.
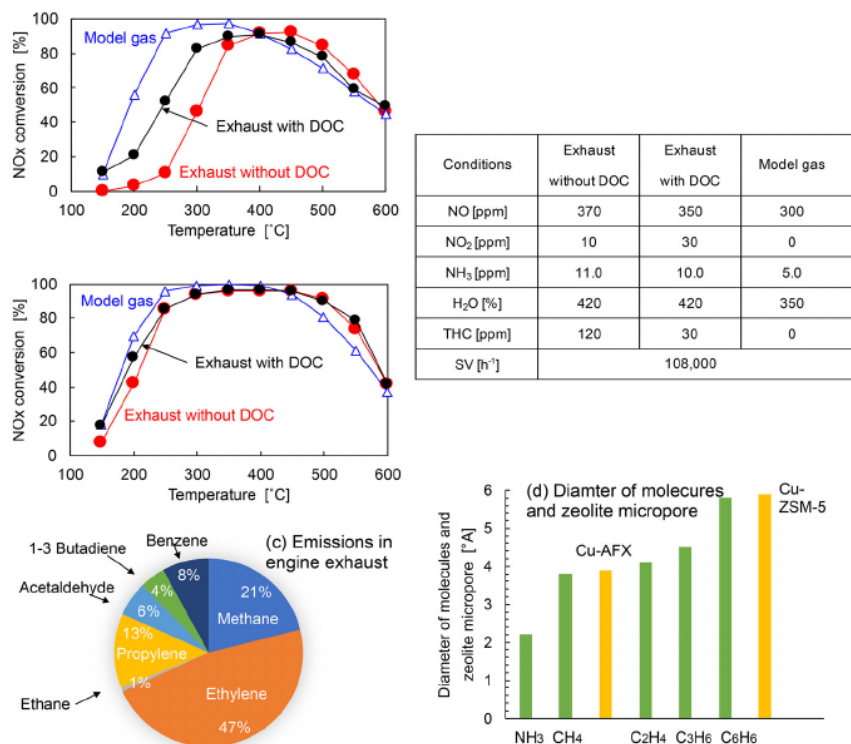
ARTICLE IN PRESS

Fig. 5. De-NOx profiles for (a) Cu-ZSM-5 (A) and (b) Cu-AFX, (c) GC analysis of hydrocarbon emissions from the diesel engine.

a diesel oxidation catalyst (DOC) heated at 300 °C is equipped at the upstream of the SCR catalyst. For the analysis of hydrocarbons in the engine exhaust in Fig. 5(c), the emissions, without passing the DOC and SCR catalysis, were sampled by a gas bag, and were analyzed by a gas chromatograph-FID.

3. The model

The NH$_3$-SCR model has been developed in Fortran, based on computational fluid dynamics (CFD) and chemical kinetics [13,14]. The initial and calculation conditions are the input data, and the initial environmental conditions in the monolithic catalyst are calculated. Then, the chemical reaction part is solved and the time step is updated. The energy transport equation, flow distribution, and mass transport equations are also solved. In the simulation with the monolithic SCR catalyst, it is assumed that the same flow and the same chemical reactions occur in all flow channels in the catalyst, making the calculations performed for one channel represent the overall exhaust. A representative channel, illustrated in Fig. 2, is modelled in quasi-2D and divided into the y-axis (the direction perpendicular to the flow) and the Z axis (the direction parallel to the flow) components. The energy transport, mass transport, and diffusion between gas-to-solid and solid-to-solid components are taken into account. The time step for calculation is 0.1 msec. The properties of monolithic catalysts for model mixed gas tests and engine exhaust test are shown in (Table 1).

The kinetic model is based on the three reactions listed in Table 2: adsorption/desorption of NH$_3$ (R1), oxidation of the adsorbed NH$_3$ (R2), and reduction of the adsorbed NH$_3$ under NO + O$_2$ (standard-SCR). We assume that the adsorbed NH$_3$ on an active site reacts with NO + O$_2$ via the Eley-Rideal mechanism. For the NH$_3$ adsorption/desorption step (R1), the reaction parameters by Olsson et al. [5] were used. The rate equations for the NH$_3$ oxidation, Eq. (1), and the standard-SCR, Eq. (2), are defined in Eqs. (3) and (4). The reaction rate constants are calculated from Eqs. (5) and (6). The activation energy

Table 1
Properties of monolithic catalysts for model mixed gas tests and engine exhaust tests.

Catalyst	Cu-ZSM-5 (A)	Cu-ZSM-5 (B)	Cu-ZSM-5 (C)	Cu-AFX
Micropore size	5.6 Å × 5.3 Å	←	←	3.9 Å × 3.7 Å
Cell density [cpsi]	600	←	400	600
Coat amount [g/L]	100	150	←	100

Table 2
Reactions and rate expressions for NH$_3$-SCR.

No.	Reaction	Reaction rate
R1	NH$_3$ + S1 ⇌ NH$_3$-S1	$r_1 = k_{1,f}$ [NH$_3$] $\theta_{S1\text{-}vacant} - k_{1,b}\theta_{NH3\text{-}S1}$
R2	4NH$_3$-S1 + 3O$_2$ → N$_2$ + 6H$_2$O + 4S1	$r_2 = k_2$[NH$_3$] $\theta_{NH3\text{-}S1}$
R3	4NH$_3$-S1 + 4NO + O$_2$ → 4N$_2$ + 6H$_2$O + 2S1	$r_3 = k_3$[NO] $\theta_{NH3\text{-}S1}$

S1: active site, k: rate constant, [X]: molar concentration, θ_i: coverage of component i.

and frequency factors were taken from the Arrhenius plot in Fig. 3 for the powder Cu-ZSM-5 catalyst.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{1}$$

$$4NO + O_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O \tag{2}$$

$$r_{NH3\,oxi} = k_{NH3\,oxi} [NH_3] \tag{3}$$

$$r_{SCR} = k_{SCR}[NO] \tag{4}$$

$$k_{NH3\,oxi} = \frac{r_{NH3\,oxi}}{[NH_3]} \tag{5}$$

3

ARTICLE IN PRESS

G. Shibata et al.　　　　　　　　　　　　　　　　　　　　　　　

$$k_{SCR} = \frac{r_{SCR}}{[NO]} \qquad (6)$$

4. Results and discussion

4.1. Estimation and validation of kinetic model for SCR by Cu-ZSM-5

Fig. 3 shows the Arrhenius plots for the NH$_3$ oxidation (335–375 °C) and standard NH$_3$-SCR (175–225 °C) by powder Cu-ZSM-5 catalyst. The activation energy and frequency factor for the NH$_3$ oxidation reaction are 169 kJ/mol and 1.9×10^{17} s^{-1}, and those for the NH$_3$-SCR are 75 kJ/mol and 1.6×10^{11} s^{-1}. These values are used in our kinetic simulation model.

Next, we carried out NH$_3$-SCR by monolithic Cu-ZSM-5 catalysts using a model gas mixture (300 ppm NO, 350 ppm NH$_3$, 5% O$_2$, 3% H$_2$O, in N$_2$ balance). Fig. 4 shows NOx conversion profiles for three monolithic Cu-ZSM-5 catalysts: (A) a catalyst with catalyst loading of 100 g/L and cell density of 600 cpsi, (B) a catalyst with catalyst loading of 150 g/L and cell density of 600 cpsi, (C) a catalyst with catalyst loading of 150 g/L and cell density of 400 cpsi. The conversions for different cell density (B and C) were quite close to each other, which indicates that mass transport in the monolith is not rate limiting process. To verify the kinetic model, the calculated NOx conversions are compared to the results of the monolithic catalyst tests. Independent of the catalyst loading and cell density, the simulated conversion curves are in good agreement with the measured curves. This indicates that our simple simulation model is validated with the experimental results for NH$_3$-SCR by monolithic catalysts with different parameters (catalyst loading and cell density). It is important to note that the experimental data used for validation were not included in the estimation of the kinetic model.

4.2. Differences between the model gas and engine exhaust emission tests

Next, we carried out NOx removal from the real diesel exhaust by monolithic catalysts using the same reactor as the above NH$_3$-SCR experiment (Fig. 4). The catalysts used in the experiments are monolithic Cu-ZSM-5 (A) and Cu-AFX with the same catalyst loading (100 g/L) and cell density (600 cpsi). Two types of the reactions with and without DOC were tested. As listed in the table in Fig. 5, the gas mixture without DOC contains larger amount of hydrocarbons than that with DOC. NH$_3$ flow was added to the exhaust between the DOC and the catalyst bed. The composition of the engine exhaust gas mixture without DOC, estimated by GC-FID analysis, is shown in Fig. 5(c). It is found that nearly 80% of the hydrocarbons in the exhaust are light hydrocarbons including methane (21% based on ppmC), ethylene (47%), and propylene (13%). The NOx conversion profiles with and without DOC by monolithic Cu-ZSM5 (A) and Cu-AFX are compared in Fig. 5(a) and (b), respectively. Clearly, the NOx conversions by Cu-AFX are higher than those by Cu-ZSM-5 (A). For the Cu-ZSM-5 (A) catalysts below 350 °C, the NOx conversions with DOC (black curve) are higher than those without DOC (red curve). In contrast, the deference in the NOx conversions with and without DOC is relatively small for Cu-AFX.

To discuss observed difference between Cu-ZSM-5 (A) and Cu-AFX, the kinetic diameter of the hydrocarbons [16] in the exhaust are compared with the diameters of micropores of ZSM-5 (5.6 Å × 5.3 Å) and AFX (3.9 Å × 3.7 Å) in Fig. 5(d). The kinetic diameters of NH$_3$ and CH$_4$ molecules are smaller than the pore size of ZSM-5 and AFX, which indicates that NH$_3$ and CH$_4$ can enter the micropores of Cu-ZSM-5 (A) and Cu-AFX catalysts. The diameters of other light hydrocarbons in the exhaust, ethylene and propylene, are larger than the pore diameter of AFX but smaller than the pore diameter of ZSM-5. This indicates that these hydrocarbons can access the active sites inside the particles of Cu-ZSM-5 but they cannot access the active sites in the particles of Cu-AFX.

hydrocarbons (ethylene and propylene) decreases the catalytic activity of Cu-zeolite catalysts for NH$_3$-SCR [17–21], the larger promotion effect of DOC on the activity of Cu-ZSM-5 (A) than Cu-AFX (Fig. 5) could be explained as follows. With DOC, or in other word with large amount of ethylene and propylene in the exhaust, the catalytic activity of the medium pore zeolite (Cu-ZSM-5) is decreased by the hydrocarbons adsorbed on the active sites. With DOC, or in other word with small amount of these hydrocarbons in the exhaust, Cu-ZSM-5 undergoes less inhibition effect. In contrast, these hydrocarbons cannot access the inner space of the small pore zeolite (Cu-AFX), resulting in less poisoning effect by the hydrocarbons.

To support the above hypothesis, NH$_3$-SCR experiments by a model gas mixture (300 ppm NO, 350 ppm NH$_3$, 5% O$_2$, 3% H$_2$O in N$_2$) were also conducted under the similar conditions as the de-NOx experiments from engine exhaust. The NOx conversion profiles for the model gas mixture tests (blue lines) by Cu-ZSM5 (A) and Cu-AFX catalysts are included in Fig. 5(a) and (b). For the Cu-ZSM-5 (A) below 350 °C, the NOx conversions for the model gas tests (blue line) are higher than those for the engine exhaust tests with DOC and without DOC. In contrast, the difference in the NOx conversions for the model gas tests and engine exhaust tests are relatively small for Cu-AFX. These results are consistent with our hypothesis that a poisoning effect of hydrocarbons on the medium pore zeolite (Cu-ZSM-5) is more significant than small pore zeolite (Cu-AFX). Thermodynamically, amount of adsorbed hydrocarbons decreases with temperature. Oxidation of the hydrocarbons by the Cu catalysts can also reduce the amount of adsorbed hydrocarbons at high temperatures. These trends can account for the experimental result that the NOx conversions for model gas and engine exhaust gas with and without DOC are rather close to each other at high temperatures (> 400 °C) for both catalysts (Cu-AFX and Cu-ZSM-5). In summary, Cu-AFX catalyst with relatively small pore (8-membered ring) undergoes less negative impact of co-existing hydrocarbons than the Cu-ZSM-5 catalyst with relatively large pore (10-membered ring).

5. Conclusions

We have developed a simple model for NH$_3$-SCR by Cu-ZSM-5 based on kinetics and parameters for heat and mass transport and structure of monolithic catalysts. In the model, adsorption and desorption reaction of NH$_3$, oxidation and SCR of the adsorbed NH$_3$ are considered. The developed simulation model can predict the steady-state NOx conversion of monolithic Cu-ZSM-5 catalysts with different parameters (cell densities and amounts of catalyst coated) in the temperature range of 150–600 °C. For NOx reduction from the diesel engine exhaust below 350 °C, the hydrocarbons in the exhaust emissions have an inhibiting effect on the NOx conversion. The inhibition effect is more significant for Cu-ZSM-5 than Cu-AFX, which has smaller micropore size than Cu-ZSM-5. It is suggested that hydrocarbons in the engine exhaust emissions (ethylene and propylene) do not enter into the micropores of the small pore zeolite (Cu-AFX), resulting in a lower inhibition effect of hydrocarbons on the activity of Cu-AFX.

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

Taking into account the reported results that the co-presence of light

online version, at doi:https://doi.org/10.1016/j.cattod.2018.06.023.

4

ARTICLE IN PRESS

G. Shibata et al.

Catalysis Today xxx (xxxx) xxx–xxx

References

[1] C. Favre, D. Bosteels, J. May, J. Andersson, S. Vries, New results from a 2015 PEMS testing campaign on a Diesel Euro 6b vehicle, 11th Integer Emissions Summit & AdBlue® Forum Europe 2015, (2015).

[2] A.M. Beale, F. Gao, I. Lezcano-Gonzales, C.H.F. Peden, J. Szanyi, Chem. Soc. Rev. 44 (2015) 7371–7405.

[3] H.J. Chae, S.T. Choo, H. Choi, I.S. Nam, H.S. Yang, S.L. Song, Ind. Eng. Chem. Res. 39 (2000) 1159–1170.

[4] J.H. Baik, S.D. Yim, I.S. Nam, Y.S. Mok, J.H. Lee, B.K. Cho, S.H. Oh, Ind. Eng. Chem. Res. 45 (2006) 5258–5267.

[5] L. Olsson, H. Sjovall, R.J. Blint, Appl. Catal. B: Environ. 81 (2008) 203–217.

[6] H. Sjovall, R.J. Blint, L. Olsson, Appl. Catal. B: Environ. 92 (2009) 138–153.

[7] H. Sjovall, R.J. Blint, A. Gopinath, L. Olsson, Ind. Eng. Chem. Res. 49 (2010) 39–52.

[8] (a) I. Nova, D. Bounechada, R. Maestri, E. Tronconi, A.K. Heibel, T.A. Collins, T. Boger, Ind. Eng. Chem. Res. 50 (2011) 299–309;
(b) M. Colombo, I. Nova, E. Tronconi, Catal. Today 197 (2012) 243–255.

[9] L. Olsson, K. Wijayanti, K. Leistner, A. Kumar, S.Y. Joshi, K. Kamasamudram, N.W. Currier, A. Yezerets, Appl. Catal. 174–175 (2015) 212–224.

[10] M. Bendrich, A. Scheuer, R.E. Hayes, M. Votsmeier, Appl. Catal. B 222 (2018) 76–87.

[11] K. Leistner, A. Kumar, K. Kamasamudram, L. Olsson, Catal. Today 307 (2018) 55–64.

[12] H. Sjovall, R.J. Blint, L. Olsson, J. Phys. Chem. C 113 (2009) 1393–1405.

[13] W. Eijima, R. Koiwai, G. Shibata, H. Ogawa, Y. Kobashi, J. Kusaka, T. Uenishi, M. Ogura, T. Ohnishi, Development of NH3-SCR reaction computation model in zeolite catalyst, JSAE Trans. Pap. 20174198 48 (2) (2017) 299–304 March.

[14] W. Eijima, R. Koiwai, G. Shibata, H. Ogawa, Y. Kobashi, "Development of Ammonia-SCR Reaction Computation Model and Experimental Studiers on Zeolite Catalysts", COMODIA 2017 Paper No. A-311, Okayama Japan, July 2017.

[15] S.V. Priya, T. Ohnishi, Y. Shimada, Y. Kubota, T. Masuda, Y. Nakasaka, M. Matsukata, K. Itabashi, T. Okubo, T. Sano, N. Tsunoji, T. Yokoi, M. Ogura, Bull, Chem. Soc. Jpn. 91 (2018) 355–361.

[16] J. Weitkamp, S. Ernst, L. Puppe, Shape-selective catalysis in zeolites, Catalysis and Zeolites Vol. 4 Springer, Berlin, 1999, pp. 327–376.

[17] Q. Ye, L. Wang, R.T. Yang, Appl. Catal. A 427–428 (2012) 24–34.

[18] J.Y. Luo, H. Oh, C. Henry, W. Epling, Appl. Catal. B 123–124 (2012) 296–305.

[19] J. Wang, Y. Ji, G. Jacobs, S. Jones, D. Kim, M. Crocker, Appl. Catal. B 148–149 (2014) 51–61.

[20] L. Ma, W. Su, Z. Li, J. Li, L. Fu, J. Hao, Catal. Today 245 (2015) 16–21.

[21] Y. Zheng, M.P. Harold, D. Luss, Catal. Today 264 (2016) 44–54.

5