RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2021, **11**, 10381

High NH_3-SCR reaction rate with low dependence on O_2 partial pressure over Al-rich Cu–*BEA zeolite†

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Received 4th February 2021
Accepted 5th March 2021

DOI: 10.1039/d1ra00943e

rsc.li/rsc-advances

Dependence of NH_3-SCR reaction rate on O_2 partial pressure was investigated at 473 K over Cu ion-exchanged MOR, MFI, CHA and *BEA zeolites with varying "Cu density in micropores". Among the zeolites, Cu–*BEA zeolite demonstrated promising potential as an effective catalyst for NH_3-SCR over a wide range of O_2 partial pressure.

Selective catalytic reduction of NO_x using NH_3 as a reducing agent (NH_3-SCR) is one of the most effective ways to remove NO_x from exhausts with O_2-rich compositions. A lot of catalysts for the reaction have been developed, such as V-based mixed oxides, Fe-zeolites, and Cu-zeolites.[1] Among the catalysts so far, Cu-zeolites exhibit a high reaction rate at a low NO_2 concentration (standard SCR) in a low temperature region (below 550 K).[1] Therefore, the current central trend of the study on the catalysts for NH_3-SCR is based on Cu-zeolites. Since the development of Cu/SSZ-13 zeolite catalyst with CHA topology, which exhibits a high reaction rate in wide temperature region, high selectivity of N_2, and a high durability under hydrothermal conditions,[2] a wide variety of zeolites were tested toward the application of NH_3-SCR.[3]

In the catalytic activity tests of NH_3-SCR, it is often the case that the O_2 concentration in the reaction feed is fixed at a certain value,[3,4] and the effect of O_2 partial pressure (P_{O_2}) on the reaction rate has attracted little attention. The current application of NH_3-SCR is mainly the removal of NO_x emitted from diesel engine. The emission contains an excess amount of O_2 (typically 2–17%).[5] A portion of the O_2 contained in the exhaust is steadily consumed over other catalysts for exhaust purification processes (*e.g.*, diesel oxidation catalyst; DOC and diesel particulate filter; DPF).[6] The DOC catalyst plays a role in oxidative removal of unburned hydrocarbon (HC) and carbon monoxide (CO) using O_2. Particulate matter (PM) is trapped on the DPF and eliminated by catalytic combustion using O_2 and NO_x. In the exhaust purification system of diesel engine, such DOC and DPF units are generally mounted at the upstream of the SCR catalyst. The state-of-the-art SCR system of diesel engines tends to be integrated to DPF to make the whole system compact.[7] Moreover, the application of exhaust gas recirculation (EGR) system, which introduces a part of exhaust into engine cylinder to make the temperature of combustion decrease, resulting in the decrease of thermal NO_x, is in progress for the combustion process.[8] These purification technologies will make the temperature of exhaust and the concentration of O_2 lower than they are.

On the other hand, a recent fundamental research[9] has shown that the reaction rate for NH_3-SCR over Cu–SSZ-13 zeolite catalyst is greatly influenced by the P_{O_2} in a low P_{O_2} region with practical conditions (P_{O_2} < 18 kPa)[5] at 473 K, where the overall rate of this reaction is largely affected by the oxidation of Cu ion on zeolites by O_2.[10] It is shown in the literature[9] that the SCR rate increases with increasing Cu volumetric density. However, the significant rate drop at the P_{O_2} below 15 kPa is a common behaviour of Cu–SSZ-13 zeolite regardless of its composition. Considering the recent trends on the composition of emission from practical diesel engines and the behaviour of Cu–SSZ-13 zeolite catalyst described above, it will be desired to widen the active window for exhaust composition at low reaction temperatures (~473 K) to pass future regulations.[11]

Herein, a comparative study is conducted regarding NH_3-SCR reaction rate dependence on the P_{O_2} at 473 K over Cu ion-exchanged MOR, MFI, CHA and *BEA zeolites from the viewpoint of "Cu density in micropores"[12] to understand the effect of zeolite topology on the dependence.

Details on the preparation of the catalysts and the measurement of the reaction rates have been written in our previous reports.[12,13] The reaction rate was calculated by determining the amount of NO converted to N_2 per second, which was divided by the amount of Cu in the catalyst. The O_2 concentration was kept at 5% during the pretreatment at 873 K, followed by cooling the temperature to 473 K. The cooling to 473 K was conducted under the feed of NH_3-SCR reactants and at least 45 min since the temperature was set to 473 K was ensured

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ra00943e

to reach stable temperature and steady-state NO conversion. Then, the O_2 concentration was altered from 1 to 15%, and more than 10 min was needed to reach initial steady-state NO conversion at each targeted O_2 concentration. Formed NO_2 was transformed to NO by a NO_2 converter catalyst unit attached to a chemical luminescence NO_x analyser (HORIBA VA-3000); therefore, the NO conversion detected by the analyser was regarded as the NO_x conversion and the effect of background NO_2 was eliminated.

First of all, the catalytic activity of a reference Cu–SSZ-13 catalyst[14] with a similar composition to the state-of-the-art commercial catalyst for NH_3-SCR was measured. It is reported that the catalyst has the composition of Si/Al and Cu/Al ratios ~9.5 and 0.3, respectively, corresponding 3.1 wt% Cu,[15] whose Cu content is higher than that of any catalyst used in the report[9] on dependence of NH_3-SCR rates on O_2 pressure.

Fig. 1a shows the rate dependence on P_{O_2} for NH_3-SCR per Cu ((mole NO to N_2) per (mole Cu) per s) by a kinetic measurement at 473 K over the reference Cu–SSZ-13 catalyst. Similar to "Langmuirian dependence" shown in the previous report by Jones *et al.*,[9] a monotonic increase of SCR rate along with P_{O_2} was observed. Note that the dependence obtained in this work could be expressed by the Langmuir–Freundlich equation better than the Langmuir equation (Fig. S1†). The reaction order with respect to O_2 for NH_3-SCR per Cu was determined according to the following power law model equation.[4a]

$$(NH_3\text{-SCR rate per Cu}) = A_0 \times \exp(-E_{app}/RT) \times (P_{O_2})^{\alpha}$$

The α in this equation expresses the reaction order for O_2. Fig. 1a was re-plotted to log–log axises (Fig. 1b) to know the slope corresponding to α. As shown in Fig. 1b, the log–log plot did not follow a liner relationship. It is observed that the slope of the plot decreased with increase in P_{O_2} in the reaction flow. This result shows that the reaction order for O_2 decreases with increase in P_{O_2}.

This phenomenon can be explained by the suggested redox mechanism between Cu^+ and Cu^{2+} in the micropore of zeolites. The reduction of Cu^{2+} to Cu^+ is thought to proceed by NH_3 + NO co-reductants,[16] and the oxidation of Cu^+ to Cu^{2+} is thought to proceed by O_2 oxidant.[17] It has been observed by several *operando* analyses that both Cu^+ and Cu^{2+} exist under a steady-state NH_3-SCR condition,[18] although the ratio between two oxidation states depends both on the composition of Cu-zeolites and the

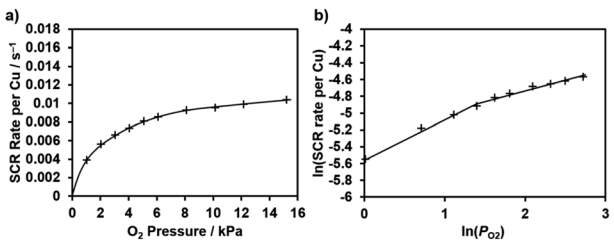

Fig. 1 (a) The dependence of NH_3-SCR rate per Cu at 473 K on O_2 pressure and (b) the log–log plot for the calculation of apparent O_2 order over the reference Cu–SSZ-13 zeolite.

Table 1 The reaction order for O_2 at 473 K over several P_{O_2} region

O_2 partial pressure region/kPa	Reaction order for O_2
1–4	0.46
5–15	0.14

reaction conditions. From these results, it has been suggested that the reaction rate is not solely limited by the rate for the Cu^{2+} reduction step (reduction half-cycle) nor Cu^+ oxidation step (oxidation half-cycle).[10] In other words, the reduction and oxidation half-cycles are kinetically relevant under the conditions below 523 K and at 5–20 kPa O_2 pressure over Cu–SSZ-13 zeolite.[10]

From the description above, the phenomenon observed in Fig. 1b can be understood as follows; the reaction is strongly influenced by the oxidation half-cycle under a low P_{O_2} reaction condition because the supply of oxidant is relatively insufficiency, and the oxidation half-cycle rate is improved with increasing the P_{O_2}. The reaction order for O_2 could be calculated in the low P_{O_2} region (≤4 kPa) and high P_{O_2} region ($5 \le P_{O_2} \le 15$ kPa). The results are shown in Table 1. The reaction order for O_2 decreased with increasing P_{O_2}, but did not reach to zero-order in the P_{O_2} region in this work. It is indicated from the results that the effect of oxidation half-cycle on the whole reaction rate remains in all the P_{O_2} region in this work, and the effect becomes stronger in a lower P_{O_2} region below 5 kPa than in the higher P_{O_2} region over this Cu–SSZ-13 catalyst. The apparent activation energy (E_{app}) for the reaction around 473 K calculated from the Arrhenius plots (Fig. S2†) was not changed obviously (Table 2) in the P_{O_2} region between 1 and 15 kPa. The value of the E_{app} was typical for the NH_3-SCR over Cu-zeolite catalysts.[4] Therefore, it is confirmed that alteration of the reaction condition does not change the apparent E_{app} for kinetically relevant step(s).

The same measurements were conducted over the Cu-zeolite catalysts with MOR, MFI, *BEA, and CHA topologies that have similar cation density in micropores of zeolites and several Cu density in micropores.[11,12] Cu-Zeolites with different topologies and cation density in micropores were applied in this study to minimize the contributions from factors other than the topology that can affect the NH_3-SCR rate.[12] Fig. 2 show the dependence of NH_3-SCR rate per Cu at 473 K on P_{O_2} over each topology. Cu density in micropores increases with light-to-dark shading (Table S1†). As shown in Fig. 2, monotonic increase of

Table 2 The apparent activation energy around 473 K in several O_2 pressure reaction over the reference Cu–SSZ-13 catalyst

O_2 partial pressure/kPa	E_{app}/kJ mol^{-1}
1	49
5	44
15	44

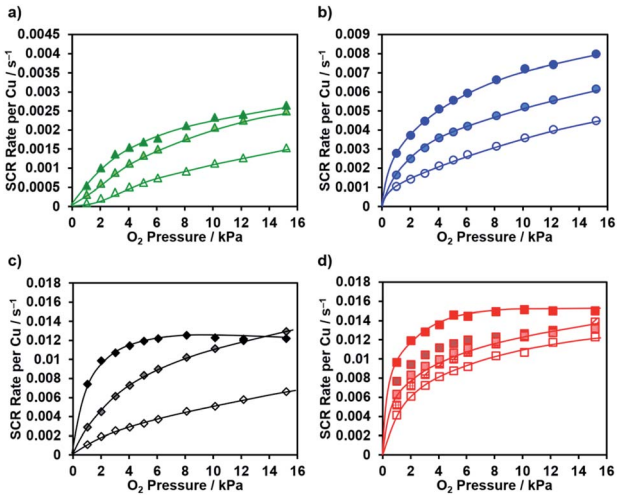

Fig. 2 The dependence of NH_3-SCR rate per Cu at 473 K on O_2 pressure over (a) MOR, (b) MFI, (c) CHA, and (d) *BEA zeolite catalyst with several Cu density in micropores. Cu density in micropores increases with light-to-dark shading.

SCR rate along with P_{O_2} increase similar to shown in Fig. 1a was observed over all Cu-zeolites. However, the changes of SCR rate along with both P_{O_2} and Cu density strongly affected by zeolite topologies and Cu density in micropores.

Cu–MOR zeolite applied in this study exhibited the lowest NH_3-SCR rate per Cu over all P_{O_2} region (Fig. 2a). Note that the scale of *Y* axis in Fig. 2a is as large as a quarter of Fig. 1a. A little increase was observed in both magnitudes and slopes of NH_3-SCR rate per Cu along with increasing Cu density in micropores. However, the rate was far smaller than that of the reference Cu–SSZ-13 zeolite catalyst, even with the higher Cu density.

Cu–MFI zeolite used in this study exhibited a higher NH_3-SCR rate per Cu over all P_{O_2} region than Cu–MOR zeolite (Fig. 2b). The scale of *Y* axis in Fig. 2b is as large as a half of that in Fig. 1a. In the case of the MFI zeolite, the increase was also observed in both magnitudes and slopes of NH_3-SCR rate per Cu with increasing Cu density in micropores. Both the reaction rate and its increase over Cu–MFI zeolite were larger than over Cu–MOR zeolite. However, the reaction rate over Cu–MFI zeolite was smaller than over the reference Cu–SSZ-13 zeolite catalyst regardless of Cu density in micropores. Even the Cu–MFI zeolite with Cu density in micropores at 7.4 $(1000\ Å^3)^{-1}$ (approximately 3 times as large as the reference Cu–SSZ-13 zeolite) did not represent an exception.

In the case of Cu–CHA zeolite, the increase behaviour in NH_3-SCR rate per Cu along with P_{O_2} was largely affected by the Cu density in micropores (Fig. 2c). The catalyst with a low Cu density in micropores showed relatively steady increase in NH_3-SCR rate per Cu along with P_{O_2}. On the other hand, the catalyst showed the rapid increase in NH_3-SCR rate per Cu in low P_{O_2} region, and the rate became constant in the higher P_{O_2} region (>6 kPa). Note that the slight decrease in NH_3-SCR rate per Cu of the Cu–CHA zeolite with the largest Cu density in micropores over 8 kPa P_{O_2} region is mainly caused by the increase in the formation of N_2O. Interestingly, the zeolites with Cu density in micropores at 1.6 and 3.4 $(1000\ Å^3)^{-1}$ exhibited almost the same NH_3-SCR rate per Cu when P_{O_2} was at 15 kPa. This result suggests that they would reach the zero-order dependence on P_{O_2}, which means that the oxidation half-cycle does not determine the overall rate in the P_{O_2} region regardless of Cu density in micropores.

Among the Cu-zeolite catalysts, Cu–*BEA zeolite employed in this study exhibited high NH_3-SCR rate per Cu with relatively low dependence of on P_{O_2} (Fig. 2d). Moreover, the effect of Cu density in micropores of the catalyst was small on the behaviour of the rate along with P_{O_2}. Surprisingly, even the Cu–*BEA zeolite catalyst with Cu density in micropores at 0.76 $(1000\ Å^3)^{-1}$ (The sample shown as hollow red square symbol in Fig. 2d and described as B12 in Table S1†) exhibited a higher NH_3-SCR rate per Cu than the reference Cu–SSZ-13 catalyst with Cu density in micropores at 2.7 $(1000\ Å^3)^{-1}$ (Fig. S3a†). This difference was more obvious in lower temperature region (Fig. S3b†). In other words, the Cu–*BEA zeolite catalyst exhibited a high NH_3-SCR rate per Cu with low dependence on both Cu density in micropores and P_{O_2} in the temperature region below 473 K.

In the case of the zeolites other than Cu–CHA, the obvious deviation from a liner relationship following a Langmuir equation was observed in the dependence of SCR rate on P_{O_2} (Fig. S4†). To analyze the relationship, the Langmuir–Freundlich equation, which introduced the order on P_{O_2} as a correction factor to the Langmuir equation, was needed. From these results, it is suggested that the dependence of SCR rate on P_{O_2} over Cu-zeolites generally follows the Langmuir–Freundlich equation.

The reaction order for O_2 was calculated in a similar manner as the reference Cu–SSZ-13 catalyst in a low P_{O_2} region (≤5 kPa). The results were displayed as a function of Cu density in micropores (Fig. 3a). As shown in Fig. 3a, the reaction order for O_2 decreased with increase in the Cu density in micropores for all the zeolites investigated in this study. This result was consistent with the previous report on Cu–SSZ-13 zeolites with several Cu densities[18] and can be understood by the increase in the rate for the oxidation half-cycle with increasing Cu density in micropores. When the reaction order for O_2 was compared among the Cu-zeolites with a similar Cu density in micropores, the tendency was observed that Cu-zeolite with a high reaction

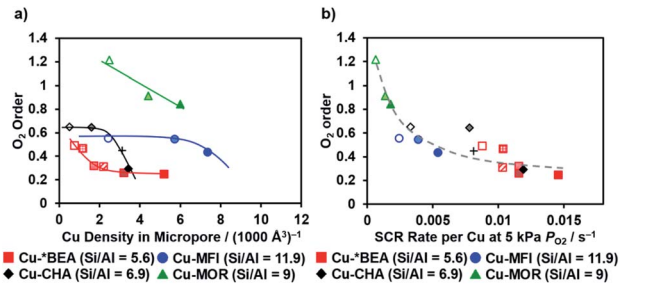

Fig. 3 The relationship between reaction order for O_2 in the O_2 pressure region (≤5 kPa) and the (a) Cu density in micropores or (b) SCR rate per Cu at 5 kPa O_2 over the MOR (▲), MFI (●), *BEA (■), and CHA (◆) zeolites. The cross symbol (+) shows the reference Cu–SSZ-13 zeolite.

rate showed a low reaction order for O_2 (Fig. 3b). This result means that the effect of P_{O_2} on the reaction rate is small over a catalyst with a high reaction rate such as Cu–CHA with high Cu density in micropores or Cu–*BEA.

Both the Cu density in micropores and P_{O_2} could play a role in the oxidation half-cycle in recently suggested mechanism of NH_3-SCR.[17] Moreover, we have reported that the dependence of SCR rate against Cu density in micropores are related to the oxidation half-cycle in a previous report,[12] which investigated SCR rate at O_2 partial pressure of 5 kPa over the same catalysts tested in this study in detail. Thus, it can be assumed that the high NH_3-SCR rate of Cu–*BEA catalyst shown in this report is derived from the oxidation property for Cu^+ ion by O_2 even insensitive to the P_{O_2}. However, detailed analysis using *operando* spectroscopic techniques will be necessary to elucidate the origin. It will be reported and discussed in the closest future.

Dependence of NH_3-SCR rate on P_{O_2} was investigated at 473 K over Cu ion-exchanged MOR, MFI, CHA and *BEA zeolites with several "Cu density in micropores". The reaction rate with respect to P_{O_2} was largely affected by the zeolite topology. Among the zeolites investigated here, Cu–*BEA zeolite catalyst exhibited a higher reaction rate regardless of the Cu density in micropores (or Cu loading) than a Cu–SSZ-13 reference catalyst in the whole range of Cu content tested in this study. The Cu–*BEA zeolite has a promising potential as the effective catalyst for NH_3-SCR in a wide range of P_{O_2}.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by "Elements Strategy Initiative for Catalysts & Batteries (ESICB)" of MEXT; Ministry of Education, Culture, Sports, Science and Technology, Japan, Grant Number JPMXP0112101003.

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