

Article

AFX Zeolite for Use as a Support of NH₃-SCR Catalyst Mining through AICE Joint Research Project of Industries–Academia–Academia

Masaru Ogura ^{1,*} , Yumiko Shimada ¹, Takeshi Ohnishi ¹, Naoto Nakazawa ², Yoshihiro Kubota ² , Toshiyuki Yokoi ³ , Masahiro Ehara ⁴, Kenichi Shimizu ⁵  and Nao Tsunoji ⁶ 

- ¹ Institute of Industrial Science, The University of Tokyo, Meguro, Tokyo 153-8505, Japan; yshimada@iis.u-tokyo.ac.jp (Y.S.); ohnishi@iis.u-tokyo.ac.jp (T.O.)
² Division of Materials and Chemical Engineering, Yokohama National University, Yokohama 240-8501, Japan; naoto-nakazawa-bd@tosoh.co.jp (N.N.); kubota-yoshihiro-sr@ynu.ac.jp (Y.K.)
³ Nanospace Catalysis Unit, Tokyo Institute of Technology, Yokohama 226-8503, Japan; yokoi@cat.res.titech.ac.jp
⁴ Research Center for Computational Science, Institute for Molecular Science, Okazaki 444-8585, Japan; ehara@ims.ac.jp
⁵ Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan; kshimizu@cat.hokudai.ac.jp
⁶ Graduate School of Advanced Science and Engineering, Hiroshima University, Higashihiroshima 739-8527, Japan; tnao7373@hiroshima-u.ac.jp
* Correspondence: oguram@iis.u-tokyo.ac.jp



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Abstract: This paper introduces a joint industries–academia–academia research project started by researchers in several automobile companies and universities working on a single theme. Our first target was to find a zeolite for NH₃-SCR, that is, zeolite mining. Zeolite AFX, having the same topology of SSZ-16, was found to be the one of the zeolites. SSZ-16 can be synthesized by using an organic structure-directing agent such as 1,1'-tetramethylenebis(1-azonia-4-azabicyclo[2.2.2]octane; Dab-4, resulting in the formation of Al-rich SSZ-16 with Si/Al below five. We found that AFX crystallized by use of *N,N,N',N'*-tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium ion, called TEBOP in this study, had the same analog as SSZ-16 having Si/Al around six and a smaller particle size than SSZ-16. The AFX demonstrated a high performance for NH₃-SCR as the zeolitic support to load a large number of divalent Cu ionic species with high hydrothermal stability.

Keywords: NO_x; ammonia-SCR; AFX; zeolite; AICE

1. Introduction

The Association for Automotive Internal Combustion Engine Technology, so-called AICE, was once an organization of eight Japanese passenger car manufacturers (Original Equipment Manufacturers: OEMs) and the Japan Automobile Research Institute (JARI), and has since grown to include two organizations and nine OEMs. At the time of its launch, joint research was conducted with subsidies from the Ministry of Economy, Trade, and Industry (METI) and investments from OEMs. The first phase of the collaboration was a three-year scheme for 2014–2016. The second phase was the following two years 2017–2018, which was an opportunity for autonomy from government subsidies. It has been more than five years since this industries–academia–academia joint research started. This paper will introduce this section, which involves the culmination of five years of our work [1].

The AICE mission originally started with the goal of increasing the combustion efficiency of internal combustion engines and reducing CO₂ emissions in the name of the national project. The AICE, which is mainly in charge of after treatment, has been launched with the following six themes at the time of its inception, targeting diesel vehicles with high combustion efficiency among internal combustion engines.

- (1) Basic research on the advancement of diesel particulate filter (DPF) functions.

- (2) Basic research on the advancement of the regeneration function of DPF.
- (3) DPF simulation application research.
- (4) Basic research on white smoke control technology.
- (5) Basic research on exhaust gas recirculation (EGR) deposit suppression technology.
- (6) Basic research on innovative NO_x reduction catalysts.

Themes (1) to (3) are related to the diesel particulate removal filter, as in diesel aftertreatment. Theme (4) deals with the suppression of relatively high boiling point fuel-derived components that precipitate on the catalytic converter during cold start, and subsequently become visible vapor (i.e., white smoke) when they are expelled by heating. Theme (5) is also related to relatively high boiling point compound-derived components that occur in diesel EGR systems. Our first mission was to develop a unique deNO_x catalyst in the theme (6).

In Japan, diesel passenger cars are very rare. The research theme of AICE, which advocates the systemization of after treatment technologies for clean diesel, reminds us that there are urgent problems to be solved in the exhaust of clean diesel, although the exhaust is cleaner than it was in the past.

In response to the aforementioned theme (6), what is required to us “chemists”, perhaps, is a detailed clarification of the reaction mechanism and the derivation of kinetic equations. First, the following proposition was put forward.

- (I) Development of a unique zeolite catalyst.
- (II) Bridging chemistry and mechanical engineering.

The first proposition is, in essence, a screening work on zeolite catalysts (worldwide termed SCR, selective catalytic reduction of NO_x, using ammonia as a reductant).

The NH₃-SCR (more precisely, using urea aqueous solution, AdBlue[®]) is actually conducted as follows: urea aqueous solution is loaded on-board in a tank and sprayed into the exhaust gas pipe, which undergoes hydrolysis to form two molecules of ammonia on-site from a single molecule of urea, as the combustion exhaust naturally contains a large quantity of water. In the 1930s, NH₃-SCR, in which ammonia aqueous solution was sprayed, was applied to purify thermal NO_x emitted from high-temperature steel melting furnaces. Due to the high concentration of water vapor in combustion flue gas, this water usually becomes a catalyst poisoning for oxide catalysts where Lewis acidity, the redox property of metal, and oxygen deficiency sites are important [2]. However, the NH₃ molecule overcame the competitive adsorption of water molecules and reacted selectively with NO_x at lower temperatures even in the exhaust gas with a high concentration of oxygen remaining. As an aside, the influence of the NO₂ concentration in NO_x on the overall reaction rate was already clarified at that time [3], at least the repetition of definitions such as “fast SCR” and “slow SCR” in the present day is seen.

At that time, an investigation of so-called first generation NH₃-SCR was considered, which was not suitable for on-board use due to the toxicity of ammonia, and the NH₃-SCR catalytic process was considered to be a countermeasure for stationary, fixed sources of NO_x. Here, we would like to stress that Japanese researchers were the leaders in this generation, especially in the reaction mechanism studies [4].

Subsequently, the rise of urea-SCR systems in Europe and the United States has become more pronounced in the 2000s. This can be regarded as the second generation investigation. First, iron ion-exchanged zeolite, and later copper ion-exchanged zeolite were found to be the most suitable catalysts.

In Japan, the selective reduction reaction HC-SCR using hydrocarbons HC for removal of NO_x from the exhaust gas, was discovered in the 1990s. Screening of copper zeolites and the other catalytic systems and examining the reaction mechanisms were the main subject. Thus, many researchers have joined the field and conducted evaluation tests as if they were filling out a candidate from the Periodic Table [5]. In the first-generation era, zeolite was not received that could survive under the severe conditions essential for automotive applications.

Zeolite was generally considered weak against heat, and did not reach practical use. There existed another question: is it possible for molecules in the exhaust gas to enter the molecular-sized pores of zeolite under such a massive stream of exhaust? Looking back at that time, the 1:1 cooperation between industry (government) and academia was not so intimate, and the exchange of information was insufficient. Finally, zeolite was not much put to use in a practical after treatment application.

The main investigation of the urea (NH_3)-SCR was carried out on copper zeolites, a group of zeolites defined as small pore zeolites with a CHA structure, SSZ-13 [6]. For iron zeolites, a large pore zeolite beta with *BEA structure was mainly used. Other complex oxides such as V_2O_5 and CeO_2 , which have been well studied by Chinese researchers, are also known [7], and their catalytic properties are summarized in a review by a certain catalyst manufacturer [8]. We do not need to compete with the catalyst technologies in the same field as the other researchers in the world [9], because we in Japan produce the world's leading researchers in zeolite synthesis. The expertise in zeolite synthesis in Japan has provided us with "durable" zeolite, where probably the first hurdle exists to be overcome. The "robustness" above-mentioned is based on the assumption that the zeolite crystal structure is not collapsed and dealumination from the zeolite framework does not occur even after exposure to 800 °C for several hours in a water vapor atmosphere, when considering the application as a catalyst for automotive exhaust purification. The original screening target was not to find a zeolite with a novel structure, but the same type of zeolite as that crystallized by the conventional hydrothermal method would be acceptable. Furthermore, we invited to test some zeolites that had been used by professors in other fields working on other reactions, but had never been used for automotive emission control before.

In this way, a journey in search of "good" zeolite was about to begin. We received a zeolite sample from a Japanese researcher who provided us with a potential new SCR catalyst candidate, and we decided to evaluate the NH_3 -SCR characteristics and hydrothermal resistance of the zeolite under unified conditions by ion exchange of Cu. It is important to note that these characterization conditions as well as catalyst evaluation have been made as the AICE standard agreed by all OEMs. Our site will become a base for comparison on the same level of evaluation, and we will form a center to aggregate the conditions, samples for testing, and the results of each analysis.

2. Results and Discussion

2.1. Catalytic Performances and Unique Properties of the Cu-AFX Zeolite

Figure 1 illustrates the catalytic performance of AFX for NH_3 -SCR under conditions so far reported, along with SSZ-13 with a higher silica composition ($\text{Si}/\text{Al} = 19$) and a similar Cu content ca. 4 wt%. As can be observed, the performance on the SSZ-13 showed a high NO conversion, but at 250–300 °C with a narrow active temperature window. It is mainly due to the worse selectivity of NH_3 usage against the SCR reaction, and the selectivity went down upon temperature increase from the ideal value of 1, where SCR reaction takes place solely on the catalyst. A large fraction of Cu species might be located as Cu oxide species on the external surface of the SSZ-13, resulting in the promotion of NH_3 oxidation by oxygen. We know that the Cu content on Cu-SSZ-13 used in this study was too much to demonstrate a better performance for SCR. Actually, in our study, Cu-SSZ-13 with a much less Cu content also gave a better NO_x conversion at a high temperature around 600 °C, thanks to the higher selectivity, as shown in Figure 2. However, the conversions at low temperatures around 200 °C were lower than those on the high Cu zeolite. Hydrothermal aging at 800 °C further deteriorated the catalytic properties, while NO conversion was not so much decreased at the maximum point of active temperature.

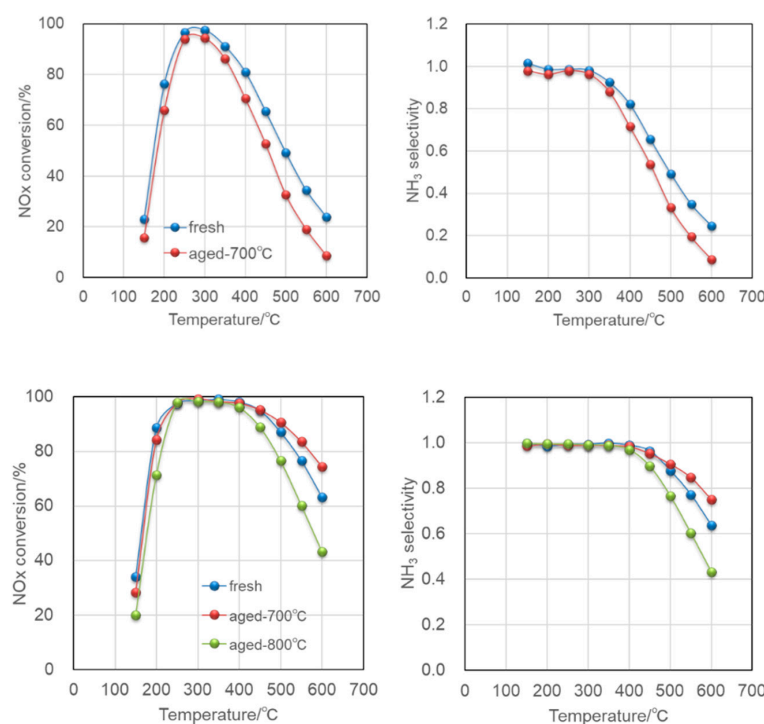


Figure 1. Catalytic performances of SSZ-13 (top) and AFX (bottom) for NH₃-SCR. (Left) NO conversions on fresh and hydrothermally-aged catalysts; (right) NH₃ selectivity for SCR.

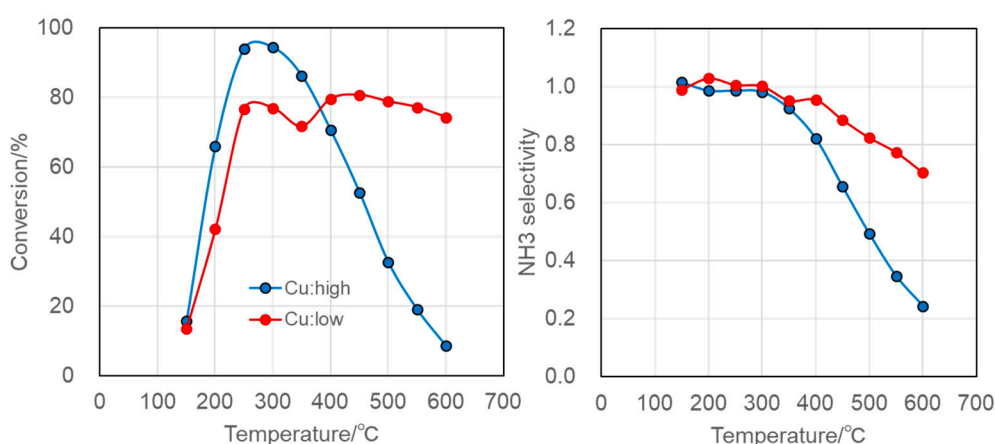


Figure 2. Catalytic performances of aged SSZ-13 with low (1.3 wt% Cu, Cu/Al = 0.30, red) and high (3.7 wt% Cu, Cu/Al = 0.89, blue) contents of Cu. (Left) NO conversions on hydrothermally-aged catalysts; (right) NH₃ selectivity for SCR.

It is amazing that the Cu-AFX zeolite showed a tremendous catalytic performance under our conditions (see Figure 1), and such a high performance could be maintained even after the hydrothermal aging. We should note first that the selectivity kept its high level up to 400 °C, compared with that on Cu-SSZ-13. This mainly reflects the framework composition, and we could say simply that a large quantity of Cu ion exchangeable site results in the higher selectivity on AFX (Si/Al = 5.3) than that on SSZ-13 (Si/Al = 19). Thanks to the high capacity as a Cu ion container, the active temperature window on AFX seems much wider than that on SSZ-13. Second, we must note that hydrothermal stability of the AFX was high, even having such a high Al content. It must be an interesting phenomenon that NO conversions at higher temperatures than 500 °C increased by hydrothermal aging. Becoming higher selectivity in the same temperature region tells us that solid state ion exchange of Cu into AFX further occurs in the aging atmosphere. Much higher performance can be expected from the consideration of ion exchange capacity of the AFX zeolite.

On SSZ-13 (Si/Al = 19), the NO conversion increased significantly with increasing Cu content at low temperatures around 200–300 °C, while at high temperatures above 400 °C, the NH₃ oxidation by oxygen progressed and the selectivity was drastically reduced, as seen in Figure 2. As a result, the window for the temperature range of high NO conversion became very narrow. On the other hand, when the amount of Cu is reduced, the conversion decreased significantly at the low temperatures, while the conversion did not decrease at higher temperatures, thanks to the selectivity remaining high. Consequently, the ion exchange capacity of zeolite is strongly needed for this application, as SSZ-13 with a low Si/Al ratio is expected to be increased in this sense. The difficulty for this is thought to also be due to the fact that a large amount of charge-compensating hydrated Na and K ions are difficult to escape from the 8-membered ring of zeolite, which is the ion exchange window, and thus the small window might inhibit the ion exchange to the Cu form. The ion exchange ability also depends on the crystalline size of SSZ-13, even though it is often without consideration.

SSZ-16 (Si/Al = 3.3) is also the same 8-membered ring zeolite, but it has a smaller Si/Al ratio and, interestingly, a larger ion exchange capacity than other zeolites. Thus, its Cu ion exchange capacity is clearly larger than SSZ-13. Furthermore, it is noteworthy that, despite such a high amount of Al, the activity of the material remains relatively high even after hydrothermal treatment. A general consensus for zeolite is that a zeolite with high Al content is structurally weak. However, the consensus is not always true, and there are several zeolites that are structurally stable even when the amount of Al is high. It might depend strongly on the synthesis of the zeolite.

The structural stability of 8-membered ring zeolites is not necessarily high. For instance, the ZK-5 zeolite was almost completely deactivated after hydrothermal treatment under our test conditions, although it is questionable whether this zeolite is suitable for this comparison. This zeolite has a low Si/Al ratio (4.3) due to the double six-membered ring enclosing the *lta* cage structure [10], but it has a poor ion exchange property, and thus, the low catalytic activity even on the fresh product. So far, we are beginning to get a sense of how the structural properties of the zeolite are linked to the NH₃-SCR properties.

Let us consider the positive difference between SSZ-16 and the AFX named in this study. SSZ-16 synthesized by an organic structure-directing agent (OSDA) [Dab-4]²⁺ was selected for this comparative study, and 5.5 wt% Cu was loaded to the obtained SSZ-16 with Si/Al = 3.3, which corresponds to Cu/Al = 0.30, the same value of Cu-AFX (Cu/Al = 0.32) synthesized by TEBOP²⁺. Figure 3 reveals that the degreened catalysts showed just the same performance. Surprisingly, significant loss in the performance was realized on Cu-SSZ-16, while the conversion was hardly changed on Cu-AFX obtained after hydrothermal aging at 800 °C. Again, we can say why AFX can be promising, even it is highly aluminated zeolite.

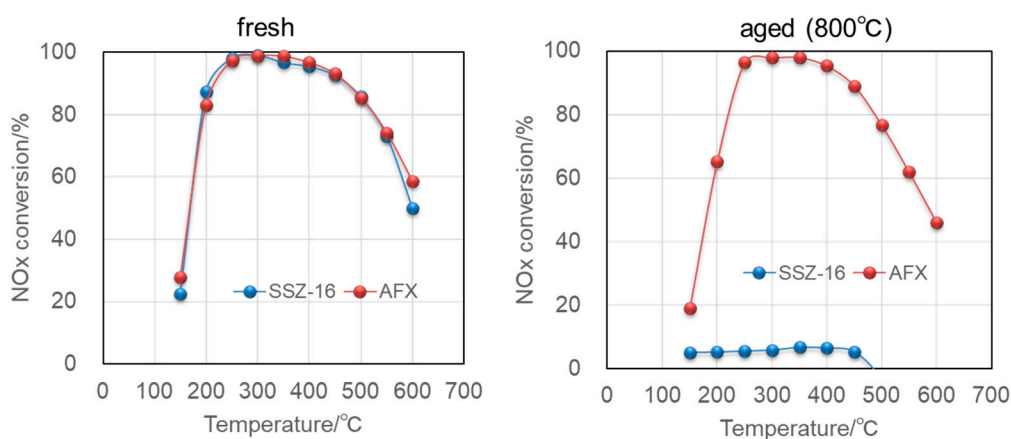


Figure 3. Catalytic performances for NH₃-SCR on fresh and hydrothermally-aged AFX (red) and SSZ-16 (blue).

2.2. Potential Role of OSDA on Al Distribution in the Framework of AFX

Figure 4 demonstrates the thermogravimetry-differential thermal analysis (TG-DTA), which compels the elimination of TEBOP^{2+} , the OSDA molecule as intact inside as-synthesized AFX zeolite. Dehydration was hardly detected under $100\text{ }^{\circ}\text{C}$, meaning that the sample does not occlude H_2O molecule in the micropores, which might be occupied by the TEBOP^{2+} molecule. Two-step weight loss with exothermic peaks was seen at $300\text{--}600\text{ }^{\circ}\text{C}$ in the TG and DTA profiles, which involves thermal decomposition of the TEBOP^{2+} molecule in two steps according to Hoffman elimination of the alkyl group in the alkylamine complex [11]. The quantitative analysis led us to identify that the weight loss assignable to OSDA occluded in the as-synthesized AFX framework corresponded to 0.86 OSDA per one *aft* cage in the AFX structure. This indicates that one molecule TEBOP^{2+} ($0.53 \times 1.35\text{ nm}$ in size) occupies one *aft* cage of the AFX ($0.55 \times 1.35\text{ nm}$ in size).

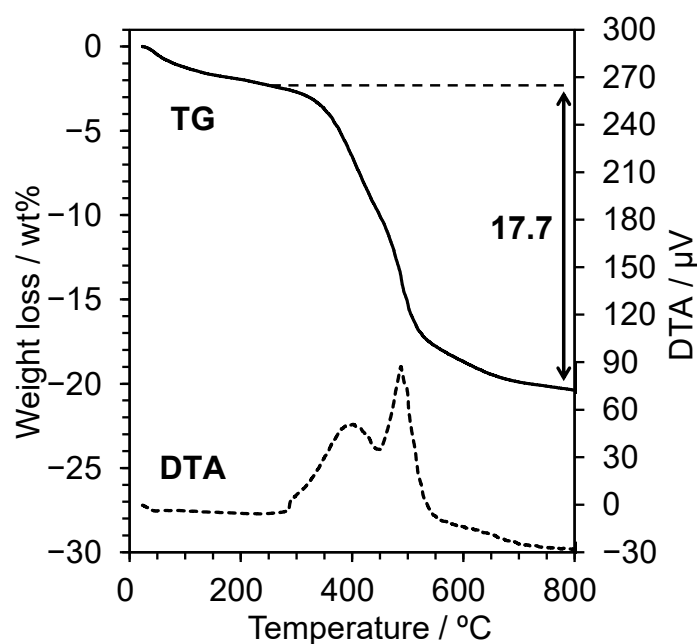


Figure 4. TG-DTA analysis for as-synthesized AFX zeolite.

The effect of an alkali source on the zeolitic phase in the crystallized product was investigated by use of Li^+ , Na^+ , K^+ , and Cs^+ as the inorganic agent in the synthesis solution. As shown in the X-ray diffraction (XRD) patterns in Figure 5, each product revealed that only Na^+ led to form AFX selectively. The diffraction patterns derived from the FAU zeolite were detected in the case studies of Li^+ , K^+ , and Cs^+ . The alkalinity of the aqueous solution for the synthesis of AFX might be changed by using such alkali agents and the FAU added in the synthesis medium as seeds, or the resources of Si and Al for AFX crystallization might not be dissolved as it was. Another promotive force of the size effect of those alkali agents might be possible to drive into consideration; the ion sizes of bare Li^+ , Na^+ , K^+ , and Cs^+ are 0.12, 0.19, 0.26, and 0.34 nm, respectively [12]. The *gme* cage found in AFX is 0.33×0.74 in size (Figure 6). When dissolution of the FAU seed takes place in the course of crystallization, the limitation of the size occluded in the *gme* cage might play a role to nucleate the AFX zeolitic structure.

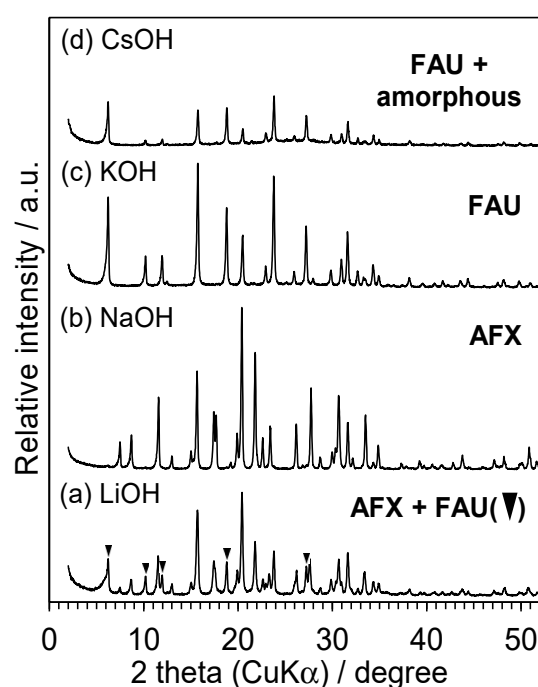


Figure 5. XRD patterns of the products crystallized with TEBOP and hydroxide of (a) Li, (b) Na, (c) K, and (d) Cs in the starting hydrogel.

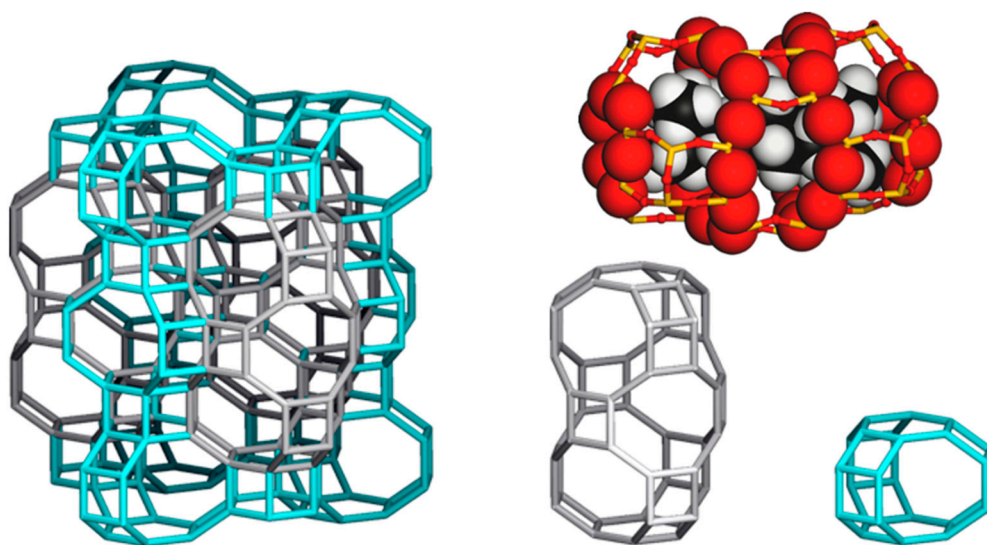


Figure 6. AFX framework composed of two cage structures of *aft* (gray lines) and *gme* (green lines). The cartoon shows that one TEBOP^{2+} cation occupies one *aft* cage.

Figure 7 illustrates the ^{29}Si MASNMR spectra for calcined and Cu ion-exchanged SSZ-16 and AFX zeolites. The three distinct peaks were detected on both samples, Q^4 (0Al), Q^4 (1Al), and Q^4 (2Al), and a minor Q^4 (3Al) might be seen on SSZ-16. The Si/Al ratios of the zeolites calculated by means of Q^4 ($n\text{Al}$) spectra quantitatively were 3.8 for SSZ-16 and 5.2 for AFX. These values are consistent with those analyzed by ICP-AES, which were 3.3 and 5.3, respectively. This could make us believe that the peak assignment is correct. AFX synthesized by TEBOP^{2+} apparently demonstrates Q^4 (0Al) as the main Si species, while SSZ-16 Q^4 (1Al), although both zeolites can be regarded as a highly aluminated zeolite. Along with the existence of Q^4 (3Al) in SSZ-16, it is possible to deduce that the Al distribution in the zeolite framework is quite divergent from each other. Here, a structural

flexibility of the OSDA molecule would be proposed to consider for the discussion of Al distribution. The TEBOP²⁺ molecule seems *rigid* thanks to the sp³ orbital connection, consisting 5- and 6-membered rings of hydrocarbon in between nitrogen atoms, so that the distance of nitrogen atoms with a positive charge keeps a long length. The location of negatively charged Al in the framework may somewhat be governed by the position of positively charged atoms. The TEBOP²⁺ molecule fits well inside the *aft* cage, as illustrated in Figure 6, and almost no space is left for additional Na⁺ insertion in the cage; therefore, Al becomes stable in the framework apart from each other, due to the rigid configuration of the TEBOP²⁺ molecule. In contrast, the [Dab-4]²⁺ molecule seems much more *flexible* than TEBOP²⁺, because the single alkyl chain in between nitrogen atoms is able to bend. There exists a space for an additional cation in the identical *aft* cage or next neighbored cages, resulting in the close location of Al in the framework such as Q⁴ (2 or 3Al). Such Al distribution delivers a preference to stabilize a multivalent cation in a local environment, but simultaneously becomes a weak point against hydrothermal aging conditions.

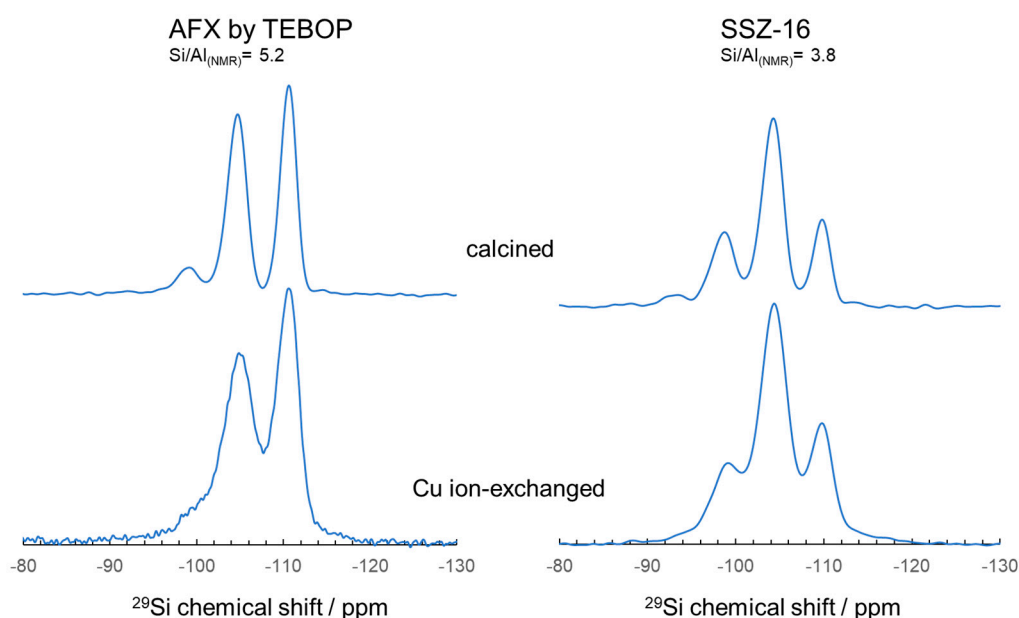


Figure 7. ²⁹Si MASNMR spectra for AFX (left) and SSZ-16 (right) as-calcined (top) or Cu ion-exchanged (bottom) samples.

How can we take into account for the Al distribution in another cage in AFX, that is the *gme* cage? Simple consideration of the Al distribution in the *aft* and *gme* cages with the Si/Al ratio reminds us that it is 5~6 Al in *aft* and 2~3 Al in *gme* cages. Additionally, the size consideration of the Na⁺ ion makes us deduce that a few Al and the corresponding Na⁺ could be present in the *gme* cage. Figure 8 summarizes the catalyst performance of the GME zeolite, which consists of *gme* cages connecting with each other by *d6r* [10]. The deNO_x performance on Cu-GME was apparently lower than other zeolites tested here in the low temperature range. Theoretical calculation has taught us that an intermediate of the SCR such as oxidized NH_x species on the Cu ion in zeolite is difficult to form, and the activation energy for SCR increased with a decrease in the cage size of the support for Cu ions [13]. The GME zeolite has a straight 12 MR channel in its framework structure, and Cu ion exchange and molecular diffusion in the micropores of the zeolite will be helped through the pore connection, which is the reason why another explanation is still possible for the low activity of Cu in GME zeolites. It is preliminarily possible to discuss that a wide space, at least larger than *cha* cage in SSZ-13, is necessary as the reaction field to form an intermediate species for the promotion of SCR.

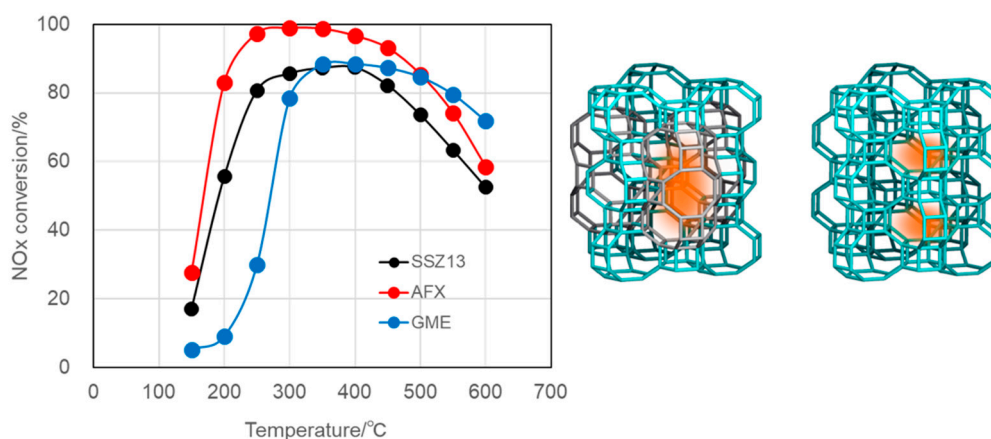


Figure 8. Catalytic performances of AFX and GME zeolites compared with other candidates for NH_3 -SCR. Frameworks of AFX (middle) and GME (right) are illustrated.

3. Method

With the aforementioned strategy, we began, in essence, to work on zeolite screening. It was decided to investigate whether there were any common “descriptors” among the various zeolites provided, without preconceptions such as that a small pore 8-membered ring zeolite is better, or that a large pore zeolite is affected by the adsorption of coexisting HCs, as is generally believed. About 30 structures of zeolites of various sizes and synthetic methods have been investigated [1] and their results are summarized by the following three items:

(1) Selectivity

As the reaction was under the standard SCR condition, and the molar ratio of NO to NH_3 supplied to the catalyst was 1:1, only this 1:1 reaction proceeded at a low temperature of about 200 °C. Based on the previous studies, this reaction was known to be catalyzed by Cu cationic species located at the ion exchange site [14]. However, at high temperatures such as 600 °C, the excess oxygen causes the ammonia to undergo oxidation [15]. Therefore, the term “ammonia selectivity toward SCR” was defined as follows: a value close to 1 indicates the presence of Cu cations and the progress of only selective reduction reaction, while a value away from 1 indicates the progress of non-selective reaction by copper oxide species located outside the zeolite framework.

$$\text{NH}_3 \text{ selectivity toward SCR} = \frac{\text{Converted NO into N}_2 \text{ [mol/min]}}{\text{Converted NH}_3 \text{ [mol/min]}}$$

(2) Si/Al ratio, Cu loading

The Si/Al molar ratio of the zeolite framework applied is one of the major basic properties of the zeolite, and it can be a parameter that controls not only the surface properties of the zeolite, but also the structural properties. A zeolite with a high Si/Al ratio is generally stable against high hydrothermal conditions, while a zeolite with a low Si/Al ratio possesses many metal ion exchange sites such as Cu ions and have a large ion exchange capacity. A zeolite with both high ion exchange capacity and high hydrothermal stability is highly desired.

(3) Large micropore

In the absence of HC, a large pore zeolite such as *BEA and EMT showed a high SCR performance. Some of them such as OSDA-free zeolite beta maintained a high NO conversion after hydrothermal treatment [1]. In general, inhibition of adsorption by coexisting HCs and structural disintegration due to the heat of combustion of HC are often pointed out as a disadvantage of large-pore to extra-large-pore zeolites. However, the size

of the pore does not seem to affect the essence of the “intrinsic” activity of Cu such as the ability to maintain active copper species and surface properties.

More unfortunate is that by-product selectivity to N_2O is unusually high in large pore zeolites, in particular EMT, accounting for more than half of the nitrogen-containing products. This can be explained by the presence of a large cage that can easily form the intermediate NH_4NO_3 for N_2O formation, as discussed in the reaction mechanism [16,17].

Figure 9 shows the preliminary summary of zeolite mining for use as the support of the NH_3 -SCR catalyst [1]. It is clearly demonstrated that NO conversion at 200 °C was increased with an increase in the amount of ionic Cu loaded on each zeolite, where the ionic Cu was detected as another desorption peak in the NH_3 -TPD profile between 150 and 300 °C, apparently different from the original NH_3 desorption derived from the Brønsted acid site in each zeolite. Apart from the discussion on the active Cu species, it must be a natural trend of the activity increment. In another word, the zeolitic framework structure seems to have little influence on the “intrinsic” activity of the Cu ion. This strongly indicates that the main and important role of zeolite support is, first of all, to hold such an active Cu ionic species while maintaining its activity not to be deactivated. Additionally, it is quite natural that a large number of Cu species result in high catalytic performance for NH_3 -SCR; therefore, a large number of ion-exchange sites, that is, Al in the framework of aluminosilicate zeolites, should be kept inside the framework even under severe conditions exposed by automobile exhaust. The plots showing above 70% NO conversion were derived from Al-rich SSZ-13 (Si/Al = 9), beta (Si/Al = 5), and SSZ-16 (Si/Al = 3.3). We focused on SSZ-16 in this study.

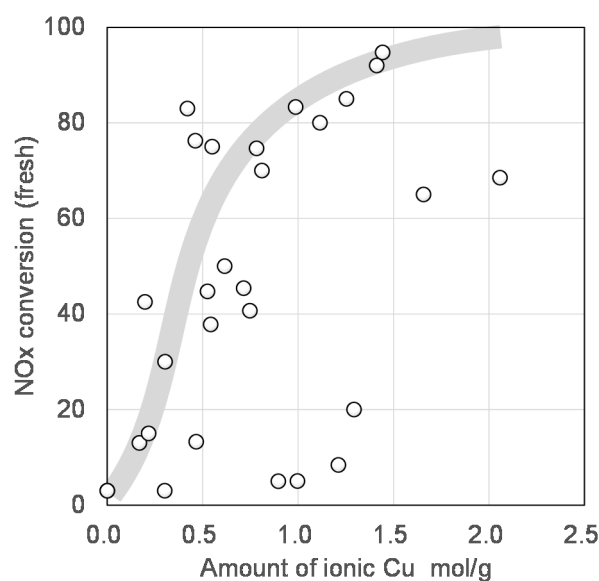


Figure 9. Catalytic performances for NH_3 -SCR at 200 °C over Cu-zeolites with various frameworks, Si/Al ratios, and Cu contents. The plot data was based on the research [1].

The framework type AFX, the three letter code of the structure of SSZ-16 [18] and SAPO-56 [19] assigned by the IZA synthesis committee in 1994, has a large cavity of 0.55×1.35 nm in size, named *aft* as the composite building unit, and a small *gme* cage of 0.33×0.74 nm, each of which is connected by a *d6r* unit [10]. Compared to the SSZ-13 CHA structure (see Figure 10), which holds only one type of medium *cha* cage of 0.70×0.83 nm in size, a large reaction field is expected even though the cages are connected through an 8-membered ring [10]. In this sense, the AFX zeolite is classified in the group of small pore zeolites, the same class of CHA. SSZ-16 was first reported to synthesize hydrothermally by use of 1,1'-tetramethylenebis(1-azonia-4-azabicyclo[2,2,2]octane, $[Dab-4]^{2+}$, a cationic compound, as an organic structure-directing agent [10,20], and the product has a well-crystalline rugby-ball-like particle of 2–3 μm in size with Si/Al = 6 or so. High silica

SSZ-16 was also synthesized by use of 1,3-bis(1-adamantyl)imidazolium cation to obtain Si/Al = 16 with a larger crystalline size of 5 μm [21].

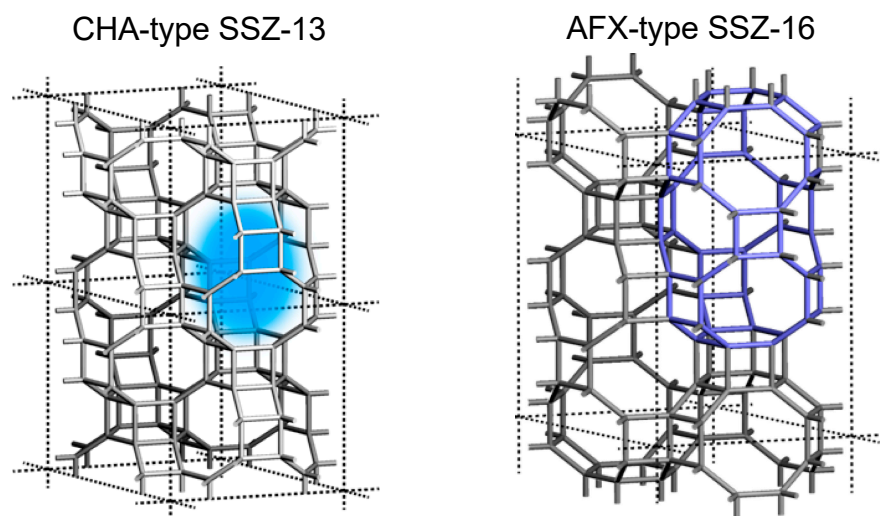


Figure 10. Frameworks of CHA-type SSZ-13 (left) and AFX-type SSZ-16 (right).

One of the coauthors of this research has already reported that the same zeolite could be crystallized by *N,N,N',N'*-tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium cation, TEBOP^{2+} , and they successfully obtained the zeolite with less than 500 nm tetragonal particles having Si/Al = 6~9 [22]. Such unique OSDA could be used to synthesize MSE or other types of zeolite by the same group. Professor Corma and his co-workers reported simultaneously that AFX was crystallized by use of TEBOP^{2+} in a similar manner (see Figure 11) [23]. This zeolite seems to deliver an ideal structure and composition in the name of automobile purification; thus we decided to call it the “AFX” zeolite in this paper to differentiate and categorize a different case with SSZ-16.

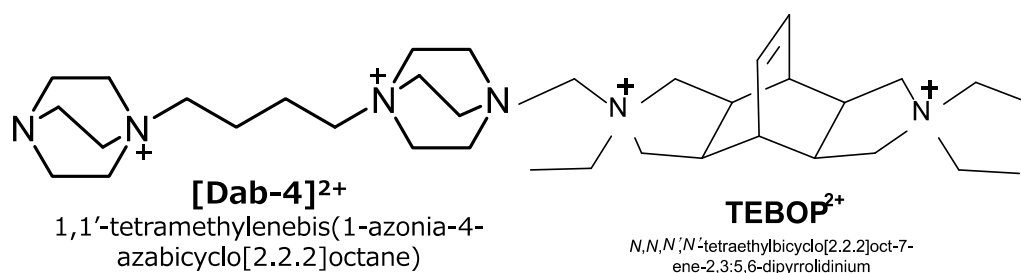


Figure 11. Organic structure-directing agents (OSDAs) synthesized for SSZ-16 (left) and for AFX defined in this study (right).

Experimental

All zeolite samples were supplied from industries or academia [1,22]. SSZ-16 and AFX zeolites were home-made according to the procedures reported elsewhere [22]. The copper ion exchange was carried out at room temperature for 24 h using an aqueous solution of copper acetate. Typically, the chemical compositions of Cu-SSZ-16 and Cu-AFX used in this study were Si/Al = 3.3 and 5.3, and Cu/Al = 0.30 and 0.32, respectively, which corresponds to 5.5 and 4.1 wt% of Cu loading. Characterization of the product with Cu ion exchange was conducted by an inductively coupled plasma-atomic emission spectrometry (ICP-AES, SPS4000, Seiko Instruments Inc., Chiba, Japan), a X-ray diffractometer (XRD, Rint2100, Rigaku, Tokyo, Japan), a N_2 sorption equipment (Quadrosorb, Quantachrome, Boynton Beach, FL, USA), a thermogravimetry-differential thermal analysis (TG-DTA, Thermoplus EVO II TG8120, Rigaku, Tokyo, Japan; TGDTA2000SA, Bruker AXS, Billerica, MA, USA),

and ^{29}Si magic angle spinning-nuclear magnetic resonance (MASNMR, ECA-600, JEOL, Tokyo, Japan).

The SCR test reaction was conducted by a plug-flow, fix-bed reactor attached with a 10 mm diameter glass tube and an electric furnace, which attained an increase in the catalyst bed temperature up to 900 °C. The mixed gas composed of NO, 300 ppm; NH_3 , 300 ppm; O_2 , 5%; H_2O , 3% was balanced by N_2 to be 200 cm^3/min , then flown onto a catalyst 30 mg ($\text{SV} = 144,000 \text{ h}^{-1}$). After degreening the catalyst at 600 °C, the catalytic performance was measured from 150 °C to 600 °C. The conditions for hydrothermal aging was as follows: temperature, 700–900 °C; duration, 16 h; composition of the feed, 5% H_2O balanced by 10% oxygen, and the remaining nitrogen. Infrared detectors and a chemiluminescence NOx analyzer (VA-5000 series, Horiba Ltd., Kyoto, Japan) were used to detect those components, quantify, and calculate the NO and NH_3 conversions. A small amount of N_2O below 10 ppm was detected in almost all of our experiments; nevertheless, the experimental conditions or catalytic nature was altered.

4. Conclusions

In summary, our zeolite mining project led us to discuss the role of zeolite as the support of the active Cu ion for SCR of NO by use of a NH_3 reductant. We focused on the selectivity of NH_3 for SCR as the key term to figure out the better candidate. From this sense, the capacity of Cu ion storage, which simply means the Al content in the zeolite framework, is quite important to at least obtain high NO conversion in a wider active temperature window.

We focused on the AFX zeolite, which we differentiated in this paper with SSZ-16 having the same topology, but with a different synthesis method using a different OSDA TEBOP $^{2+}$ in the synthesis media. The *rigid* feature of the OSDA molecule led to adjusting the Al location in the topology, resulting in a large amount of highly isolated Cu ionic species on zeolites with high hydrothermal stability, even at 800–900 °C.

Based on the above characteristic samples, the next generation of zeolites will be possibly developed, and people may think that this is not going to be easy. After all, it is still the largest common SCR candidate zeolite (distinguished as a new zeolite in our opinion) within the nine Japanese automobile OEMs. From these findings, it seems that it is not so easy to find out the common descriptor of activity and durability. In this sense, we could figure out the common descriptor for high NH_3 selectivity against SCR and the wide temperature window of SCR. The zeolitic catalyst carrier should be capable of providing ion exchange sites (stable retention of active Cu ion species) and inhibiting Al removal from its framework. Finally, these functions result in high selectivity and wide temperature window. It is important to note that Cu ion capacity is a key obtained from the examination of our AFX zeolites and many zeolites, and Al retention is a key obtained from our P-modified zeolites [24,25]. Both researchers who are familiar with this field will submit maximal common descriptors and solutions that are considered to be “natural”. The knowledge provided by the zeolite synthesizer, which is the pride of Japan, is very important.

Not only that, what we should do is to make the greatest common descriptor into a least common multiple. Each OEM has developed their own engine philosophy, its own exhaust gas concepts, its actual exhaust composition, and its own measures. The proposal from the academic world would become common for OEMs to come up with each solution. In this AICE project, both parties could make the best performance in identical research.

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