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A Collective Case Screening of the Zeolites made in Japan for High Performance NH_3-SCR of NOx

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Abstract

Zeolites demonstrating better SCR of NOx performance due to wide temperature activity, hydrothermal stability and N_2 selectivity have been identified under a joint research initiative by the Research Association of Automotive Internal Combustion Engines (AICE), Japan. Based on the AICE's standards, over 25 zeolites with different structures and pore dimensions were investigated and their SCR efficiency and durability have been compared. While the performances of the top contenders cannot be related to a single parameter, the results suggest that the SAR, Cu quality/quantity, pore dimensions, diffusivity and acidity play a combined role in deciding the SCR activity and selectivity.

1. Introduction

The regulations to limit emissions from automotive exhaust for the foreseeable future are much more stringent than ever before, since these emissions have already caused damage to our environment and health. The previous regulatory initiatives to limit them were drawn more loosely.[1,2] Under the current scenario, there is a growing interest in developing advanced engines with robust emission control strategies for fuel efficiency and treating nitrogen oxides (NOx), respectively. Although recent advances in engine designs have been quite impressive, designing high performance materials to control NOx emissions in compliance with new regulations is still ongoing. Selective catalytic reduction (SCR) has emerged as a robust

management tool for treating NOx effectively. The first commercial inception of SCR in automobiles began in 2005 and required plenty of urea on-board. Though urea-SCR exhibited high NOx remediation efficiency, it suffered from technical challenges largely due to the airless system causing secondary emission of isocyanic acid. Since then, ammonia-SCR (NH_3-SCR) has been considered as a viable alternate to overcome issues from urea usage.[3–5] The first generation SCR catalyst was based on vanadium, tungsten and titanium oxides, and found more suitable for treating emissions from stationary sources. As the catalyst in stationary sources is placed within a heat recovery steam generator, their hydrothermal stability was considered critical. During the conventional inception of SCR technology for treating NOx the hydrothermal stability of zeolites had not been fully explored and metal oxides were considered superior in this regard. Therefore, metal oxides found effective usage for the SCR of NOx from stationary sources. However, the durability of these metal oxides is seemingly inferior to zeolites in treating emissions from automobile sources as the latter's activity is better over a broad temperature window and are very tolerant to secondary emissions. Therefore, the second generation SCR system was based on zeolite catalysts i.e. metal exchanged zeolites such as Cu or Fe for the effective reduction of NOx from automobile sources.[3,6]

Since the pioneering work of Barrer in the mid 20th century on the synthesis and adsorption properties of zeolites,[7–10] the field of zeolite science has grown massively, with its industrial usage exceeding one billion tons and discovery of new structures every year. Owing to their structural uniqueness, zeolites are involved in a wide range of industrial applications such as catalysis, ion-exchange and molecular sieving which makes the design of new topologies particularly appealing. Among wide ranging application potentials, catalysis is one of the most sought after properties. Especially, its role in the selective catalytic reduction of NOx with ammonia (NH_3-SCR of NOx) is of paramount significance for safeguarding the environment by treating effluent gas from automobiles and reducing air pollution. The commercial exploitation of copper (Cu) metal exchanged SSZ-13 zeolite with chabazite (CHA) structure as an automotive exhaust catalyst is a well-known example.[11,12]

Nevertheless, the SSZ-13 with an almost monopolized SCR market has been proven vulnerable to structural collapse as well as severe loss in NOx reduction ability, due to the formation of copper oxides at high temperatures.[13,14] Also, investigations of the qualitative and quantitative analysis of Cu species in SSZ-13 revealed how their hydrothermal stability and SCR activity is significantly affected by the type of Cu, their loading and interactions.[15,16] The interactions of the Cu species are thought to be influenced by various factors from cold start to high temperature exhaust conditions. These hypotheses inspired several groups to investigate every possible factor from material synthesis to NH_3-SCR of NOx reactions to envisage how the activities of these materials are related to Cu species.[17–23] Primary investigations by different groups have revealed that there exist two types of Cu species in Cu-zeolite under ambient and oxidized conditions.[18–20] In this regard, Clemens et al. reported details of how external CuO driven by the NH_3-SCR reaction (as a function of time on stream) increases the Cu(I) and Cu(II) species within the zeolite (SSZ-13) pores and therefore enhance their SCR activity.[21] Further, Pereda-Ayo et al. noted that the SCR activity of Cu zeolite catalysts varied based on the type of Cu species involved. While the CuO species favored low-temperature deNOx, the isolated Cu^{2+} species were found to aid high temperature NOx conversion.[22] In a recent study, in situ DRIFTS and TPSR were used to investigate SCR reaction pathways and active intermediates. This gave insights on how NH_3 adsorbed on Lewis acid sites tends to react faster than that adsorbed on Bronsted acid sites.[23]

The mainstay of the current investigation is to exhibit the identification of zeolite systems that provide viable options to address the issues faced with the stereotypic SSZ-13 in terms of wide temperature activity, high hydrothermal stability and N_2 selectivity for NH_3-SCR of NOx under the realistic conditions of automotive exhaust. Though there are several reports about zeolite based NH_3-SCR of NOx, the conditions in each of these studies were not essentially the same and it becomes increasingly difficult to arrive at a general conclusion. Therefore, investigating the efficiency of these materials under a global standard of automotive exhaust conditions is needed for the effective screening of zeolite catalysts based on both the cost and functionality. In particular, International Organization for Standardization (ISO) and Original Equipment Manufacturer (OEM) have set certain standards in vehicle manufacturing and auto parts production. These standards vary in accordance to each country's own jurisdiction requirements.[24] In this regard, a new joint research organization combining nine of the Japanese automobile manufactures and two academic organizations in Japan known as the Research Association of Automotive Internal Combustion Engines (AICE) was established in 2014. Since then AICE supports fundamental and applied research through joint academic and industrial initiatives to develop advanced clean low exhaust gas reduction technologies. Hence, the current study has been conducted over the AICE prescribed standards using ca. 30 zeolite based catalysts (from researchers in Japan) to formulate the ideal knowledge about their catalytic activities for NH_3-SCR of NOx as well as their improvement. Given the extent of environmental damage from automobile exhaust the current study indexes zeolites based mainly on their NH_3-SCR of NOx functionality (ion-exchange capacity, activity and hydrothermal durability) rather than their production cost. Further, the NH_3-SCR of NOx experiments were carried out by overlooking the existing diversities (in terms of synthesis conditions, molar Si/Al ratio, surface chemistry, porosity, Cu content, etc.,) of zeolites investigated so as to represent the good performance of each zeolite within their family.

2. Experimental

2.1 Characterization of Materials. Structural elucidation of the parent and Cu ion-exchanged samples were performed using a RINT2100 X-ray diffraction instrument with Cu Kα radiation (Wavelength, $\lambda = 1.54$ Å). The diffraction measurement was observed in the 2θ range between 5 and 50° with a scan speed of 0.02/s. The Quantochrome Quadrosorb-evo BET analyzer involving N_2 adsorption-desorption method was employed to measure the porosity. Prior to measurement all the samples were degassed under N_2 atmosphere for up to 300 °C for 3 h. Inductively coupled plasma atomic emission

spectrometry (ICP-AES) was used to quantify the elemental compositions.

Temperature programmed desorption of ammonia (NH_3-TPD) was carried out using a BELCAT instrument. The pre-treatment of the samples was done at 500 °C with a rise of 10 °C min^{-1} for 1 h under He atmosphere. The samples were heated up to 610 °C with a temperature rate of 10 °C min^{-1}. Temperature-programmed reduction (TPR) using H_2 was carried out in the BELCAT analyzer fitted with a TCD detector. Sample pre-treatment was done under Ar environment at 500 °C for 1 h and then cooled down to 50 °C, then the temperature was raised by 10 °C min^{-1} from 50 to 800 °C with a flow of 30 mL min^{-1} of H_2 (5 vol%) in Ar for TPR measurements.

2.2 Selective Catalytic Reduction of NOx Using NH_3. In a fixed bed reactor, the NOx decomposition using NH_3-SCR technique was performed with a quartz reactor. In a small quartz-tube reactor of 8 mm in height, 20 mg of catalyst with 280 mg of SiC were stuffed together with a maximum packing limit of 6 mm. The pre-treatment of the catalyst was done by introducing a mixture of gases (O_2:5%, H_2O:3%, N_2:92%) into the system using a mass flow controller. The study was conducted for each 50 °C rise in temperature from 150 to 600 °C with a mixture of NO:300 ppm, NH_3:300 ppm, O_2:5%, H_2O:3% N_2, with a total flow rate of 200 cm^3 min^{-1} GHSV is 50,000 h^{-1}. Hydrothermal aging of the catalyst was done at 700 °C for 15 h using O_2 5%, H_2O 3%, and N_2 3% with a flow rate of 200 cm^3 min^{-1} and was analyzed with a quadrupole mass spectrometer (Q-MS). The same catalyst was hydrothermally aged and the analyses were done at temperatures between 150 and 600 °C.

3. Results and Discussion

In order to facilitate discussion, results summing up the top contenders in terms of NOx conversion as a function of temperature have been put forth in Figure 1 and interpreted in this section. The details of other zeolites involved have been presented in the supporting information. The NOx conversion efficiency of the top nine zeolites as influenced by their Cu content (i.e. low or high Cu) is shown in Figure 1a and 1b, respectively. Increasing Cu content imparts a considerable rise in the NOx conversion of four kinds of zeolites (Cu-P-SSZ-39, Cu-FER, Cu-SSZ-13 and Cu-SSZ-39), while four others (Cu-beta, Cu-EMT, Cu-SSZ-16 and Cu-SZR) exhibit negligibly small or no change (Figure 1). The cause for such divergence in NOx conversion efficiency with varying Cu content of these zeolites is probably related to their Si/Al ratio (SAR) shown in Table 1. As can be seen in Table 1, the former four zeolites possess higher SAR ranging between 6 to 19 in stark contrast to the latter's 3 to 5. In other words, the latter four zeolites possessed aluminum-rich framework favorable for incorporating more Cu at positions desirable for SCR activity than the former four. Therefore, any attempts to load Cu excessively to the Cu-Beta, Cu-EMT, Cu-SSZ-16 and Cu-SZR catalysts fails to make an impact over their SCR activity as they attained maximum NOx conversions even with a lower Cu loading. In addition, the excess Cu species might exist as CuO, which

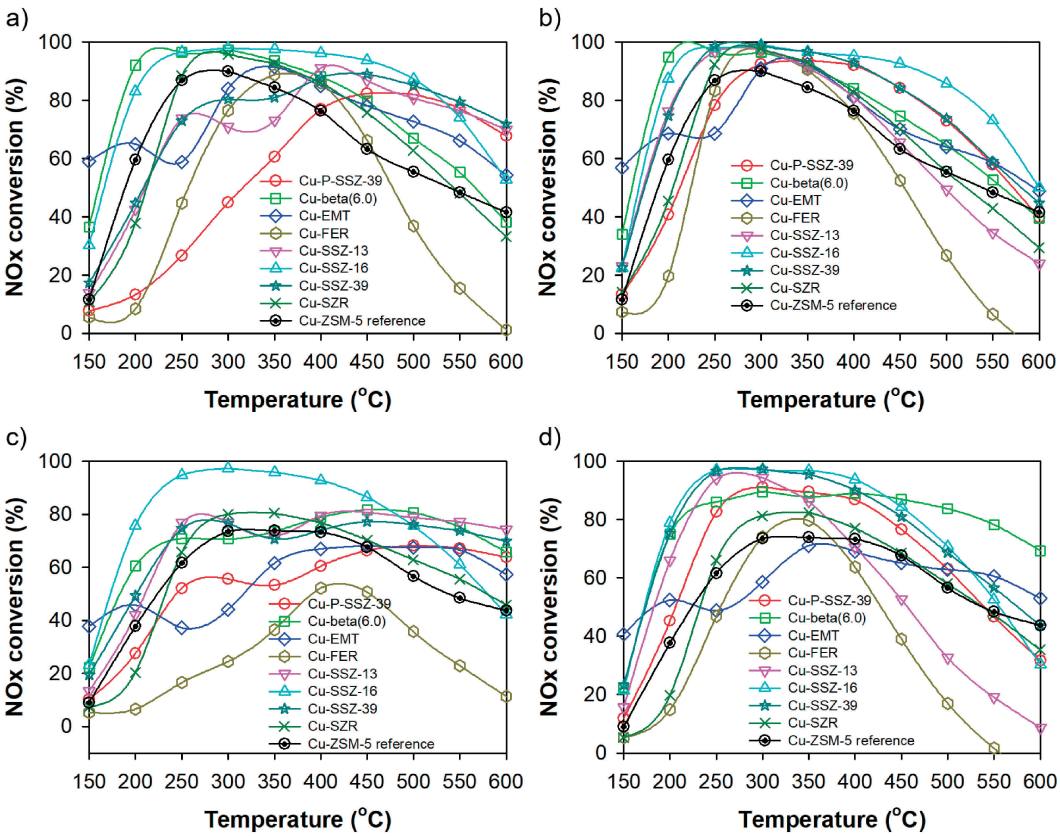

Figure 1. The activities of the top nine zeolites in the NH_3-SCR of NOx reaction performed from 150 °C to 600 °C: a) fresh (Low Cu), b) fresh (High Cu), c) aged (Low Cu) and d) aged (High Cu). Note the Cu content of the Cu-ZSM-5 was not changed as it was supplied as a reference commercially.

Table 1. Comparison of physicochemical traits of the top nine selective zeolites

Zeolite	Molar Si/Al ratio (mol/mol)	Cu loading (wt%)		Cu/Al		MDS* (Å)^{IZA}	MDS# (Å)^{IZA}	MPV (cm^3/g)	Total Acidity (mmol/g) of Cu zeolite		NH_3-TPD (mmol/g)	
		Low	High	Low	High				Low	High	Low	High
Cu-P-SSZ-39	12	1.4	3.2	0.22	0.49	7.3	3.8 3.8 3.8	0.24	1.1	0.96	0.72	0.47
Cu-Beta	5.1	3.6	6.0	0.28	0.48	6.7	5.9 5.9 5.9	0.35	1.4	1.8	1.4	1.4
Cu-EMT	3.5	4.5	5.4	0.27	0.34	12	6.5 6.5 7.3	0.29	2.1	1.7	2.1	1.7
Cu-FER	8.9	2.3	4.2	0.27	0.50	6.3	1.5 3.4 4.6	0.13	2.1	1.7	1.3	1.2
Cu-SSZ-13	19	1.3	3.7	0.30	0.89	7.4	3.7 3.7 3.7	0.17	1.0	0.6	0.66	0.20
Cu-SSZ-16	3.3	4.2	5.5	0.23	0.30	7.8	3.7 3.7 3.7	0.21	2.7	2.1	1.5	0.99
Cu-SSZ-39	12	1.9	3.5	0.28	0.53	7.3	3.8 3.8 3.6	0.43	1.10	1.1	0.52	0.52
Cu-SZR	6.0	2.3	3.3	0.18	0.27	6.3	3.3 3.3 4.6	0.08	1.29	0.91	0.72	0.54
Cu-ZSM-5	11	3.90		0.56		6.4	4.7 4.4 4.4	0.18	1.0		0.81	

^{IZA} – Data according to International Zeolite Association (IZA); Note, Cu-ZSM-5 was supplied commercially as a reference with one type of Cu loading; SZR-Sunbury zeolite with sequence number four; MDS* - maximum diameter of a sphere that can be included; MDS# - maximum diameter of a sphere that can diffuse along a, b and c axes; MPV – micropore volume

enhances undesirable NH_3 oxidation leading to the decrease of NH_3 usage.

At 150 °C, Cu-EMT exhibited NOx conversions of 57% when fresh and 40% when aged, nearly twice the amount put forth by the other contenders (Figure 1b & 1d). Notwithstanding its performance at low temperature, Cu-EMT (high Cu) barely reached its maximum of 90% (fresh) and 71% (aged) NOx conversions at 350 °C before it started to decline at higher temperatures. At 200 °C, Cu-beta hit the highest point of the chart with 95% NOx conversion followed by Cu-SSZ-16 (87% with high Cu loading), which is far higher than the rest. At low temperatures, the activity of the catalysts solely depends on the availability of active Cu ionic species, which enhance the adsorption of reactants. However, contributions from other CuO as well as the diffusivity of zeolite channels begin to influence the conversion of NOx into desired and/or undesired products as we move up the temperature scale. Once the temperature reached 300 °C, all the nine zeolites have attained their maximum activity for NOx conversion i.e. 90% and above. Though the activity of most zeolites started to wither off after 300 °C, each showing random decrease in NOx conversion, some lingered till 350 °C (Cu-EMT) and/or 400 °C (Cu-P-SSZ-39), which might be attributed to the nature of copper species and their contents.

Additionally, the SCR activities of their respective aged zeolites are also shown in Figures 1c and 1d to identify the effects of ageing over their catalytic performances. At 150 °C, the trend in the SCR activity of the aged samples (Figure 1c, d) is quite similar to that of fresh (Figure 1a, b). However, at higher temperatures (200 °C to 600 °C) the aged samples (with the exception of Cu-SSZ-39) exhibited lower NOx conversions and differed in trend as compared to fresh. Interestingly, the activity of the Cu-beta dropped at a snail's phase as it registered a meager 21% drop in NOx conversion from 90% to 69% (Figure 1b), which is the highlight of this study. On the other hand, the activity of Cu-SSZ-13 zeolite used in this study shows a steep decrease from 94% to 9%, which is well over an 80% drop in NOx conversion in the temperature range performed here. Despite this, exhibiting higher activity, the NOx conversion of Cu-SSZ-16 and Cu-SSZ-39 dropped 67% and 54% respectively (Figure 1b). Though SSZ-16 possessed an acidity twice that of SSZ-39, the latter still exhibited a competitive NOx conversion, which might be attributed to the variation in their pore aperture size, their connectivity and volume (Table 1).

At this juncture it is noteworthy to mention that the practical applicability of most copper zeolites for SCR of NOx with NH_3 (despite exhibiting higher activity) is hindered by their limited hydrothermal stability. At high temperatures, hydrothermal ageing can cause dealumination of framework aluminum and/or loss of active Cu ionic species leading to reduced SCR performance. In this regard, one can easily predict from Figure 1b that Cu-beta possess higher hydrothermal stability than other zeolites as it exhibited just 21% overall drop in NOx conversion. In addition, Cu-beta exhibited higher NOx conversion (ranging from 16% to 37%) than Cu-EMT at any given temperature from 200 to 600 °C. Further, the activity of all zeolites dropped drastically above 400 °C with the exception of Cu-Beta, which can be correlated to its ion-exchangeable capacity to hold a greater amount of Cu ionic species.

The Si/Al ratio (SAR) of the copper zeolites listed in Table 1 varies from a minimum of 3.3 (Cu-SSZ-16) to a maximum of 19.2 (Cu-SSZ-13). At low SAR it is easier for isolated Cu^{2+} ions to bind with tetrahedral (T) 'Al' sites as the latter's quantity and distribution would be relatively abundant. In contrast, at higher SAR, the isolated Cu^{2+} species undergo an inappropriate complex formation for charge balancing the negative framework.[16–20,25–27] However, one has to be careful in deciding the SAR as each of the zeolites investigated have unique requirements, disturbing of which might result in formation of undesired phases and/or physicochemical traits that are non-conducive for SCR of NOx with NH_3. In general, SAR 10 and below can be considered low, however, Figure 1 and Table 1 revealed a SAR-SCR activity correlation with a partial contradiction to the aforementioned theory. Because, the low temperature activity of fresh Cu-EMT and Cu-beta if attributed to their low SAR alone then the Cu-SSZ-16 (fresh) with the lowest SAR should have exhibited highest NOx conversion.

Interestingly, both the fresh and aged Cu-SSZ-13, Cu-SSZ-16 and Cu-SSZ-39 catalysts exhibited higher NOx conversions that cannot be reasoned with the SAR-SCR activity correlation, because their respective SAR are quite the extremes.

Based on ICP elemental analysis (Table 1), it was found that the amount of copper among the top nine contenders varied from 3.2 to 6.0 (wt %). Not much difference was found in the amount of Cu ion-exchanged in Cu-EMT, Cu-beta and Cu-SSZ-16 samples so as to clarify the contradictory SAR-SCR activity correlation. Instead, it supports the SAR-Cu content correlation wherein low SAR promoting copper loadings in zeolites with Cu-Beta, Cu-EMT and Cu-SSZ-16 possessing the highest Cu loadings relative to their number of tetrahedral 'Al' sites. Pore dimension and diffusivity data of respective zeolites were obtained from "International Zeolite Association" (IZA) to explore their influence over NH_3-SCR activity and correlate with 'SAR', 'Cu' loading and pore volume data (Table 1). The three-dimensional geometry combined with high diffusivity enables most of the zeolites higher activity for NH_3-SCR of NOx (Figure 1 & Table 1). Because they have enough diffusivity (Table 1) to allow the unhindered mobility of the guest molecules such as NH_3 (2.60 Å), NO (3.17 Å), N_2 (3.64 Å), N_2O (3.30 Å) and NO_2 (~5.12 Å) formed during the SCR reactions. In this regard Cu-FER, despite exhibiting competitive NOx conversions of 97% (fresh catalyst at 300 °C) and 80% (aged catalyst at 350 °C), registered an early loss in catalytic activity (i.e. fresh catalyst-10% and aged catalysts-0% both at 550 °C) compared to others (Figure 1b and 1d). Further, Cu-SZR with a lower acidity and micro-pore volume than Cu-FER exhibited better NOx conversion, which highlights the significance of three-dimensional framework related diffusivity for higher NH_3-SCR activity (Figure 1 & Table 1).

A well-known fact about zeolites is their shape selectivity, which is a prerequisite for catalysts to tackle complex reactions involving the formation of undesired products. Accordingly, the results of SCR reveal that the porosity and diffusivity of Cu zeolites in conjunction with the type of Cu species present as critical for the formation of desired or undesired products. At high temperatures, an anomaly related to preferential formation of N_2O over N_2 exists among these nine kinds of zeolite as large pore zeolites produced the former while small pores lost their activity. Such an anomaly can be related to the pore opening, cage size and dimensionality of the intersecting channels as well as their diffusivity within the zeolite structure. Since the cages of small pore zeolites are comparable to those of large pores (Table 1), the formation of N_2O within the cages of the small pore zeolites cannot be ruled out completely. However, the diffusivity along their narrow (3.72–3.84 Å) pore channels is such that N_2O is trapped and therefore, their NOx conversion appears to drop drastically. Though the size of the rings, diffusivity along the channels (3.72–3.84 Å) and pore dimensions (3D) of the small pore zeolites are close to each other, they show difference in their respective SAR, Cu content and acidity, yet they exhibit similar SCR activity at low temperature. Cu-P-SSZ-39 is the least active among the small pore zeolites at temperatures 200 °C and below, which can be related to the presence of phosphorous in their framework. Among the small pore zeolites Cu-SSZ-13 exhibited higher N_2O formation at higher temperature. Also, zeolites such as Cu-Beta and Cu-EMT exhibited high N_2O emission at higher temperatures as their large pores offer unhindered diffusion and provides a large cavity to accommodate the intermediate for N_2O.[28]

The total acidity of each zeolite calculated from the NH_3-TPD is shown in Table 1 and the details on its type and strength are presented in Figure 2a. Since the adsorption and desorption of ammonia is a complicated process, especially with zeolites where it forms a multi-layer, the relative desorption below 250 °C might be attributed to weakly adsorbed ammonia. Further, framework structure (pore connectivity and aperture size) plays a critical role in promoting the diffusivity of ammonia because bigger ring size higher would provide freedom for Cu species to access the internal tetrahedral 'Al' sites. As discussed earlier, Cu-FER though possessed higher acidity than Cu-EMT and Cu-beta failed to exhibit higher activity. Similarly, the acid sites in Cu-SSZ-13 were quite low as it registered a total of 0.66 mmol g^{-1} of acidity. Therefore, at high temperatures the activity of Cu-SSZ-13 dropped rapidly.

After ion-exchange, the loaded copper can either be present as Cu (Cu^+/Cu^{2+}) cations and or CuO species, H_2-TPR was used to determine the same. The Cu^+/Cu^{2+} acts as redox active centers and plays a significant role in the SCR activity of zeolites. Besides, the nature of the Cu species in zeolites alters their selectivity towards SCR reactions. At low temperature, the high N_2 selectivity is related to Cu^+/Cu^{2+} species. Therefore, correlating TPR profiles with the selectivity of zeolites could provide details on the nature and/or locations of Cu species. As

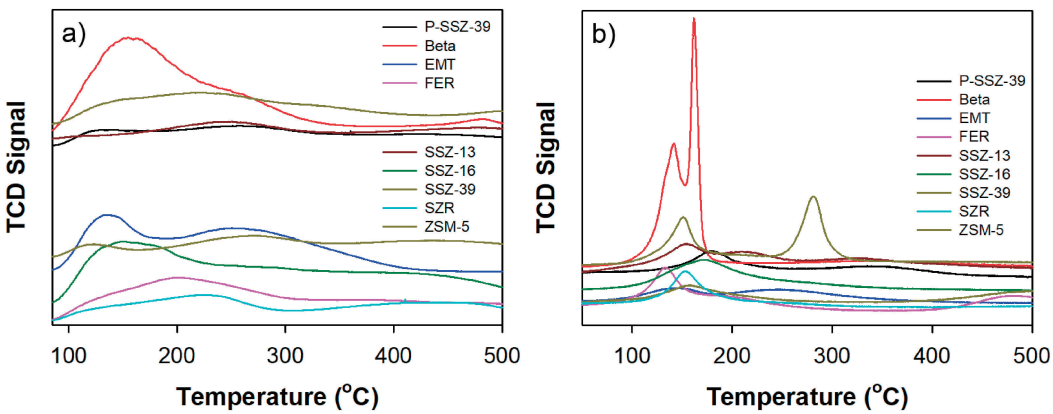

Figure 2. Comparison of the TPD of NH_3 and H_2-TPR profiles of fresh zeolites loaded with high copper content.

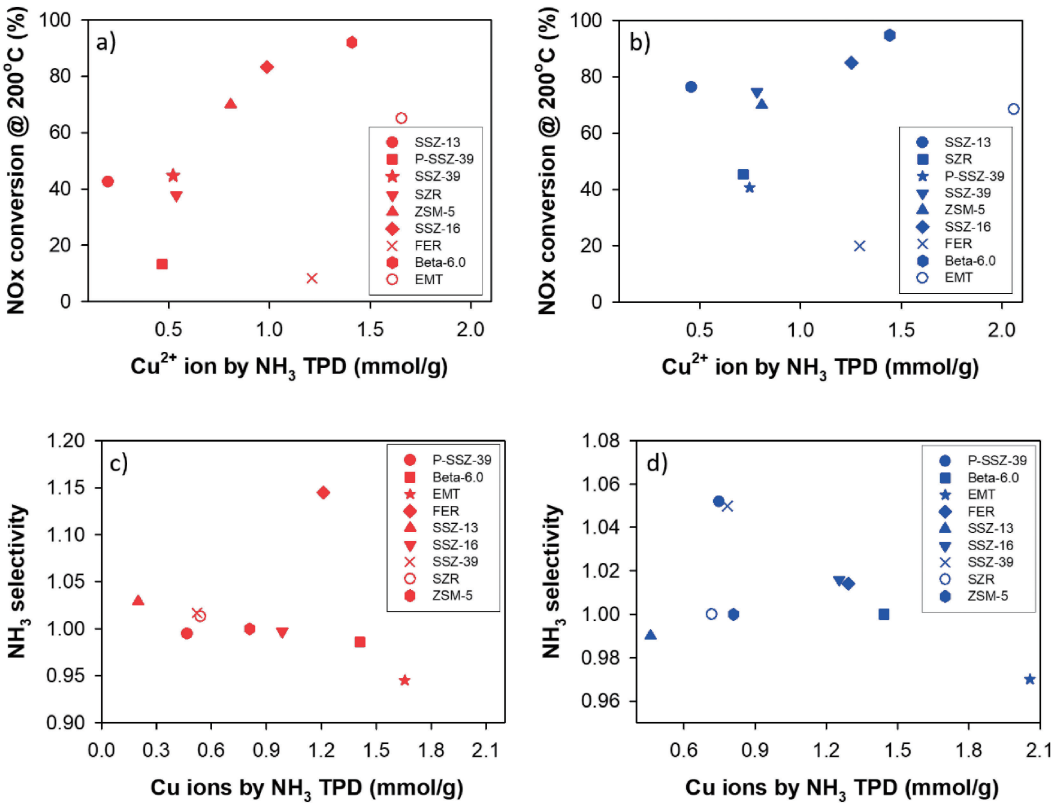

Figure 3. Influence of copper ion content over (a, b) the NOx conversion and (c, d) NH_3 selectivity of each zeolite catalyst at 200 °C. (a, c) Low-Cu and (b, d) high-Cu.

can be seen from the TPR profiles (Figure 2b), some exhibit two or more peaks, while some have tailing and the rest show a single peak. It has been previously concluded that the peaks at low temperature might be due to the reduction of either CuO or $[Cu(OH)]^+$.[19] Cu-SSZ-16 and Cu-SZR each show a single peak around 200 °C while Cu-ZSM-5, Cu-AEI, Cu-SSZ-39 and Cu-EMT all showed two discrete peaks as a result of redox reactions i.e. Cu^{2+} to Cu^+ and CuO to Cu^+. The 'Al' rich Cu-beta showed two peaks within close proximity to each other, which can be due to the placement of two Cu ions very close to each other within the same 12 and/or 6 membered rings (MR) of the framework. The overlapping of TPR peaks is reported to be linked to higher copper content,[29] which was the case of Cu-beta as judged from its Cu loading (Table 1) and TPR profiles (Figure 2b).

The influence of copper ion content (which is calculated by the amount of h-peak from NH_3-TPD i.e. Figure 2a) over the NOx conversion ability and NH_3 selectivity of the zeolites at 200 °C are compared in Figure 3 for both low and high copper loaded fresh zeolites. These Cu ions are active at low temperatures and enhance the NOx conversion (Figure 3a, b). At low temperatures these Cu ions show higher selectivity for NH_3 (Figure 3b) and tend to convert NOx swiftly (Figure 3a).

4. Conclusion

NH_3-SCR activity for treating NOx from automotive exhausts was conducted over a wide range of Cu exchanged zeolites with different structures and pore dimensions using various conditions recommended by OEM. The typical results demonstrated here in this paper that the NH_3-SCR of NOx activity of the investigated zeolites cannot be limited solely to a single parameter i.e. SAR, Cu content/distribution, pore dimensions, diffusivity and acidity. Instead, the study revealed the involvement of a combined role from two or more of the aforementioned parameters to decide on the SCR activity and selectivity. Furthermore, this study allowed the overall comparison of physico-chemical traits with conventional NH_3-SCR protocols, since preparation of each zeolite was diverse. When fresh, the activity of most copper zeolites for NOx conversion was overall satisfactory. However, in the long run they might become vulnerable to the unpredictable temperature variations at the automotive exhausts and start to lose their SCR activity. Therefore, possessing stability towards hydrothermal ageing even after repeated exposure to high temperatures is of paramount significance to be successful in SCR applications. In this regard, Cu-Beta, Cu-SSZ-16, Cu-P-SSZ-39 and Cu-SSZ-39 not only offer excellent SCR activity of NOx and selectivity for N_2 but also high hydrothermal stability over a broad temperature window and could be suitable alternatives to overcome the drawbacks faced by the stereotypic SSZ-13 systems in conventional SCR applications.

Supporting Information

This material is available on http://dx.doi.org/10.1246/bcsj.20170352.

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