



Advances and perspectives from a decade of collaborative efforts on zeolites for selective catalytic reduction of NO_x

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ABSTRACT

Nitrogen oxides (NO_x) is a major air pollutant and its release is regulated by increasingly stringent legislation. Selective catalytic reduction using ammonia as a reductant (NH₃-SCR) is the most widely applied method to reduce NO_x from diesel vehicle exhaust. Significant technological achievements have been developed in the last 10–15 years to minimize NO_x by NH₃-SCR, particularly using Cu-containing small-pore zeolites as active and stable catalysts. In the present perspective, we highlight some of the most noteworthy advances achieved by industry and academia on the understanding of the unique reaction mechanism of NH₃-SCR over Cu-zeolites. With the increased understanding, researchers have been able to rationalize the design and realization of new Cu-zeolite catalysts. Although light-duty diesel vehicles will be electrified in the near future, heavy-duty diesel vehicles will continue to play a large role in future powertrain solutions even beyond 2030. Hence, we highlight some of the challenges and perspectives moving forward.

Preface

We congratulate Prof. Avelino Corma on his 70 years birthday and thank him for his passionate mentorship, fruitful collaboration, strong urge to drive zeolite research towards industrial application and for his warm personality.

1. Introduction

“Emission” has several meanings today ranging from greenhouse gas emissions to air pollution emissions that have an impact on climate and environment, respectively. One of the biggest challenges our society urgently faces is global warming leading to dramatic climate change and extreme weather events [1]. At the same time, clean breathable air has a direct impact on human health. The two types of emissions are typically confused with each other, most likely because they traditionally originate from the same source and sometimes have an impact on both climate and environment.

During combustion of fossil fuels, CO₂ (climate emission) is released as the product of the reaction. At the same time several pollutants, such as NO_x (mainly NO and NO₂), are also created and emitted. It is formed by combination of N₂ and O₂ from the air during the high temperatures of the combustion. NO_x is directly related to human respiratory health issues, but it also reacts in the atmosphere to form ozone and acid rain [2]. Nitrous oxide (N₂O) may also be obtained in minor quantities from fuel combustion or be produced in exhaust systems. This specific molecule has a global warming potential ~300 times more detrimental compared to CO₂ and is a good example of a pollutant as well as a climate emission gas. Today the majority of NO_x is released from mobile sources, such as cars and trucks (automotive applications). In most regions around the world, pollution emissions are controlled by legislation and reduction is made possible by the technological achievements, especially from environmental catalytic innovations.

The most applied technology to reduce NO_x emissions is selective catalytic reduction using ammonia as the reductant (NH₃-SCR). Metal promoted zeolites are excellent catalysts for this reaction, but

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historically suffered from hydrothermal stability issues. A little more than a decade ago, an important contribution from industry appeared, which described Cu-containing small-pore-zeolites and especially chabazite (CHA) as a solution [3]. This description clearly revealed a tremendous improvement of the hydrothermal stability compared to former reports in the 80s using Cu-containing medium and large pore zeolites, as MFI and BEA, respectively [4,5]. The discovery of small pore zeolites for NH₃-SCR, and in particular Cu-CHA, is a milestone in environmental catalysis and opened intense research programs on a class of zeolites that up until this discovery had been limited to use in gas adsorption and separations [6,7].

Before the discovery of small-pore Cu-CHA for NH₃-SCR, researchers at the “Instituto de Tecnología Química” (ITQ) led by Prof. Avelino Corma were already active in the synthesis of new small-pore zeolite topologies, particularly in their high-silica or even pure silica forms [8–10]. This previous experience on designing novel small-pore zeolites at the ITQ, positioned Corma’s group in an ideal situation in the late ‘00s to initiate a research program with both a fundamental character and an industrial link. With this in mind, ITQ and the industrial catalyst company Haldor Topsøe A/S (today Topsoe) initiated a joint research program on these topics at the end of 2009. Currently, this long-term academia-industry collaboration is still maintained between ITQ and Umicore after the acquisition of Topsoe’s heavy-duty diesel and stationary deNO_x catalyst businesses at the end of 2017.

Along the present perspective article, the most important and relevant results obtained through this fruitful collaboration will be highlighted within the context of concurrent efforts by other research groups.

2. Cu-zeolites: From large to small pore zeolites

2.1. Initial discovery of Cu-CHA for NH₃-SCR and influence of framework stability

Shortly after the first industrial reports of enhanced performance of Cu-CHA and small-pore zeolites for NH₃-SCR of NO_x [3] several academic groups started to study this class of materials. Fickel and Lobo first showed that Cu enhanced the stability of Cu-CHA (Cu-SSZ-13) compared to the NH₄⁺- or H⁺-form using Rietveld refinement of variable-temperature PXRD data [11]. Peden et al. also compared the NH₃-SCR performance of Cu-CHA to Cu-MFI and Cu-BEA [12]. They found that Cu-CHA presents improved NO_x conversion values over a broad temperature range (200–550 °C), as well as higher selectivity towards N₂ (less undesired NO₂ and N₂O by-products), compared to Cu-BEA and Cu-MFI under the same reaction conditions (350 ppm NO, 350 ppm NH₃, 14% O₂, 2% H₂O, GHSV~30,000 h⁻¹) [12]. Later studies also compared the impact of hydrothermal aging (16h at 800 °C) on the NO_x conversion in the NH₃-SCR reaction and confirmed the high stability of Cu-CHA, whereas Cu-MFI (Cu-ZSM-5), Cu-BEA (Cu-Beta) and Cu-FAU (Cu-Y) suffered from extensive activity loss (see Fig. 1) [13].

During severe ageing treatments, CuO and Cu-aluminate species were found to form in Cu-MFI and Cu-BEA, whereas for Cu-CHA little changes could be observed. They also found that Cu could easily reduce from Cu²⁺ to Cu⁰ in Cu-BEA and Cu-MFI, while it would only reduce to Cu⁺ in Cu-CHA during H₂-TPR studies [13]. These results seemed to suggest that the enhanced performance of Cu-CHA could be attributed to a higher resistance towards dealumination and a higher stabilization of the Cu-ions within the framework of small-pore zeolites. Similar conclusions were proposed by Fickel and Lobo, who argued that the small diameter in small-pore zeolites would not allow Al(OH)₃ formed during dealumination to migrate towards the surface and that Cu stabilize the structure by coordination to the 6-ring of the Cu-CHA framework [11].

At this point, it was not evident how much the framework stability would influence the hydrothermal stability of a Cu-exchanged zeolite catalyst. Since Cu-CHA showed very little deactivation and other studied frameworks both had very different window sizes and framework

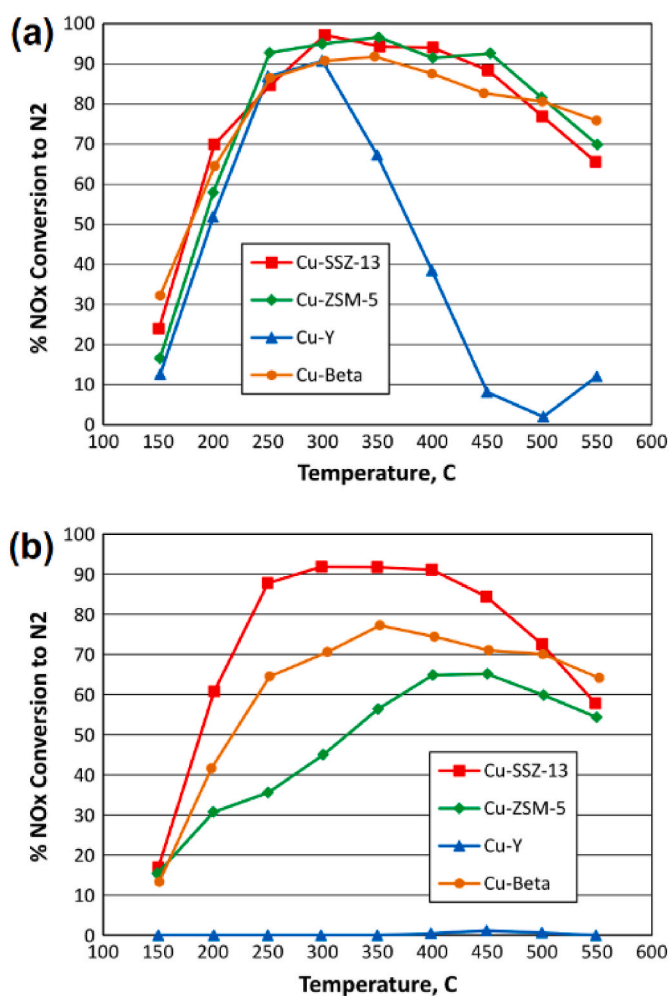


Fig. 1. NO_x conversion values over different Cu-zeolites in the fresh state (a) and after ageing treatments at 800 °C in 10% H₂O in air for 16 h (b). Reproduced from Ref. [13].

connectivities, one of the first joint study between ITQ and Umicore (formerly Topsoe) investigated Cu-MFI and Cu-IMF (IM-5 zeolite) [14]. The two frameworks are very similar in terms of window size and connectivity, but the IMF structure is less susceptible towards dealumination. After hydrothermal aging (650 and 750 °C), Cu-IMF showed less deactivation than Cu-MFI indeed indicating that the lattice stability plays a role in the deactivation of Cu-zeolites. The study also concluded: (i) if CuO species are formed, it is a reversible reaction under NH₃-SCR conditions as long as the Al species remain attached to the framework (see Fig. 2a); and (ii) once dealumination of framework Al into extra-framework positions (see Fig. 2b and c) has occurred, it can irreversibly react with Cu-species to form Cu–Al clusters with a resemblance to CuAl₂O₄ spinel-type species. Altogether, this highlights the important role of Al-stability in the zeolite framework, but also indicates that the stabilization of the Al by Cu-coordination in the framework towards dealumination could be unique for Cu-CHA and similar structures with double-6-ring units.

2.2. Small-pore zeolites for increased hydrothermal stability: from Cu-CHA to Cu-AEI and Cu-LTA

The biggest obstacle for commercialization of Cu-zeolites for NH₃-SCR in automotive applications had been the hydrothermal stability. Hence the discovery of the more stable Cu-CHA zeolite compared to Cu-MFI and Cu-Beta [13,14], motivated researchers to look for other

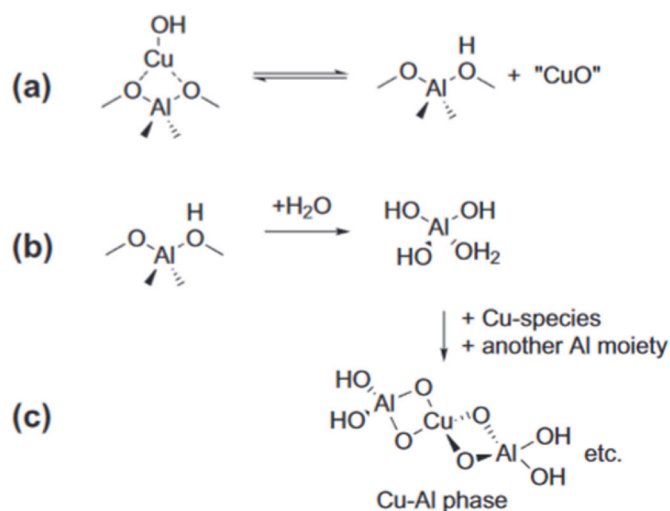


Fig. 2. Proposed hydrothermal deactivation mechanisms. Reproduced from Ref. [14].

small-pore zeolites with analogous structural features to CHA that could lead to similar, or even improved, catalytic performance as well as hydrothermal stability.

Lobo et al. first reported the catalytic performance of various Cu-exchanged small-pore zeolites, CHA (SSZ-13), AFX (SSZ-16), DDR (Sigma-1), and LEV (Nu-3) in the NH_3 -SCR reaction [15]. From these early results, two zeolites showed improved performance compared to Cu-MFI, namely the already reported Cu-CHA, but also Cu-AFX. Both frameworks are members of the ABC-6 family, which consist of hexagonal arrays of non-connected planar 6-rings. The difference between CHA and AFX is the stacking sequence of the 6-rings (AABBCC vs. AABCCBB for CHA and AFX, respectively), resulting in similar structural features, but different framework topologies. Each structure is exclusively formed by interconnected double six-rings (D6Rs), but the difference in stacking sequence leads to a *cha* cage in the CHA structure and a larger *afx* cage in the AFX topology. As mentioned before, the D6R in both structures offered an optimal location for Cu^{2+} coordination [11], but the Cu-CHA showed the highest stability in the study by Lobo et al. [15].

Having in mind the necessity of finding alternative zeolites to Cu-CHA with improved hydrothermal stability, we first proposed to evaluate Cu-AEI (Cu-SSZ-39) in the NH_3 -SCR reaction based on the facts that both CHA and AEI have: 1) identical framework density (15.1 T atoms per 1000 \AA^3), 2) three-dimensional small-pore channels, and 3) are solely composed of D6Rs (see Fig. 3) [16,17]. The main structural difference between these two materials is the shape of their cavities, where *cha* and *aei* are elongated and a basket-type cages, respectively (see Fig. 3c and d), resulting in a different tortuosity in the channel system (see Fig. 3e and f).

The catalytic results of the Cu-AEI zeolite for NH_3 -SCR of NO_x showed competitive catalytic activity compared to the Cu-CHA catalyst, but also an improved hydrothermal stability when subjected to severe hydrothermal treatments at temperatures above 750 $^\circ\text{C}$ [16,17], which makes it particularly useful for applications with very high temperature excursions. It is worth noting that up to that moment, the aluminosilicate AEI synthesis and/or its use as catalyst was limited in the literature to its original synthesis patent and the posterior description of its framework structure [18,19]. However, soon after our first report describing the high hydrothermal stability of Cu-AEI, an extensive research from academia as well as industry started with the aim of optimizing its preparation [20–25], which has ended up in successful use of Cu-containing AEI-type catalysts for NH_3 -SCR of NO_x in vehicle applications. The enhanced hydrothermal stability of AEI has been recently explained for Al-rich AEI materials by the combination of two

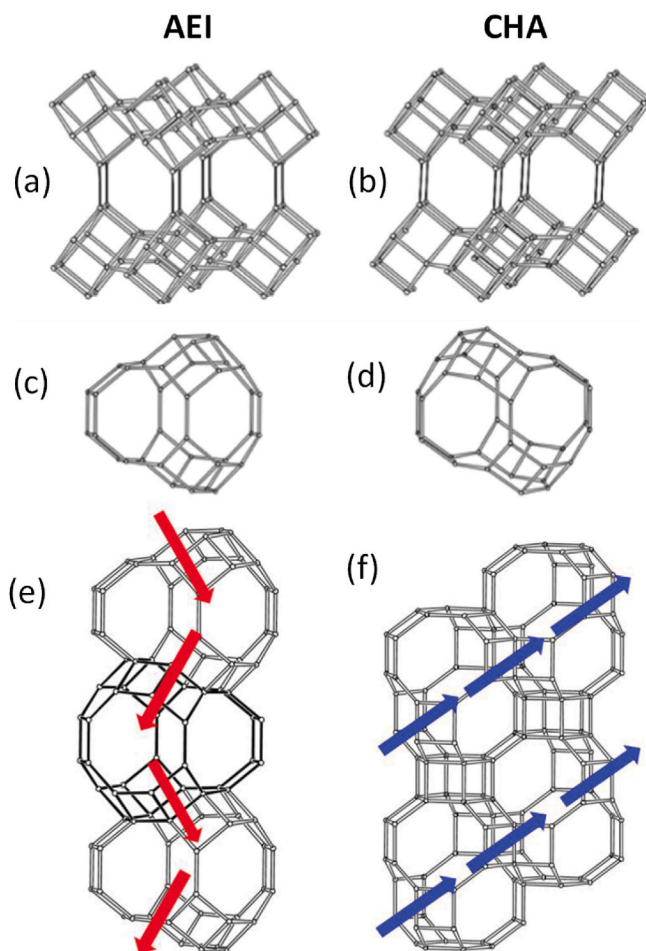


Fig. 3. Framework topologies of AEI (left) and CHA (right) zeolites. Reproduced from Refs. [26,27].

main factors: 1) AEI presents more Al-paired species than CHA, which stabilizes the catalyst by the more stable Z_2Cu species; and 2) the more tortuous channel structure in AEI (see Fig. 3e) can facilitate the reincorporation in framework positions of detached Al(OH)_3 when the catalyst cools down, minimizing undesired dealumination processes [26,27]. In addition, it is also observed that AEI, in general, crystallizes with less structural defects, which is another characteristic that also enhances the hydrothermal stability.

In addition to AEI, Hong et al. have recently described the superior hydrothermal stability of Cu-containing high-silica LTA for the NH_3 -SCR of NO_x reaction compared to other Cu-zeolites, even after hydrothermal treatments at 900 $^\circ\text{C}$ [28–30]. This result is interesting because all promising materials up to this point has been composed of D6R units whereas LTA does not possess D6Rs in its structure. The origin of the unexpected high hydrothermal stability was ascribed to the migration of Cu^+ ions from inside *sod* cages of Cu-LTA to unoccupied single 6-rings in *lta* cages, accompanied by their oxidation to Cu^{2+} during the hydrothermal treatment [29].

3. Key features of an active and stable Cu-zeolite catalyst for NH_3 -SCR of NO_x

3.1. Hydrothermal stability: zeolite topology and Al distribution

Hydrothermal stability has been the main requirement for successful implementation of Cu-zeolites for NH_3 -SCR in automotive applications. Engine exhaust contains about 5–15% H_2O and temperatures can typically reach 500–600 $^\circ\text{C}$. The hydrothermal stability has been even more

detrimental in exhaust systems for light-duty diesel (LDD) and active diesel particulate filter regeneration, where diesel is directly injected into the exhaust systems upfront of an oxidation catalyst to increase the temperature for soot combustion in the filter. In such systems, temperature requirements for the SCR component may reach as high as ca. 850 °C. As mentioned before, one key feature to achieve the hydrothermal stability is the application of small-pore zeolites, and going from e.g. Cu-CHA to Cu-AEI represents a further improvement.

Beyond the zeolite framework topology, the composition of the zeolite itself has a large effect on the hydrothermal stability. Any defect will lower the stability of the material. This can be a structural defect, such as an internal silanol, but also an isomorphous substitution of Si with Al should be considered a defect, since it will affect the local coordination geometry by its large ionic radius, as well as the accompanying proton. Dealumination is typically an acid catalyzed reaction, so the presence of a Brønsted acid site will even accelerate the deactivation. Generally, the stability of zeolites decreases with higher Al-content in the structure [31]. This is of course a paradox because the presence of Al in the framework is also required to charge balance both the protons and Cu sites required for the catalytic reaction. Hence an optimum must exist.

Following this line of thinking, the first apparent feature to control for improved stability is the Al density or Si/Al molar ratio [32–34]. Preparation of Cu-containing small pore zeolites with relatively high Si/Al molar ratios was initially explored to minimize undesired dealumination events [32,35]. However, these early experimental studies showed that Cu-CHA samples with relatively high Si/Al molar ratios (above 20) and similar Cu contents (~2–3 wt%) were not only less active under fresh conditions, but also showed more deactivation than their slightly lower Si/Al ratio counterparts [32,35]. Thus, it is not merely a matter of the Al density, but also the Cu and H⁺ density (i.e. Si/Al as well as Cu/Al molar ratios) must be taken into account [32]. Peden and Gao et al. explained the importance of controlling the Si/Al molar ratio in Cu-CHA catalysts at low-intermediate values (<15) by: 1) influencing the location/stabilization of the Cu ions, and 2) altering the Brønsted acidity of the Cu-zeolite, and, consequently, the NH₃ storage capacity of the catalyst during the NH₃-SCR reaction [33,34]. According to these studies, the different ability to stabilize Cu ion species, Z₂-Cu²⁺ or Z-[Cu(OH)]⁺ (see Fig. 4), in Cu-CHA will also dramatically impact the hydrothermal stability.

The notion of e.g. Z₂-Cu²⁺ and Z-[Cu(OH)]⁺ refers to the counter balance of the copper species by one or two Al atoms in the framework of the zeolite, and only exist in the dehydrated zeolite. Upon introduction of copper into e.g. CHA, the first Al environments that will populate are the Z₂-Cu²⁺, which also suggest that such sites are most stable and has been confirmed by theoretical methods [36]. In the Z₂-Cu²⁺ site, the Cu is coordinated in the plane of the 6-ring of the CHA structure, whereas

Z-[Cu(OH)]⁺ is mainly associated with the 8-ring window between the *cha* cavities [37]. The stability of the Z₂-Cu²⁺ is in good agreement with the early notation from Lobo et al. of a stabilizing effect from Cu located in the plane of the 6-ring of the CHA zeolite [15]. The stability effect of Z₂-Cu²⁺ vs. Z-[Cu(OH)]⁺ has been studied in greater detail by Gao and Szanyi, showing that it is mainly Z-[Cu(OH)]⁺ sites, which degrade and that even Al migration during aging leads to an increase in the amount of Z₂-Cu²⁺ sites [38]. Altogether, this mean that not only the density, but also the distribution of Al combined with the occupation of Cu in the 6-ring will have an effect on the hydrothermal stability.

3.2. Active sites and Cu-mobility

Besides hydrothermal stability, it is obvious to say that a suited Cu-zeolite catalyst must also be as active as possible. Important fundamental work has been carried out in the last decade to understand the role of the active copper sites in the complex NH₃-SCR reaction mechanism [39–41]. In general, the major development in the understanding of low-temperature reaction (<ca. 300 °C) is that the reaction involves an oxidation half-cycle where Cu⁺ is oxidized to Cu²⁺ and a reduction half-cycle where Cu²⁺ is reduced to Cu⁺ by the joint effect of NH₃, NO and O₂. During the oxidation half-cycle, molecular oxygen is activated by Cu-pair formation, which is only possible because mobile linear [Cu(NH₃)₂]⁺ complexes are formed in the reduction half-cycle (see Fig. 5).

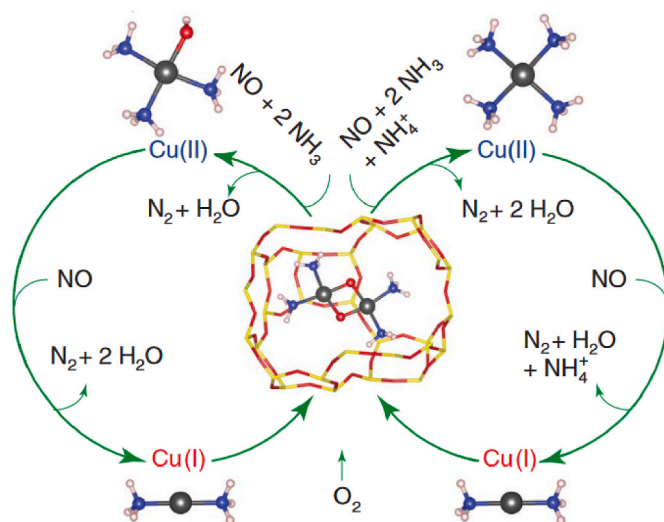


Fig. 5. Proposed low-temperature SCR catalytic cycle by Gounder et al. Reproduced from Ref. [41].

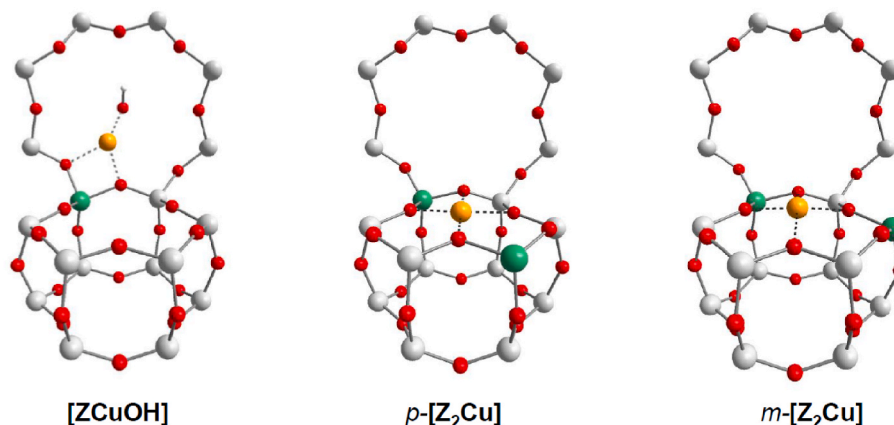


Fig. 4. Structures of Z-[Cu(OH)]⁺ and Z₂-Cu²⁺ in the Cu-CHA catalyst.

Upon oxygen activation, a Cu-peroxo-compound is formed, which is a key step in the NH_3 -SCR reaction. The NO and later NH_3 can react on the Cu-peroxo-compound whereupon the active site is dissolved and will have to form again for a new reaction cycle to proceed. Gao et al. and Paolucci et al. showed independently and almost simultaneously that the reaction rate depends quadratically on the Cu density at low copper loadings [40,41]. This can be explained by the low probability of two $[\text{Cu}(\text{NH}_3)_2]^+$ complexes to meet each other to activate the oxygen. Paolucci worked out a scenario to calculate the maximum distance a $[\text{Cu}(\text{NH}_3)_2]^+$ ion would migrate on the time scale of the NH_3 -SCR reaction and came to the conclusion that it would migrate approximately 9 Å to meet another Cu ion. Otherwise, it will not participate in the SCR reaction [41]. The reaction cycle (assuming that two Cu ions are already present in the same cage) has later been investigated in detail for each fundamental step by DFT calculations, leading to a full microkinetic model from first principle calculations. The analysis indicated that NH_3 can also poison the active Cu-peroxo-complex, that NO activation on the Cu-peroxo-complex is a key step and that also the H^+/NH_4^+ sites play a role in decomposition of reaction intermediates [42].

The formation and dissolution of the active site is interesting in itself and represents a new category in the field of heterogenous catalysis, as the active site is not a stable entity. Diffusion of the $[\text{Cu}(\text{NH}_3)_2]^+$ happens on a length scale where the complex must migrate through the 8-ring windows of the small-pore zeolite. It is therefore likely to assume that the mobility is controlled by the ease of migration through windows (e.g. topology and crystallinity dependent), counter-diffusion of e.g. NH_4^+ as well as the Al-distribution.

To evaluate the effect of such multiple variables, a first principle based molecular dynamics approach has been developed to estimate free energy diffusion barriers in complex molecular environments, where the effect of temperature and interactions of $[\text{Cu}(\text{NH}_3)_2]^+$ complexes with other molecules have been studied by using regular *ab-initio* molecular dynamics (AIMD) simulations [43,44]. These preliminary AIMD simulation studies reveal that also the local concentration of particular reactants, such as NO and NH_3 , in the close environment of the copper active sites severely hinder the low-temperature mobility of $[\text{Cu}(\text{NH}_3)_2]^+$ species.

3.3. Additional features of small pore-zeolites on NH_3 -SCR performance

3.3.1. N_2O formation

Another feature of small-pore zeolites is the apparent lower N_2O formation during NH_3 -SCR compared to medium and large pore zeolites [10]. N_2O is a by-product in the reaction, and due to its ~300 times higher greenhouse gas effect compared to CO_2 , it is undesired and is expected to be more stringently controlled in future legislations. The fundamental understanding of the origin of N_2O in the NH_3 -SCR reaction over Cu-zeolites is not well described. Peden et al. studied variable feed compositions with different NO_2/NO_x ratios on Cu-CHA and Cu-BEA catalysts [45]. The N_2O yield increased for both catalysts for higher NO_2/NO_x ratios, suggesting that N_2O is preferentially formed by decomposition from a type of “ NH_4NO_3 ” inside the zeolite pore system (its structure and interaction is not well described). Peden et al. also demonstrated that Cu-CHA is less effective for the NO oxidation reaction than Cu-BEA, lowering the formation of nitrate groups, resulting in less N_2O formed over Cu-CHA. In addition, the authors also observed that what they describe as “ NH_4NO_3 ” species were more stable in Cu-CHA than in Cu-BEA preventing their decomposition to N_2O [45]. Recent studies from Xi et al. however exclude the formation of surface nitrate or NH_4NO_3 as a precursor for the major part of N_2O formation at low temperatures and, instead, correlate the level of oxidized Cu-species to the steady and dynamic formation of N_2O [46]. Feng et al. recently considered unselective decomposition of H_2NNO over copper sites as the origin of the low-temperature N_2O formation, highlighting the impact of the Cu site and H^+/NH_4^+ on by-product formation [42]. Early work in the ITQ-Umicore (former ITQ-Topsoe) collaboration noted a clear effect of

the pore size and dimensionality of the zeolite on the N_2O formation, where lower window size and lower pore dimensionality decrease the N_2O selectivity (see Fig. 6) [47]. Altogether, it shows that there is an impact of the Cu-sites as well as zeolite topology on the N_2O formation, but the exact origin is not yet fully understood.

3.3.2. Hydrocarbon and sulfur resistance

Small-pore Cu-zeolites must accomplish even further features as NH_3 -SCR catalysts for automotive applications. Of particular importance is also a high resistance towards hydrocarbons and sulfur [48]. The Cu-zeolite may be exposed to various hydrocarbons due to insufficient fuel combustion during the “cold-start” stage or when an upstream diesel oxidation catalyst (DOC) does not perform, which can result in the deactivation of the SCR catalyst by HC fouling [48]. The negative effect of different hydrocarbons, such as propylene (C_3H_6), toluene (C_7H_8) or decane ($\text{C}_{10}\text{H}_{22}$), on the NH_3 -SCR performance when using medium and large pore Cu-zeolites (MFI and BEA) as catalysts has been well-described elsewhere [49,50]. In general, the issue of hydrocarbon fouling or deactivation is mostly remedied by the use of small-pore zeolites since the smaller window size (<4 Å) hinders the diffusion of hydrocarbons into the zeolite interior due to the larger kinetic diameters of most of the hydrocarbons [51,52].

Sulfur poisoning is another issue that needs to be taken into account when designing Cu-zeolite NH_3 -SCR catalysts. Typical diesel fuels contain up to 10 ppm S, which over the lifetime of a vehicle results in the exposure of the catalysts in the exhaust system to several fold more S than the Cu present in the catalyst on a molar basis. Even small amounts of S will influence the NO_x conversion and, especially, the low-temperature performance will be impacted. In general, a distinguishment is made between *reversible* and *irreversible* deactivation (at least for HDD applications), arbitrarily defined as the part of S, which can be removed by heating to 550 °C, and what remains on the catalyst after such heat treatment [53]. This distinguishment indicates either various degrees of sulfation or various copper species formed upon sulfur exposure. Reaction of SO_2 with various intermediates of the NH_3 -SCR reaction has recently shown that SO_2 mostly interacts with the Cu-peroxo-complex and explains why the low-temperature performance is impacted [54]. Recent investigations have also shown that the sulfur-resistance of Cu-CHA can be enhanced by performing a preceding hydrothermal treatment, which facilitates the formation of less S-sensitive $\text{Z}_2\text{-Cu}^{2+}$ species instead of $\text{Z-}[\text{Cu}(\text{OH})]^+$ [55], or by including other metal oxides together with the Cu-CHA catalyst acting as

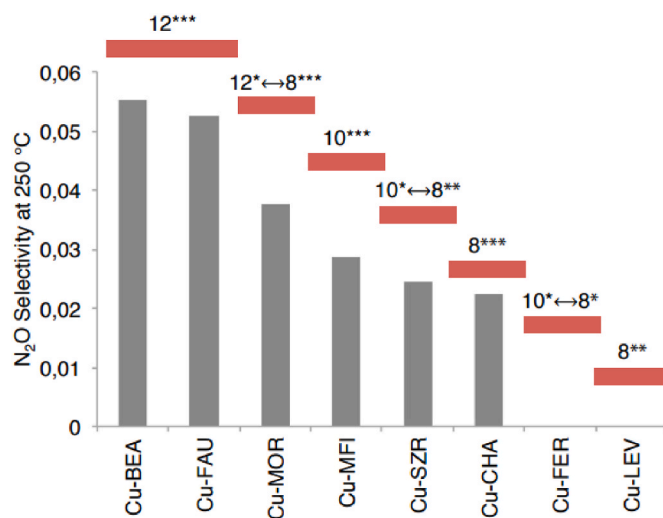


Fig. 6. Effect of the pore size and dimensionality of the zeolite on the N_2O formation at similar Cu and Al densities. Reproduced from Ref. [47].

sacrificial component [56]. We note however that deactivation by SO₂ happens faster at low temperatures and is thus not limited by the oxidation of the SO₂. Little description exists for the topology impact of the zeolite on sulfur resistance, but we note that any future design of Cu-zeolites for NH₃-SCR must also take into account the sulfur resistance as long as the diesel fuel originates from fossil sources.

4. Rationalizing the synthesis of Cu-containing small pore zeolites

Based on the key features that a Cu-zeolite NH₃-SCR catalyst must accomplish, ITQ and Umicore (formerly Topsoe) researchers have jointly explored various approaches to the preparation of small pore Cu-zeolites/zeotypes in order to make their synthesis either more efficient or to improve their catalytic performance. The most relevant achievements are highlighted below.

4.1. Solid Cu-exchange incorporation procedures

One of the first joint descriptions between ITQ and Umicore (formerly Topsoe collaboration) describes Cu-migration in the silicoaluminophosphate (SAPO) form of CHA (SAPO-34) [57]. Although today SAPO-type materials are not industrially-attractive materials for SCR applications due to their limited low-temperature hydrolytic stability [58], they were earlier considered as good candidates due to their excellent hydrothermal stabilities at high temperatures [15]. In this context, the incorporation of copper active sites into the SAPO-34 zeotype was difficult due to the combination of the presence of small pores with the high hydrophilic nature of SAPOs. During aqueous ion exchange of Cu into SAPO-34 most of the Cu species remained in the outer parts of the zeotype particles (see Fig. 7a-left), limiting the overall catalytic activity [57]. We then showed that a homogenous distribution of copper species along the particles could be achieved by activation at high temperatures (e.g. 750 °C) well above normal calcination temperatures (see Fig. 7a-right). This simple activation procedure on the as-prepared Cu-SAPO-34 lead to an increase in the catalytic performance for the NH₃-SCR of NO_x reaction, being even more active than conventional Cu-SSZ-13 per Cu active site [57].

This example clearly suggests that copper migration on a length scale of micrometers within small-pore zeotypes/zeolites is possible by application of thermal energy. In fact, the incorporation of metal active

sites into zeolites by solid-state ion exchange (SSIE) procedures at high temperatures (above 700 °C), normally in air, was broadly employed as an alternative to more traditional aqueous-exchange treatments at the time [59–61].

During another study of the impact of lattice stability on Cu-zeolite NH₃-SCR catalysts, we noted that when a physical mixture of CuO and a H-zeolite was exposed to SCR conditions (NH₃, NO, O₂ and H₂O) at normal reaction temperatures, the catalytic fingerprint was identical to that of a fully exchanged Cu-zeolite [14]. Based on this observation the facilitation of solid-state ion exchange by gas phase components at low temperatures (typically 250 °C) was explored in detail (see Fig. 7b). When copper was present in oxidation state +2 or +1, it was found that the presence of NO and NH₃ or NH₃ alone, respectively, would facilitate SSIE even below 250 °C. This was the first study to propose how [Cu(NH₃)₂]⁺ complexes, once formed, can migrate between the cages of CHA as they are linear and loosely bound to the framework [62]. This sparked a series of studies confirming the mobility of the [Cu(NH₃)₂]⁺ complex and how it can be used to facilitate ion exchange at low temperatures, which again shows mobility at the micrometer scale, but now at low temperatures and under typical reaction conditions [63,64]. Interestingly, several research groups demonstrated, in parallel, how similar mobile [Cu(NH₃)₂]⁺ species are involved in the NH₃-SCR reaction, which is also dependent on Cu-mobility, but on an Angstrom to nanometer length scale (see Section 3.2) [39–41].

4.2. One-pot synthesis of Cu-containing zeotypes and zeolites

One of the main objectives of the joint ITQ-Umicore collaboration (formerly part of Topsoe collaboration) has been to optimize the preparation of Cu-containing small pore zeotypes/zeolites to minimize the barrier for industrial application. A step to optimize is the incorporation of cationic metals in zeotypes/zeolites, which is traditionally carried out by several post-synthetic treatments. These post-synthetic treatments not only require several unit operations to obtain the desired metal-containing zeotype/zeolite, but also the dispersion of metals along the small pore zeolitic particles can be limited, as it was shown earlier for SAPO-34 [57].

A one-pot synthesis approach, where Cu ions are already introduced into the ion-exchange positions of the zeolite/zeotype, would therefore represent an improvement. Previous works from Wright and Xiao demonstrated the use of metal-complexes formed by cationic metals (Ni²⁺ or Cu²⁺) as single and inexpensive templates in the synthesis of Ni-SAPOs or Cu-CHA, respectively [65,66]. However, the final amount of the metal content in the catalysts as well as the chemical composition/distribution of the framework heteroatoms were not optimal for their catalytic application. Inspired by the use of the metal-complexes, we investigated the synthesis of Cu-containing small pore zeotypes and zeolites by rationalizing the use of cooperative templates (see Fig. 8). By combination of inexpensive Cu-complexes (i.e. Cu-tetraethylenepentamine, Cu-TEPA) with specific OSDA molecules, the direct incorporation of Cu species into extra-framework positions of the desired zeolitic structure with desired Al (or Si) and Cu densities could be achieved [35,67–69].

This cooperative one-pot approach was rationalized for the preparation of Cu-SAPO-34 catalysts by use of Cu-TEPA in combination with diethylamine and tetraethylammonium (TEA) organic molecules, which allowed for the fine-tuning of the physico-chemical properties, thereby maximizing the hydrothermal stability and catalytic performance as well as maximizing solid yields [68,70]. Interestingly, the enhanced hydrothermal stability of these Cu-SAPO-34 materials could not be ascribed to the control of the Cu-content alone, but was explained by an improved distribution of framework Si atoms as isolated species. This shows that the heteroatom incorporation is affected when e.g. the divalent Cu-TEPA is introduced in the synthesis mixture. One may speculate that the heteroatom incorporation is directed when the zeolite/zeotype crystallizes around the complex towards the most stable

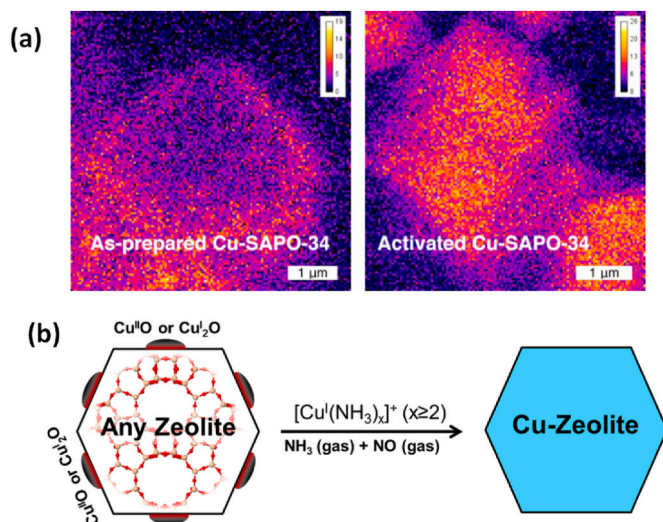


Fig. 7. (a) Cu dispersion in the as-prepared Cu-SAPO-34 (left) and after activation at 750 °C (right); (b) Scheme for the solid-state ion-exchange (SSIE) method of copper facilitated by ammonia at low temperature. Reproduced from Refs. [57,62], respectively.

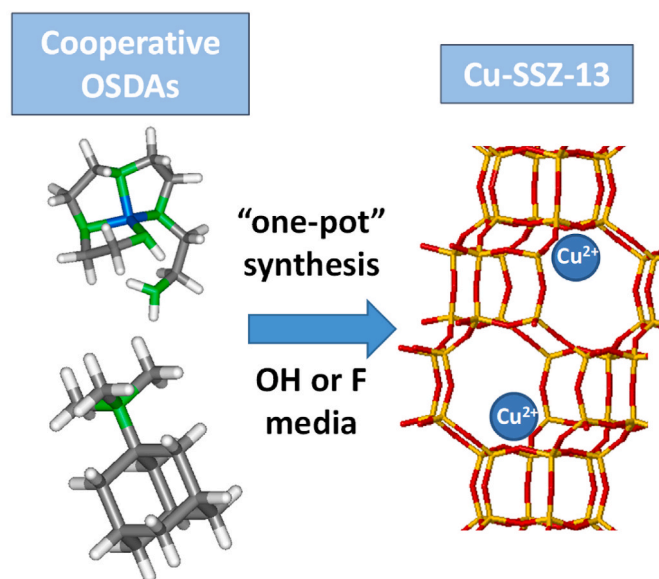


Fig. 8. Strategy for the one-pot synthesis of Cu-containing small-pore zeolitic materials by using cooperative OSDA molecules. Reproduced from ref. [35].

configuration to host the divalent cation. The approach was later successfully extended to the aluminosilicate and silicoaluminophosphate forms of both AEI and CHA framework topologies, as summarized in Table 1 [35,69,71,72].

4.3. Rationalized selection of the OSDA molecules to guide the preparation of target small-pore zeolites

In general, the OSDA molecules employed in the synthesis of high silica zeolites typically represent the highest cost-contribution in the preparation of said zeolite. Therefore, it has always been the target of several research groups to identify less cost-intensive and potentially more benign OSDA-molecules without compromising the structure directing effect during crystallization of the desired zeolite. At the same time, the physico-chemical properties of the target zeolite must not be compromised when alternative OSDAs or synthesis routes are identified to facilitate industrial-scale preparations. To do this, we have employed both chemical intuition based on the large experience of our groups in the field as well as advanced computational-guidance in many of our recent zeolite optimizations [73]. Some of the most relevant achievements are highlighted in the following sections.

4.3.1. Synthesis of pure zeolite phases

4.3.1.1. CHA and AEI zeolites. Since the first description of the high-silica CHA zeolite (SSZ-13) reported by Zones in 1985 [74], the preferred OSDA employed for the synthesis of CHA has been N,N,N-trimethyladamantylammonium (TMAda). This OSDA molecule

Table 1

Cu-zeolite or zeotypes achieved by the ITQ-Umicore (formerly part of Haldor Topsoe) through the use of a cooperative one-pot synthesis approach.

Achieved phase	Cooperative OSDA	Ref
Cu-CHA (Cu-SAPO-34)	Cu-TEPA + diethylamine and tetraethylammonium	[68, 70]
Cu-AEI (SAPO-18)	Cu-TETA + N,N-dimethyl-3,5-dimethylpiperidinium	[69]
Cu-CHA (Cu-SSZ-13)	Cu-TEPA + N,N,N-trimethyl-1-adamantammonium	[35, 71]
Cu-AEI (Cu-SSZ-39)	Cu-TEPA + N,N-dimethyl-3,5-dimethylpiperidinium	[72]

shows an extraordinary strong templating role towards CHA, allowing its preparation under very broad synthesis conditions and with different physico-chemical properties (chemical composition and/or particle sizes, among others). However, right after the claim of Cu-CHA as a commercial SCR catalyst for controlling NO_x emissions in automotive applications [3], there was a vast interest from industry to find OSDA alternatives to TMAda because this molecule presented a very high economical cost. Indeed, different cheaper OSDA molecules have been described since then for the synthesis of high-silica CHA, i.e. benzyl-trimethylammonium [75,76], N-alkyl-1,4-diazabicyclo[2.2.2]octane cations [77], or diverse cycloalkylammonium cations [78,79], among others.

At this point, we proposed the use of tetraethylammonium (TEA) as a simple, inexpensive and commercially-available OSDA molecule for the synthesis of the CHA zeolite [80,81]. We rationalized the proposal of this OSDA on the basis of TEA was one of the preferred OSDA molecules for the synthesis of SAPO-34, which is the silicoaluminophosphate form of CHA. To achieve the CHA structure, it was initially required to use another zeolite, namely FAU, as the source of Si and in particular as a source of Al. Interestingly, the one-pot Cu-CHA zeolite can also be achieved by combining Cu-TEPA and TEA as cooperative and inexpensive co-OSDAs.

Beyond chemical intuition, we have employed high-throughput atomistic simulations of the entire set of OSDA molecules described in the literature in collaboration with Prof. Gómez-Bombarelli at MIT, with the aim of finding alternative OSDA candidates with excellent templating energies towards CHA while presenting lower preparation costs [82]. This Machine-Learning (ML) analysis permitted us to confirm that previously-described TEA and some simple cycloalkylammonium cations, as for instance N,N,N-trimethylcyclohexylammonium, present a good balance between templating energies and low preparation complexities (see 6 and 9 in Fig. 9a and c) [82]. Interestingly, the ML analysis also showed that a few simple aza-spiro ammonium molecules, such as 6-azaspiro[5.6]dodecan-6-ium (see 12 in Fig. 9a and c), which was never reported before for the synthesis of CHA, not only present a great templating energy for CHA, but also a very different distinct charge distribution compared to the other reported OSDAs. Considering this remarkable and novel outcome from the ML analysis, different aluminum distributions in CHA were first theoretically predicted and later experimentally achieved by using this novel aza-spiro ammonium cation [82].

Similarly to the ML analysis performed for CHA, an exhaustive OSDA evaluation has also been carried out for the synthesis of AEI (see Fig. 9b) [82]. This advanced in-silico evaluation demonstrated that some of the former cyclic OSDA molecules reported by Zones for the synthesis of SSZ-39 (see for instance 2 in Fig. 9a and b) [18], show excellent templating energies towards AEI. Beyond those organic molecules, the ML analysis clearly reveals that the previously theoretically-predicted OSDA by Deem et al. [83] presents the best templating energy to guide the synthesis of AEI (see 1 in Fig. 9a and b). However, these alkyl-substituted cyclic amines are complex and expensive, being highly recommendable to find less complex OSDA molecules.

The synthesis of the high-silica AEI zeolite tends to present an additional limitation beyond the use of relatively expensive OSDA molecules, which is the relatively low solid yields associated to its preparation [84]. Having that in mind, we proposed the use of pre-crystallized Si and Al sources, preferentially FAU zeolites, to facilitate the nucleation process and increase the final AEI yields [72]. In one of our later studies, we highlighted the unique role of zeolite-to-zeolite transformations [85,86]. In particular, the role of a starting zeolite as a source of Al is critical, where dissolution and nucleation/crystallization rates has to be synchronized. If this is achieved, difficult zeolite phases could be assessed, particularly when employed OSDAs can direct different phases [85]. The use of other pre-crystallized zeolites, such as MFI and Beta, was later reported by other authors as efficient silicate precursors to crystallize AEI [87]. Other industrial descriptions to

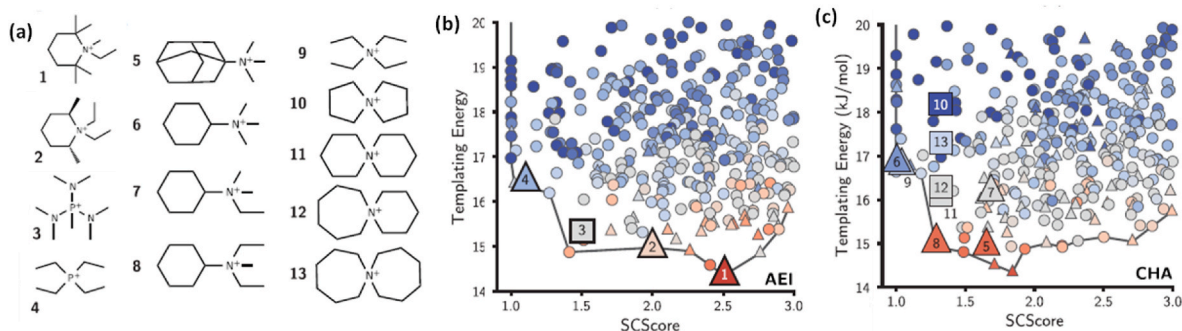


Fig. 9. (a) OSDA candidates for the synthesis of AEI (1–4) and CHA (5–13); (b–c) Templating energy of OSDAs against their SCScore for AEI (b) and CHA (c). Reproduced from ref. [82].

enhance the efficiency of the AEI synthesis involve the recyclability of the supernatant liquids to employ the inorganic and organic species that remained in solution and, consequently, improving the overall synthesis yields while minimizing costs [20].

Additional recent improvements in the AEI synthesis include its direct preparation with conventional colloidal silica and sodium aluminate instead of pre-crystallized sources as raw materials [24], as well as its ultrafast synthesis within 80 min from amorphous sources by using a fast heated tubular reactor [25].

4.3.1.2. AFX and ERI zeolites. AFX and ERI zeolites present similar small-pore topologies to CHA and AEI zeolites but with larger cavities than those of the *cha* and *aei* cages. In fact, these structures were originally considered as potential good catalyst candidates for the NH_3 -SCR of NO_x [11,15,88]. However, the number of reports including AFX or ERI was initially limited, which is most likely explained by the relatively low Si/Al molar ratios that permitted their preparation (below 5–6) and, in the particular case of ERI, the formation of intergrown crystals with large pore offretite (OFF) was broadly described, limiting in both cases their hydrothermal stabilities.

Taking into account the larger size of *afx* and *eri* cages together with the fact that, up to that moment, the preferred OSDA molecules employed for their syntheses were low-selective flexible dicationic large molecules (see 1 and 2 in Fig. 10) [89,90], we rationally proposed the use of bulky polycyclic organic molecules prepared through simple cycloaddition reactions (i.e. Diels-Alder), as potential OSDAs for these materials (see 3 and 4 in Fig. 10) [91]. The synthesis of AFX and ERI was achieved by combining these Diels-Alder derived bulky OSDA molecules with Na^+ and K^+ , respectively. The resultant AFX and ERI materials presented smaller crystal sizes that those previously reported in the literature, probably as a direct result of increased nucleation rates by employing better template-type organic molecules. Although the resultant Cu-exchanged AFX and ERI materials showed good activities for the NH_3 -SCR reaction, limited Si/Al molar ratios were still achieved for both materials (~5–6). It is worth noting that afterwards an excellent hydrothermal stability has been reported by other research groups for Cu-containing AFX materials with similar Si/Al molar ratios (~5–6), which have been prepared using an analogous bulky Diels-Alder derived molecule [92,93].

In order to attempt to increase the Si/Al molar ratio within the AFX zeolite, the number of positive charges incorporated by the OSDA molecules must be lowered. Having that in mind, two independent industrial research groups from Chevron and Johnson-Matthey have proposed the use of the same mono-cationic bulky imidazolium molecule as OSDA (see 5 in Fig. 10) for the preparation of the AFX zeolite with higher Si/Al molar ratios (between 10 and 30) [94,95]. However, the use of adamantyl-substituents in the OSDAs results in high production costs and hinder its potential industrial use. Alternatively, researchers at Tosoh Corp. have rationalized the preparation of the

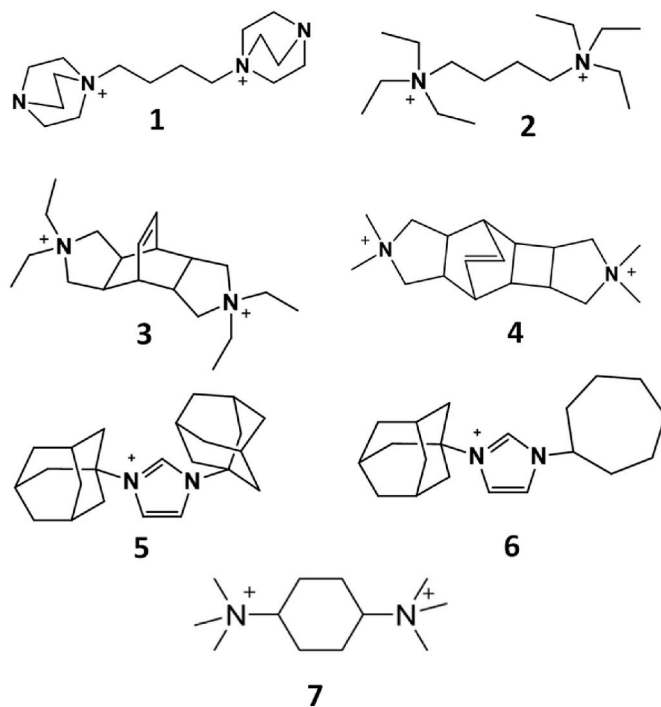


Fig. 10. OSDA molecules described for the synthesis of ERI and/or AFX zeolites.

adamantyl-substituted imidazolium by incorporating a less expensive cyclic-substituent (see 6 in Fig. 10) while maintaining high Si/Al molar ratios (above 11) [96].

In the course of the computationally-guided synthesis of a hypothetical small pore-zeolite highly related to AFX and ERI, we found that by precisely using the simple cyclohexane-1,4-bis(trimethylammonium) molecule as OSDA (see 7 in Fig. 10), a high-silica ERI with a Si/Al molar ratio of ~11 was obtained when potassium hydroxide was used as a mineralizing agent [97,98]. This was a sound-breaking advance in the preparation of high-silica pure ERI crystalline phase compared to the previous reports in the literature and, thus, showing promising features for improving the hydrothermal stability if this material is to be explored further.

4.3.2. Synthesis of zeolite intergrowths

Intergrown zeolites present disordered structures at least in one-dimension and, compared to the phase-pure counterparts, they can provide different and distinctive properties affecting to diffusional pathways, molecular confinements or specific crystallographic

environments. Thus, the ability to rationalize the preparation of intergrown zeolites with specific pore topologies and stacking control is a matter of great importance from both fundamental and applied perspectives [99].

4.3.2.1. CHA/AEI zeolite intergrowth. As it has been discussed above, CHA and AEI are the two-zeolite small-pore frameworks that have found their way to vehicle applications. However, different preparative and/or operational advantages can be observed for each of these two materials. In general, Cu-exchanged AEI shows an improved hydrothermal stability compared to Cu-CHA, while the preparation of CHA-type materials is achievable under broader synthesis conditions than those required to synthesize AEI [7,72]. Thus, the efficient design of CHA/AEI intergrowth materials could combine the preparative and operational benefits of each independent phase. Having that in mind, we have employed ML-based high-throughput simulations to propose single OSDA molecules with a dual selectivity that can guide the crystallization of the target CHA/AEI intergrowth, where these proposed single OSDA molecules must have similar strong binding energies as well as favorable shapes towards both CHA and AEI [82,99,100]. Among potential OSDA candidates, *N*-ethyl-*N*-isopropyl-*N*-methylpropan-2-ammonium and 1-ethyl-1-isopropylpyrrolidin-1-ium (see 3 and 4, respectively, in Fig. 11a) allowed the synthesis of high-silica CHA/AEI intergrowths with controlled phase enrichment [100]. Interestingly, the resultant Cu-exchanged CHA/AEI materials are active and show stability in between AEI and CHA, which represents an improvement to the classical Cu-containing CHA-type catalysts when subjected to severe aging conditions [100].

4.3.2.2. CHA/GME zeolite intergrowth. Building on our use of TEA as the OSDA for CHA as a method to achieve less cost-intensive zeolites relevant for future heavy-duty diesel automotive applications (see section 5), we undertook a computer-aided approach to find attractive low-cost OSDA molecules to facilitate the crystallization of Al-rich CHA-type zeolites [101]. One of the issues in using TEA is its competing directional effect towards the BEA phase. Among the different simple and

commercially-available alkylammonium cations, we theoretically and experimentally found that methyltriethylammonium (MTEA) is the preferred candidate towards Al-rich pure crystalline CHA (see Fig. 11b), which also avoids BEA formation [101]. In contrast, the slightly larger tetraethylammonium (TEA) cation facilitates the formation of a disordered structure when targeting relatively low Si/Al ratios (ca. 4–8), which mostly contains domains of CHA with AABBCCAA type stacking with twinning to AACCBBA stacking (see Fig. 11c). These twinning locally forms GME-type stacking, but apparent extended regions of GME are not observed by HRTEM. Interestingly, the twin boundary is able to create a larger cavity in the resultant disordered structure than the *cha* cages (see green and red cavities, respectively, in Fig. 11c). Both Cu-containing CHA and CHA/GME materials present excellent NH₃-SCR catalytic performance and sufficient hydrothermal stability for heavy-duty diesel applications after being aged under steam at moderate temperatures (i.e. 600 °C) [101].

5. Perspectives for Cu-zeolites in automotive applications

A decade of collaborative efforts have led to remarkable innovations in small pore zeolites for NH₃-SCR in automotive applications. With ongoing efforts to reduce the impact from climate gas emissions on global warming, passenger vehicles and light-duty diesel vehicles are electrifying fast. On the other hand, heavy-duty diesel (HDD) vehicles, especially for long haulage trucks, are expected to continue to play a dominant role in future powertrain solutions. As an example, the expected percentage of internal combustion engines for heavy-duty vehicles is 78% in 2030 [102], and continues to play a significant role even further into the future. Interestingly, it has mainly been light-duty diesel vehicle requirements that have required extremely high-temperature Cu-zeolite NH₃-SCR solutions. However, the thermal requirements are considerably lower for HDD. They still require the use of small-pore zeolites, but lower Si/Al ratios can be used, which opens up for new preparation routes that do not require the same specificity as for high Si/Al routes.

N₂O will be regulated in future legislations (e.g. CNVII and EUVII).

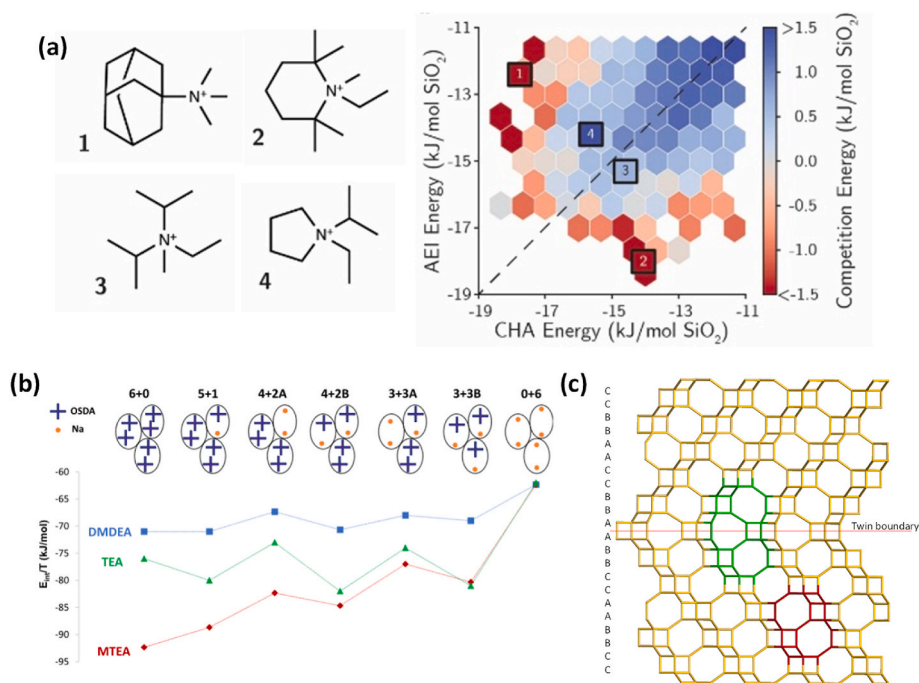


Fig. 11. (a) Comparison between binding energies of OSDAs in CHA and AEI and selected OSDA candidates for CHA and/or AEI; (b) Theoretical stabilization energies calculated for the different OSDA and Na configurations within the unit cell of CHA (DMDEA: dimethyldiethylammonium, MTEA: methyltriethylammonium, TEA: tetraethylammonium); (c) Structure for the twin boundary in CHA when using TEA as OSDA. Reproduced from ref. [100,101].

SO_x tolerance and easy regeneration remain as important features when fossil fuels are used. For these two features, researchers are still lacking good descriptors to rationalize design of new materials.

With future (pollutant) emissions legislations becoming more stringent, truck manufacturers are introducing new catalytic exhaust systems. For HDD, dual urea dosing systems seems to be a viable path forward. This will require two different SCR catalyst bricks in the system, one close-coupled to the engine and another one downstream. With this setup, the close-coupled catalyst can heat up faster to help reduce cold-start emissions even further. However, it also means the SCR catalyst will operate under more dynamic conditions and will operate part of the time under sub-stoichiometric ammonia-to-NO_x ratios. CNG, LNG and even hydrogen will also be part of the fuel mix for the internal combustion engine. This will lead to new conditions and different aging requirements e.g. when more H₂O will be present in the exhaust.

Altogether, these new or adapted requirements will translate into new material designs. Beyond automotive, clean fuels (e.g. NH₃ and MeOH) will also require exhaust treatment solutions, as they will produce (pollutant) emissions even though they will be climate neutral. In conclusion, zeolite-based exhaust treatment remains one of the key technologies to continue being able to provide breathable air.

CRedit authorship contribution statement

Peter N.R. Vennestrom: Writing – review & editing, Writing – original draft, Conceptualization. **Joakim R. Thøgersen:** Writing – review & editing. **Pär L.T. Gabriellson:** Writing – review & editing. **Leen Van Tendeloo:** Writing – review & editing. **Frank-W. Schütze:** Writing – review & editing. **Manuel Moliner:** Writing – review & editing, Writing – original draft, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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