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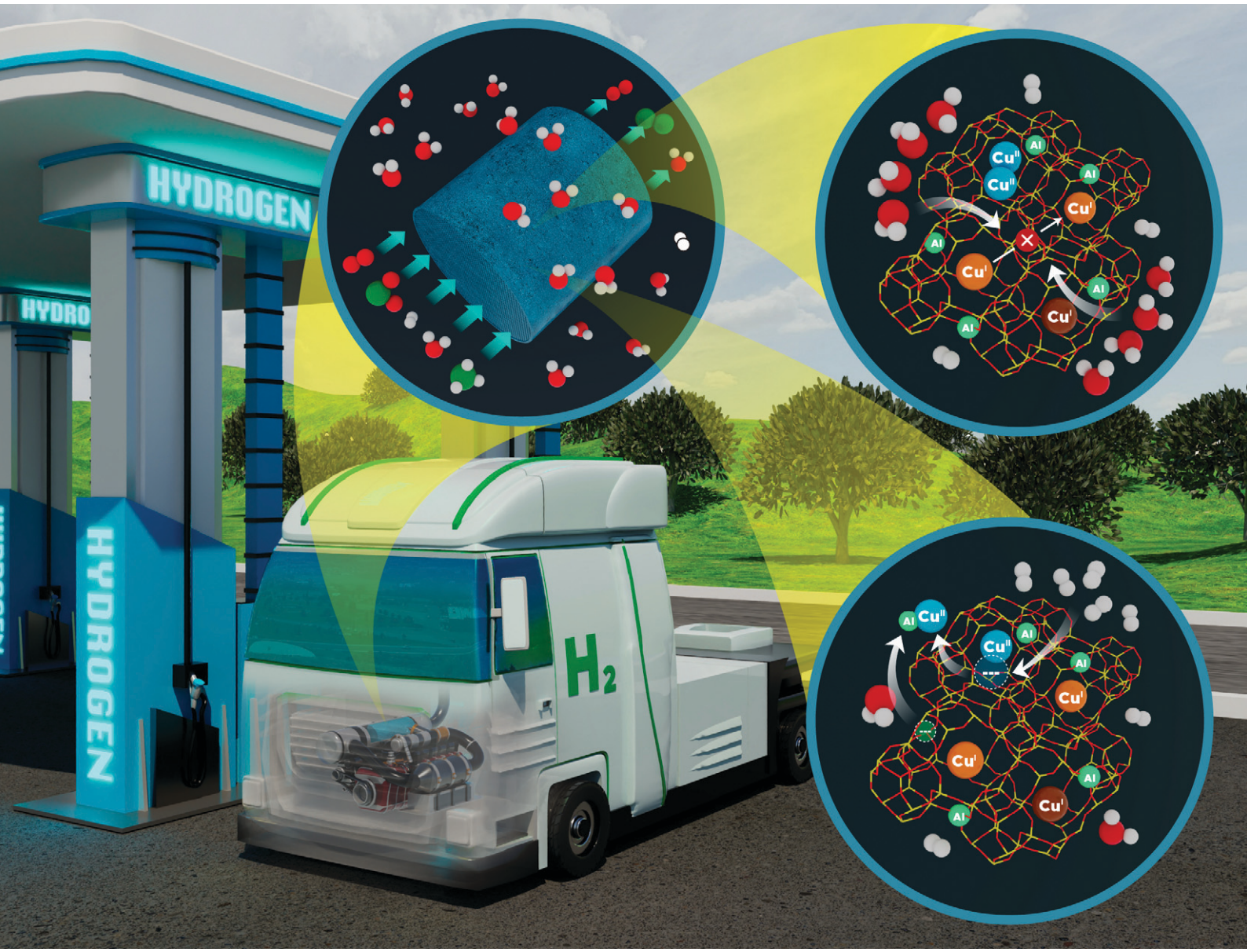

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Influence of H_2-ICE specific exhaust conditions on the activity and stability of Cu-SSZ-13 deNO_x catalysts†

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NO_x abatement from H_2 internal combustion engines (H_2-ICEs) is challenging due to high H_2O content and unburned H_2 in the exhaust. This study examines Cu-SSZ-13 SCR catalysts, focusing on the effects of high H_2O and H_2 levels on its activity and stability. High H_2O content typical of H_2-ICE exhaust hinders low-temperature SCR activity by impeding Cu migration and oxidation half cycle efficacy. H_2 slip decreases high-temperature SCR activity by reducing active Cu sites to the inactive Cu^I state. Combined, high H_2O and H_2 slip reduce SCR performance across all temperatures, making it less effective than in diesel applications. Additionally, aging under high H_2O and H_2 contents induce a severe deterioration of Cu-SSZ-13 *via* CuO_x formation and dealumination, further degrading catalyst performance. This suggests Cu-SSZ-13 may not be suitable for H_2-ICE aftertreatment, especially given the ongoing development of H_2-ICE itself. Parallel efforts in H_2-ICE and catalyst development are essential to accelerate H_2-ICE deployment.

Use of hydrogen in internal combustion engines (ICEs) has recently garnered significant attention, especially for heavy-duty machinery and vehicles.[1,2] Along with being a low-to-zero carbon strategy, H_2-ICEs also offer higher power output and thermal efficiency than traditional fossil fuel ICEs.[3] The major pollutants emitted by H_2-ICEs are oxides of nitrogen (NO_x: NO, NO_2, N_2O).

Copper-exchanged small pore zeolite Cu-SSZ-13 is a state-of-the-art catalyst used in diesel exhaust aftertreatment to remove NO_x *via* selective catalytic reduction (SCR) with NH_3 ($4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$).[4] Years of research have provided a detailed understanding of the reaction mechanisms of these catalysts under typical diesel-ICE exhaust conditions.[5–9] These studies have identified isolated Cu sites in two geometries as active sites for SCR: (1) Z_1CuOH where Cu-ions are coordinated with a single framework Al in 8-membered rings (MR), and (2) Z_2Cu where they are coordinated with two Al sites in 6MRs. The SCR reaction cycles Cu sites between Cu^{II} and Cu^I states through reduction and oxidation half-cycles (RHC and OHC). However, little is known about the behavior of these active sites and their stability in H_2-ICE exhaust, which is characterized by high H_2O content (up to 25 vol%) and the likely presence of unburned H_2.[10] Such information gap must be addressed to determine whether Cu-SSZ-13 is viable for H_2-ICEs, or if alternative catalysts should be developed. This study offers a crucial step towards closing this gap.

Here, we conducted detailed activity measurements and electron paramagnetic resonance (EPR) spectroscopy characterization of a commercially relevant Cu-SSZ-13 catalyst in simulated H_2-ICE exhaust, containing high H_2O content (up to 20%) and H_2 (up to 4000 ppm). Details on experimental setup and methods are provided in ESI† (Note S1).

We first focused on the impact of H_2O content (0, 3, 6, 10, and 20 vol%) on NO_x conversion efficiency, presented in Fig. 1a, with low-temperature data (100–300 °C) replotted in Fig. S1.† Compared to dry conditions, 3% H_2O significantly increased NO_x conversion at ≥280 °C and moderately increased it below this temperature, particularly above 150 °C. The improvement at >280 °C is primarily due to decreased parasitic NH_3 oxidation, as evident from NH_3 oxidation activity in Fig. S2† and a decreased N_2O production at temperatures >300 °C.[11] H_2O competes for active Cu sites (confirmed by NH_3 adsorption data in Fig. S3†), reducing their ability to oxidize NH_3, which in turn improves NH_3 utilization in the SCR reaction. At <280 °C, the mechanisms by which H_2O promotes NO_x conversion are complex and multi-faceted. Ma *et al.* showed that H_2O promotes surface nitrates and NO_2 formation at temperatures >250 °C which

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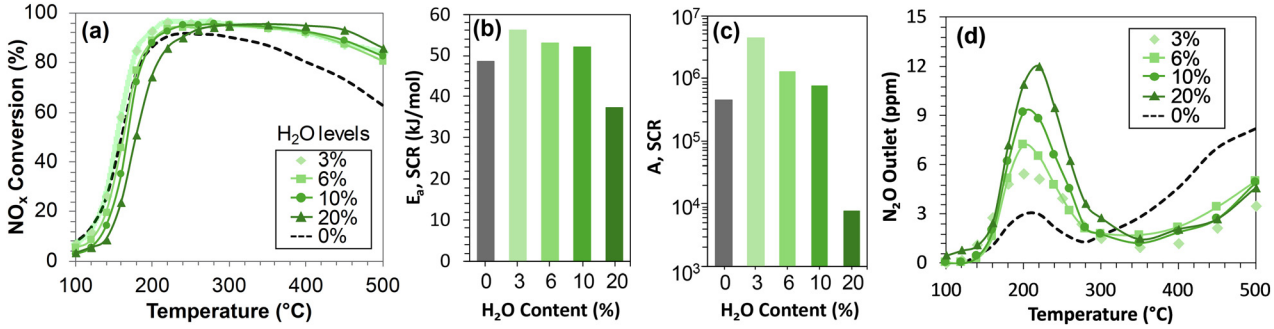

Fig. 1 (a) Steady state standard SCR NO_x conversion at different feed H_2O content (0, 3, 6, 10, 20%) on Cu-SSZ-13, (b) SCR activation energy, (c) SCR pre-exponential factor, (d) N_2O byproduct formation during SCR.

then react with Brønsted acid bound NH_3, leading to improved NO_x conversion.[12] The SCR performance below 280 °C is greatly affected by the migration and hydrolysis of active Cu centers. Utilizing *in situ* DRIFTS and XANES, Lee *et al.* concluded that H_2O promotes the mobility of Cu^I ions during the OHC.[13] In addition, Hu *et al.*[14] and Wu *et al.*[15] showed that H_2O facilitates hydrolysis of $Cu^{II}(NH_3)_4$ intermediates to more reactive $Cu^{II}(OH)(NH_3)_3$ species, which improves Cu^{II} mobility and allows formation of two-proximate Cu^{II} configuration, thereby promoting the RHC. Consequently, it is likely that the improved low-temperature SCR activity under 3% H_2O *versus* dry conditions is due to enhanced OHC and RHC facilitated by improved Cu^I/Cu^{II} migration and Cu^{II} hydrolysis. H_2O-induced promotion of both half cycles was also reported by Nasello *et al.*[16]

However, NO_x conversion behavior and the interaction of H_2O at low temperature is not altogether straightforward. Ottinger *et al.* observed a positive impact of H_2O on NO_x conversion at $NO_x > 200$ ppm but a negative impact at lower concentrations.[17] While we did not change feed NO_x in our experiments, variations in H_2O content were investigated. As seen in Fig. 1a and S1,† low-temperature NO_x conversion decreases with increased H_2O concentration above 3%. For instance, at 20% H_2O, representative of H_2-ICE exhaust, NO_x conversion at 200 °C is only 74% compared to 93% with 3% H_2O present. The low-temperature NO_x conversion data were used in Arrhenius analysis, yielding the $\ln(k)$ *vs.* $1/T$ plots shown in Fig. S4a.† The SCR activation energy (E_a) and pre-exponential factors (A) were calculated at varying H_2O contents. Previous studies have established that SCR with RHC as the rate limiting half cycle has an E_a of ~80 kJ mol^{-1}, while an OHC-limited SCR has E_a of ~35 kJ mol^{-1}.[6,18] As seen in Fig. 1b and c, the E_a and A values increases from dry to 3–10% H_2O, which is attributed to improved Cu^I mobility and O_2 activation on Cu-dimers.[13,15] These factors shift the SCR kinetics away from OHC-limited regime, which increases the E_a and A. An activation energy between 50–60 kJ mol^{-1} indicates both half cycles are kinetically relevant. However, both E_a and A decrease at 20% H_2O, indicating SCR becomes OHC-limited at high H_2O levels. The A value is nearly three orders of magnitude lower at 20% H_2O compared to 3% H_2O. Such low A indicates less efficient collisions between reactants and active Cu sites. Millan *et al.* observed in a recent DFT study that the activation barrier for $Cu^I(NH_3)_2$ inter-cage diffusion increases in the presence of excess H_2O molecules within zeolite cages.[19] This hindered diffusion would reduce the likelihood of $Cu(NH_3)_2$-O_2-$Cu(NH_3)_2$ dimer formation, necessary to facilitate the OHC, thus decreasing SCR efficiency which aligns with our findings. Hence, while a small amount of H_2O can enhance SCR activity by improving Cu mobility and hydrolysis, excess H_2O on the other hand could reduce SCR performance by impeding Cu movement.

Additionally, water content in the simulated H_2-ICE exhaust also impacts Cu-SSZ-13 SCR selectivity at low temperatures. Fig. 1d and S4b† show nitrous oxide (N_2O) byproduct formation and N_2O selectivity from Cu-SSZ-13 during SCR at various H_2O levels. The differences in N_2O formation with and without water at >280 °C are attributed to NH_3 oxidation.[11] However, below 280 °C, N_2O formation increases with H_2O content. At 20% H_2O, typical of H_2-ICE exhaust, N_2O levels are twice as high compared to those at 6% H_2O, typical of diesel exhaust. This is concerning because N_2O has a global warming potential ~300 times greater than CO_2.[20] Increased N_2O selectivity likely arises, at least in part, from hindered inter-cage diffusion of $Cu^I(NH_3)_2$ species, making them more prone to non-SCR reaction pathways. Our ongoing efforts focus on uncovering the exact mechanism behind H_2O-promotion of N_2O formation, which will be addressed in future publications.

We now focus on the impact of H_2 on the NO_x conversion efficiency on Cu-SSZ-13. To simulate SCR performance in the presence of H_2 slip from the ICE (*i.e.*, unburned H_2), experiments were conducted to measure NO_x conversion in a feed containing 20% H_2O with 200, 1000, and 4000 ppm H_2. These results are shown in Fig. 2a combined with NO_x conversion performance with 20% H_2O without H_2 previously shown. The presence of H_2 with 20% H_2O decreases NO_x conversion by up to 10% at >200 °C, with this effect being relatively insensitive to the level of H_2 within the range studied. This temperature range where NOx conversion decreases align well with the range where H_2 conversion takes place on Cu-CHA (Fig. S5†). Additionally, H_2-temperature programmed reduction (H_2-TPR) of Cu-SSZ-13

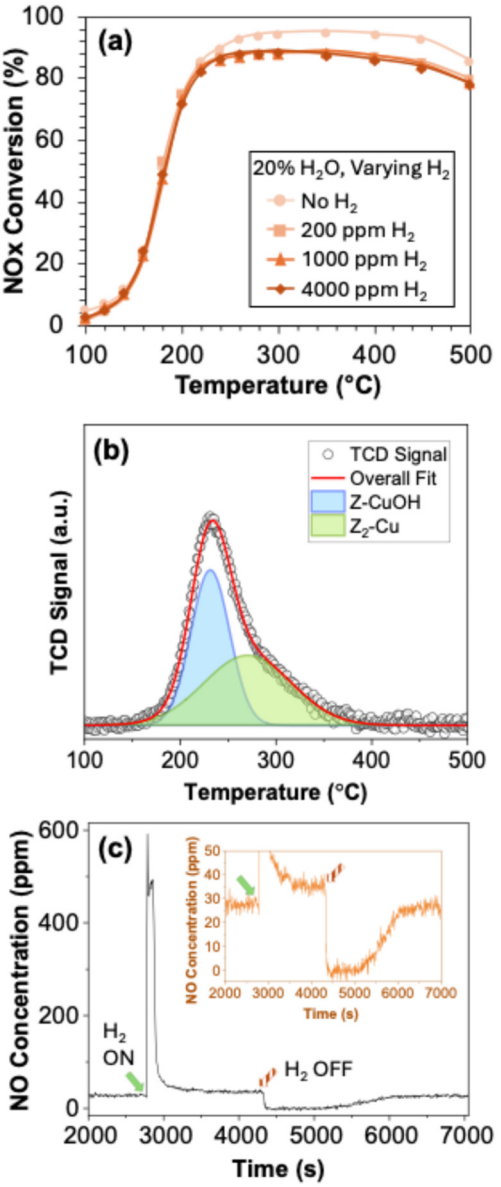

Fig. 2 (a) Steady-state SCR NO_x conversion under 0, 200 ppm, 1000 ppm, and 4000 ppm H_2, (b) H_2-TPR of Cu-SSZ-13, (c) NO transient during SCR at 250 °C with and without 200 ppm H_2.

catalyst, as shown in Fig. 2b, indicates that Cu sites reduce from Cu^{II} to Cu^{I} under H_2 at >200 °C. It is likely that under SCR conditions, H_2 has a similar reducing effect, creating a steady-state pool of Cu^{I} sites that do not participate in SCR redox activities. Although O_2 is present in the reaction mixture, a decreased NO_x conversion and an incomplete H_2 conversion (Fig. S5†) implies that Cu^{II} reduction by H_2 to Cu^{I} is faster than Cu^{I} re-oxidation by O_2.

To further elucidate the impact of H_2 on Cu-SSZ-13 SCR performance, Fig. 2c presents reactor outlet NO concentration with and without 200 ppm H_2 at 250 °C, and Fig. S6a† shows analogous results at 1000 and 4000 ppm H_2. Initially without H_2, ~26 ppm NO was measured. When H_2 is introduced at ~2800 s, an NO spike to 600 ppm is observed, after which a steady state is reached at ~37 ppm NO. This spike in NO can be directly attributed to H_2 reducing a portion of Cu^{II} sites to Cu^{I}, leading to the rapid desorption of NO_x species previously bound to Cu^{II}. Adsorbed nitrate species form at temperatures >250 °C due to an increased NO oxidation activity.[21] The subsequent higher steady state NO outlet is the result of H_2 shifting the Cu inventory preferentially to Cu^{I}, thus impeding the effective redox capacity of the catalyst. Next, when H_2 is turned off at ~4300 s, NO concentration drops to 0 ppm for a while (through ~5000 s) before it slowly returns to the original 26 ppm value observed at the start of the test. This NO consumption occurs due to an the accelerated (re)oxidation of Cu^{I} to Cu^{II} when H_2 is removed, thereby leading to (re)adsorption of NO_x species. Fig. S6b† shows the integrated quantities NO desorbed with H_2 introduction and NO adsorbed with H_2 removal. These results show that the quantities of NO desorbed and adsorbed at 200, 1000, and 4000 ppm H_2 are very similar. Consistent N_2O production during the SCR reaction tests with H_2, as presented in Fig. S7,† indicates no influence of H_2 on N_2O selectivity; this is expected since H_2 has minimal impact on low-temperature SCR activity.

Finally, the stability of Cu-SSZ-13 samples in the presence of high H_2O and H_2 was investigated by hydrothermally aging them under three different environments, followed by testing under standard SCR conditions with 6% H_2O and no H_2. HTA-1 was aged under 6% H_2O to provide a reference to diesel exhaust conditions, HTA-2 was aged under 20% H_2O to assess the impact of high-water content, and HTA-3 was aged under 20% H_2O + 1000 ppm H_2 to assess the impact of both high-water content and H_2 slip. All aging treatments were done at 650 °C for 50 hours with air as the balance gas, and the subsequent NO_x conversion results on these samples under 6% H_2O are shown in Fig. 3a. As expected, HTA-1 exhibits decreased NO_x conversion at <350 °C *versus* the fresh sample (FR) with little impact at high temperature; this can be attributed to the conversion of a portion of Z_1CuOH sites to Z_2Cu and concomitant depletion of Brønsted acid sites.[22] HTA-2 shows a modest further decrease in low-temperature activity along with markedly lower high-temperature NO_x conversion compared to HTA-1. Decreases in both high- and low-temperature NO_x conversions indicate that along with Z_1CuOH to Z_2Cu conversion, the HTA-2 sample also forms CuO_x particles (evident from EPR discussed below), increasing the magnitude of non-selective NH_3 oxidation, thereby decreasing the SCR activity.

HTA-3 shows similar high-temperature performance as HTA-2 (attributed to CuO_x particles) but significantly reduced low-temperature NO_x conversion. These results suggest that the presence of H_2 along with H_2O during aging has a detrimental effect on the stability of Cu-SSZ-13 catalysts that is not solely attributed to CuO_x particle formation. To further elucidate the impact of aging conditions on Cu-SSZ-13, the E_a and A of low-temperature SCR on the aged catalysts are tabulated inside Fig. 3a, providing two important insights: (1) similar activation energies for all catalysts indicate the same SCR reaction mechanism and rate-determining step, and (2)

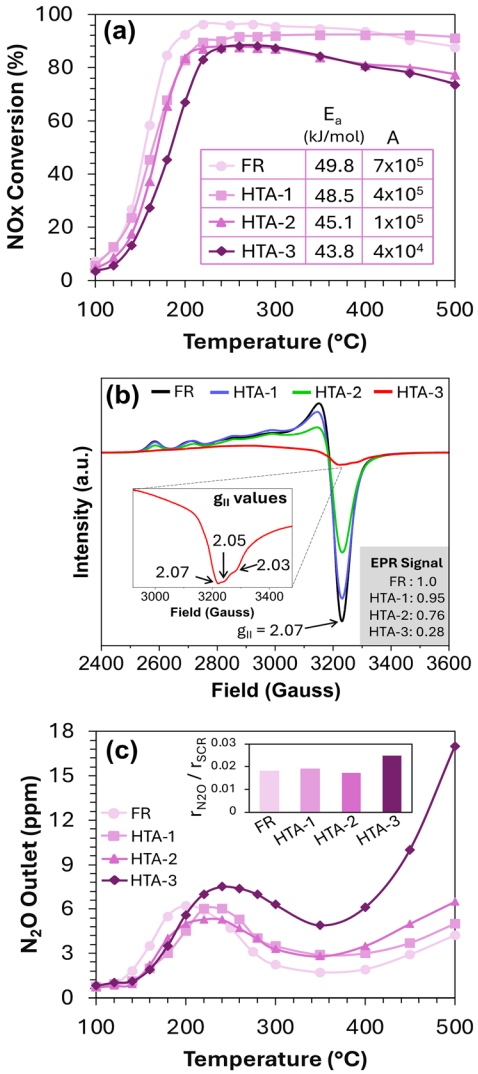

Fig. 3 (a) SCR NO_x conversion on four Cu-SSZ-13 samples with varied aging treatment: FR, HTA-1, HTA-2, HTA-3, (b) X-band EPR spectra of FR, HTA-1, HTA-2 and HTA-3 samples. Insets show ratios of total EPR signal relative to FR and high field region of HTA-3. (c) N_2O byproduct formation during SCR.

a strikingly lower pre-exponential factor for HTA-3 suggests a pronounced decrease in active Cu sites. To confirm this, we used EPR to determine the speciation and concentration of isolated Cu ions, widely regarded as the primary active sites for the SCR reaction. Fig. 3b shows the *ex situ* EPR spectra of hydrated FR, HTA-1, HTA-2, and HTA-3 at −150 °C. The high-field EPR regions of FR, HTA-1, and HTA-2 show a consistent single peak at $g_{//}$ = 2.07 attributed to anisotropic Cu^{II} ions typical of Cu-SSZ-13 (more details in ESI† Fig. S8).[18] The loss of isolated Cu sites to CuO_x clusters (which are not EPR active) is reflected in a decreased overall EPR signal. As shown in Fig. S8,† the total EPR signal of HTA-1 is similar to that of FR, confirming negligible CuO_x formation at 6% H_2O (typical of diesel exhaust conditions). HTA-2 also shows similar EPR patterns but with ~24% decreased EPR signal, confirming that high H_2O content increases CuO_x, leading to decreased performance. The EPR spectra of HTA-3, however, is notably different, with significant reductions in both the hyperfine and high-field regions. The high-field region shows features at $g_{//}$ = 2.05 and $g_{//}$ = 2.03, which Wang *et al.* identified as belonging to $CuAl_2O_4$ species.[23] Since H_2 is oxidized over Cu sites (Fig. S5†), the ensued exothermicity may lead to a reaction between Cu and Al to from $CuAl_2O_4$-type species. This indicates that the presence of H_2 and high H_2O content, typical of H_2-ICE exhaust conditions during hydrothermal aging, leads to a significant loss of isolated Cu (~72% based on Fig. S8†). Some of the lost Cu exits the zeolite framework, interacts with Al, and causes dealumination, leading to the formation of $CuAl_2O_4$. While CuO_x particles could still assist low-temperature SCR activity by oxidizing NO to form NO_2 *in situ*, facilitating the fast-SCR reaction, $CuAl_2O_4$ does not, resulting in a significant decrease in low-temperature SCR activity on HTA-3.

The detrimental impact of H_2-ICE exhaust goes beyond decreased SCR activity and the loss of active Cu sites; it also affects N_2O formation. As shown in Fig. 3c, HTA-3 generates significantly more N_2O compared to the other samples. The exact cause of N_2O formation remains unclear, whether it stems from reduced OHC efficacy or the formation of CuO_x or $CuAl_2O_4$ species. Nevertheless, it is evident that HTA-3 degradation due to high H_2O content and H_2 increases harmful N_2O emissions at both low and high temperatures.

In summary, this study evaluates the feasibility of Cu-SSZ-13 as an NH_3-SCR deNO_x catalyst under in H_2-ICE exhaust conditions. The high H_2O concentration typical of H_2-ICE exhaust reduces low-temperature SCR activity by hindering Cu migration and limiting the oxidation half-cycle efficacy. Additionally, H_2 slip decreases high-temperature SCR activity by converting active Cu sites to the inactive Cu^{I} state. Our findings show that the simultaneous presence of high H_2O and unburned H_2 significantly decreases the SCR performance of Cu-SSZ-13 across the entire temperature range when compared to diesel exhaust. Hydrothermal aging under high H_2O results in a noticeable decrease in isolated Cu sites due to increased CuO_x formation. Moreover, the co-presence of high H_2O and H_2 causes severe deterioration of Cu-SSZ-13, including dealumination and the formation of inactive CuO_x and $CuAl_2O_4$ species. This evidence suggests that Cu-SSZ-13 may not be a suitable SCR catalyst for H_2-ICE applications. Molecular level understanding of these observations will be key to developing the next generation of SCR catalysts optimized for H_2-ICE applications. Reducibility of different isolated Cu species (Z_1CuOH *vs.* Z_2Cu) and changes in support acidity caused by Si/Al ratio and topology differences should be exploited to design new catalysts. The development of more resilient catalysts is further complicated by the evolving nature of H_2-ICE technology, with variables like NO_x levels, unburned H_2, and exhaust temperature still largely undefined. Therefore, maintaining open communication between catalyst developers and OEMs will be crucial for the successful deployment of H_2-ICE technologies.

Data availability

The data supporting this article have been included as part of the manuscript and ESI.†

Author contributions

D. J. Deka: investigation, data curation, writing – original draft. G. Lee: investigation, data curation, writing – review and editing. K. Rappe: conceptualization, supervision, funding acquisition, writing – review & editing. E. Walter: investigation, writing – review & editing. J. Szanyi: supervision, writing – review and editing. Y. Wang: conceptualization, supervision, funding acquisition, writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

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