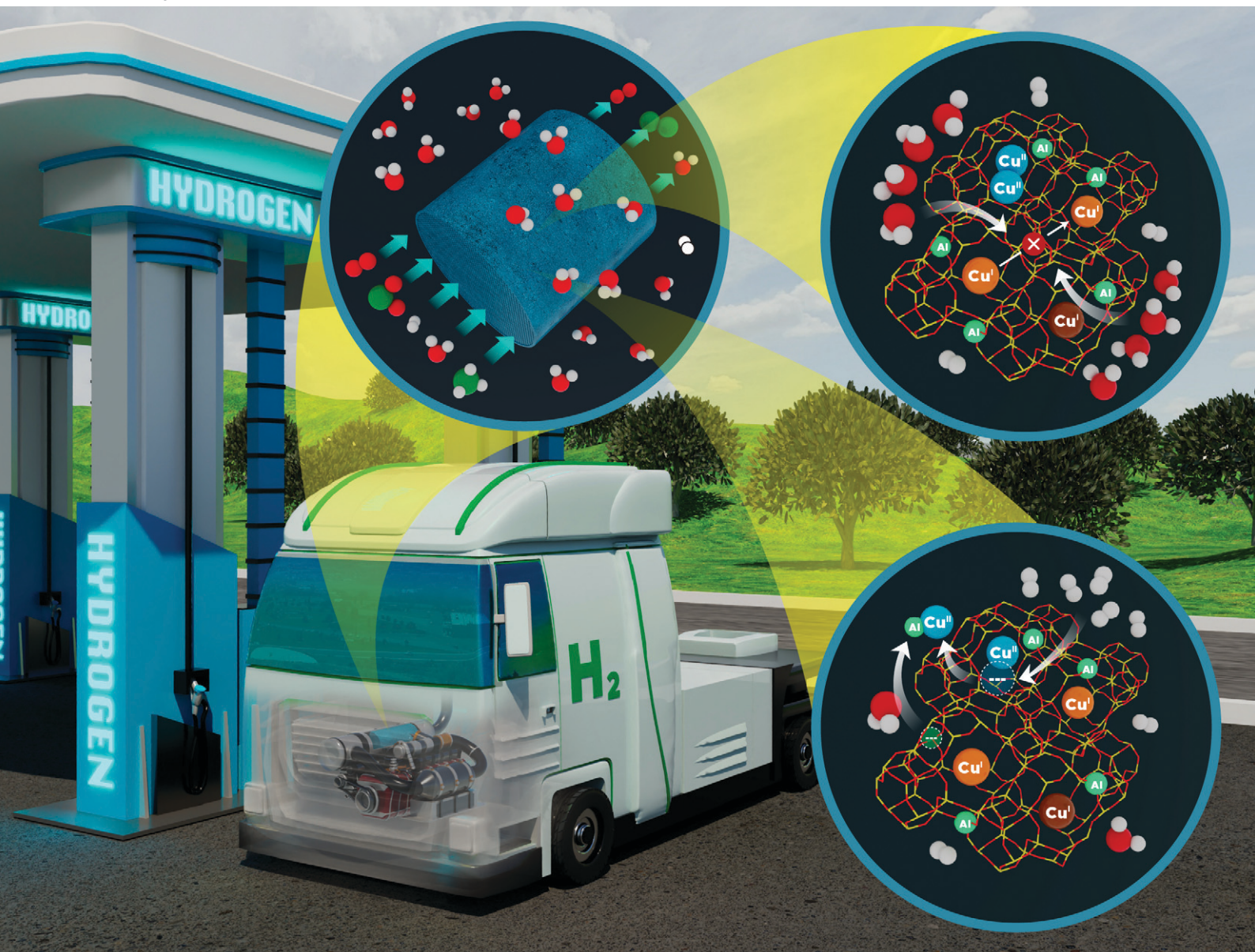


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rsc.li/catalysisInfluence of H₂-ICE specific exhaust conditions on the activity and stability of Cu-SSZ-13 deNO_x catalysts†Dhruba J. Deka, ^{*,a} Garam Lee, ^a Kenneth G. Rappé, ^a Eric Walter, ^a
Janos Szanyi ^a and Yong Wang ^{ab}

NO_x abatement from H₂ internal combustion engines (H₂-ICEs) is challenging due to high H₂O content and unburned H₂ in the exhaust. This study examines Cu-SSZ-13 SCR catalysts, focusing on the effects of high H₂O and H₂ levels on its activity and stability. High H₂O content typical of H₂-ICE exhaust hinders low-temperature SCR activity by impeding Cu migration and oxidation half cycle efficacy. H₂ slip decreases high-temperature SCR activity by reducing active Cu sites to the inactive Cu^I state. Combined, high H₂O and H₂ slip reduce SCR performance across all temperatures, making it less effective than in diesel applications. Additionally, aging under high H₂O and H₂ 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 H₂-ICE aftertreatment, especially given the ongoing development of H₂-ICE itself. Parallel efforts in H₂-ICE and catalyst development are essential to accelerate H₂-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, H₂-ICEs also offer higher power output and thermal efficiency than traditional fossil fuel ICEs.³ The major pollutants emitted by H₂-ICEs are oxides of nitrogen (NO_x: NO, NO₂, N₂O).

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 NH₃ (4NO + 4NH₃ + O₂ → 4N₂ + 6H₂O).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) Z₁CuOH where Cu-ions are coordinated with a single framework Al in 8-membered rings (MR), and (2) Z₂Cu 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 H₂-ICE exhaust, which is characterized by high H₂O content (up to 25 vol%) and the likely presence of unburned H₂.¹⁰ Such information gap must be addressed to determine whether Cu-SSZ-13 is viable for H₂-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 H₂-ICE exhaust, containing high H₂O content (up to 20%) and H₂ (up to 4000 ppm). Details on experimental setup and methods are provided in ESI† (Note S1).

We first focused on the impact of H₂O 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% H₂O 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 NH₃ oxidation, as evident from NH₃ oxidation activity in Fig. S2† and a decreased N₂O production at temperatures >300 °C.¹¹ H₂O competes for active Cu sites (confirmed by NH₃ adsorption data in Fig. S3†), reducing their ability to oxidize NH₃, which in turn improves NH₃ utilization in the SCR reaction. At <280 °C, the mechanisms by which H₂O promotes NO_x conversion are complex and multi-faceted. Ma *et al.* showed that H₂O promotes surface nitrates and NO₂ formation at temperatures >250 °C which

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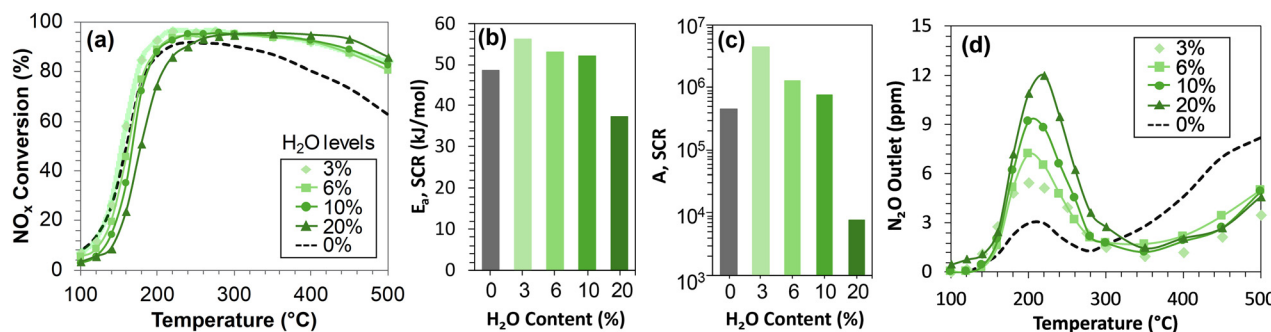


Fig. 1 (a) Steady state standard SCR NO_x conversion at different feed H₂O content (0, 3, 6, 10, 20%) on Cu-SSZ-13, (b) SCR activation energy, (c) SCR pre-exponential factor, (d) N₂O byproduct formation during SCR.

then react with Brønsted acid bound NH₃, 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 H₂O promotes the mobility of Cu^I ions during the OHC.¹³ In addition, Hu *et al.*¹⁴ and Wu *et al.*¹⁵ showed that H₂O facilitates hydrolysis of Cu^{II}(NH₃)₄ intermediates to more reactive Cu^{II}(OH)(NH₃)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% H₂O *versus* dry conditions is due to enhanced OHC and RHC facilitated by improved Cu^I/Cu^{II} migration and Cu^{II} hydrolysis. H₂O-induced promotion of both half cycles was also reported by Nasello *et al.*¹⁶

However, NO_x conversion behavior and the interaction of H₂O at low temperature is not altogether straightforward. Ottinger *et al.* observed a positive impact of H₂O 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 H₂O content were investigated. As seen in Fig. 1a and S1†, low-temperature NO_x conversion decreases with increased H₂O concentration above 3%. For instance, at 20% H₂O, representative of H₂-ICE exhaust, NO_x conversion at 200 °C is only 74% compared to 93% with 3% H₂O 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 H₂O 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% H₂O, which is attributed to improved Cu^I mobility and O₂ 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% H₂O, indicating SCR becomes OHC-limited at high H₂O levels. The *A* value is nearly three orders of magnitude lower at 20% H₂O compared to 3% H₂O. 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(NH₃)₂ inter-cage diffusion increases in the presence of excess H₂O molecules within zeolite cages.¹⁹ This hindered diffusion would reduce the likelihood of Cu(NH₃)₂-O₂-Cu(NH₃)₂ dimer formation, necessary to facilitate the OHC, thus decreasing SCR efficiency which aligns with our findings. Hence, while a small amount of H₂O can enhance SCR activity by improving Cu mobility and hydrolysis, excess H₂O on the other hand could reduce SCR performance by impeding Cu movement.

Additionally, water content in the simulated H₂-ICE exhaust also impacts Cu-SSZ-13 SCR selectivity at low temperatures. Fig. 1d and S4b† show nitrous oxide (N₂O) byproduct formation and N₂O selectivity from Cu-SSZ-13 during SCR at various H₂O levels. The differences in N₂O formation with and without water at >280 °C are attributed to NH₃ oxidation.¹¹ However, below 280 °C, N₂O formation increases with H₂O content. At 20% H₂O, typical of H₂-ICE exhaust, N₂O levels are twice as high compared to those at 6% H₂O, typical of diesel exhaust. This is concerning because N₂O has a global warming potential ~300 times greater than CO₂.²⁰ Increased N₂O selectivity likely arises, at least in part, from hindered inter-cage diffusion of Cu^I(NH₃)₂ species, making them more prone to non-SCR reaction pathways. Our ongoing efforts focus on uncovering the exact mechanism behind H₂O-promotion of N₂O formation, which will be addressed in future publications.

We now focus on the impact of H₂ on the NO_x conversion efficiency on Cu-SSZ-13. To simulate SCR performance in the presence of H₂ slip from the ICE (*i.e.*, unburned H₂), experiments were conducted to measure NO_x conversion in a feed containing 20% H₂O with 200, 1000, and 4000 ppm H₂. These results are shown in Fig. 2a combined with NO_x conversion performance with 20% H₂O without H₂ previously shown. The presence of H₂ with 20% H₂O decreases NO_x conversion by up to 10% at >200 °C, with this effect being relatively insensitive to the level of H₂ within the range studied. This temperature range where NO_x conversion decreases align well with the range where H₂ conversion takes place on Cu-CHA (Fig. S5†). Additionally, H₂-temperature programmed reduction (H₂-TPR) of Cu-SSZ-13



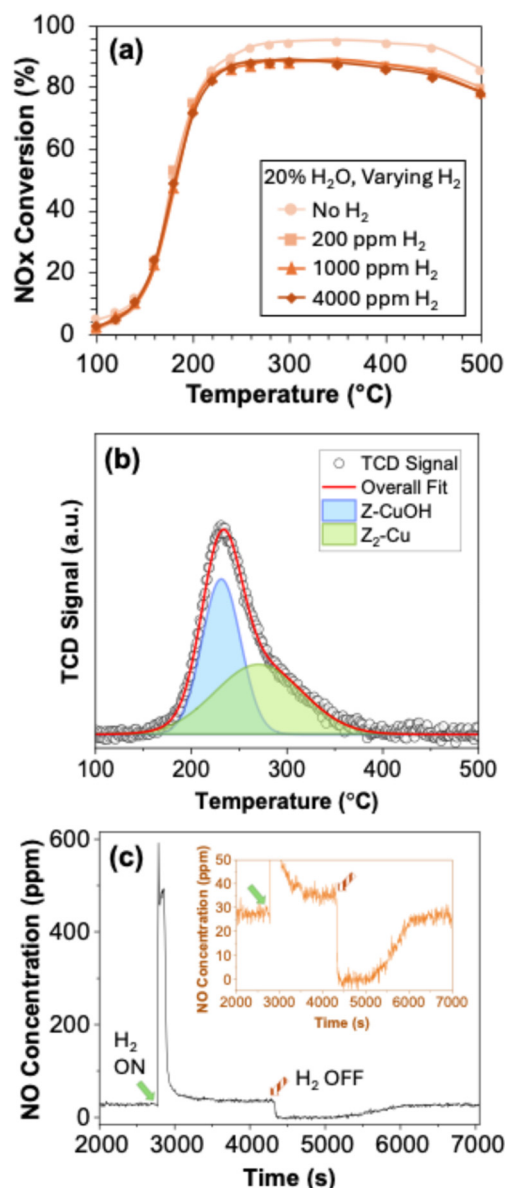


Fig. 2 (a) Steady-state SCR NO_x conversion under 0, 200 ppm, 1000 ppm, and 4000 ppm H₂, (b) H₂-TPR of Cu-SSZ-13, (c) NO transient during SCR at 250 °C with and without 200 ppm H₂.

catalyst, as shown in Fig. 2b, indicates that Cu sites reduce from Cu^{II} to Cu^I under H₂ at >200 °C. It is likely that under SCR conditions, H₂ has a similar reducing effect, creating a steady-state pool of Cu^I sites that do not participate in SCR redox activities. Although O₂ is present in the reaction mixture, a decreased NO_x conversion and an incomplete H₂ conversion (Fig. S5†) implies that Cu^{II} reduction by H₂ to Cu^I is faster than Cu^I re-oxidation by O₂.

To further elucidate the impact of H₂ on Cu-SSZ-13 SCR performance, Fig. 2c presents reactor outlet NO concentration with and without 200 ppm H₂ at 250 °C, and Fig. S6a† shows analogous results at 1000 and 4000 ppm H₂. Initially without H₂, ~26 ppm NO was measured. When H₂ 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 H₂ 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 H₂ shifting the Cu inventory preferentially to Cu^I, thus impeding the effective redox capacity of the catalyst. Next, when H₂ 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 the accelerated (re)oxidation of Cu^I to Cu^{II} when H₂ is removed, thereby leading to (re)adsorption of NO_x species. Fig. S6b† shows the integrated quantities NO desorbed with H₂ introduction and NO adsorbed with H₂ removal. These results show that the quantities of NO desorbed and adsorbed at 200, 1000, and 4000 ppm H₂ are very similar. Consistent N₂O production during the SCR reaction tests with H₂, as presented in Fig. S7,† indicates no influence of H₂ on N₂O selectivity; this is expected since H₂ has minimal impact on low-temperature SCR activity.

Finally, the stability of Cu-SSZ-13 samples in the presence of high H₂O and H₂ was investigated by hydrothermally aging them under three different environments, followed by testing under standard SCR conditions with 6% H₂O and no H₂. HTA-1 was aged under 6% H₂O to provide a reference to diesel exhaust conditions, HTA-2 was aged under 20% H₂O to assess the impact of high-water content, and HTA-3 was aged under 20% H₂O + 1000 ppm H₂ to assess the impact of both high-water content and H₂ 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% H₂O 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 Z₁CuOH sites to Z₂Cu 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 Z₁CuOH to Z₂Cu conversion, the HTA-2 sample also forms CuO_x particles (evident from EPR discussed below), increasing the magnitude of non-selective NH₃ 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 H₂ along with H₂O 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)



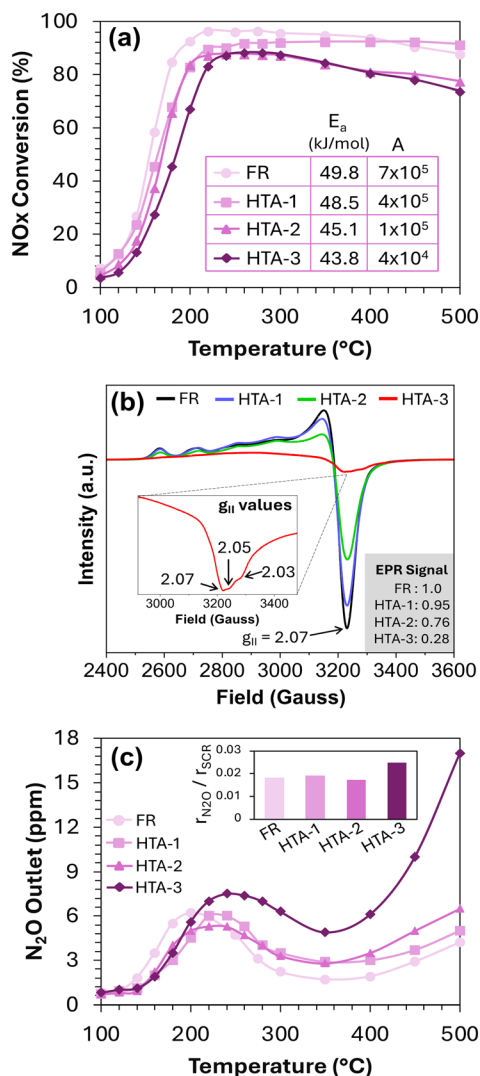


Fig. 3 (a) SCR NO_x conversion on four Cu-SSZ-13 samples with varied aging treatment: FR, HTA-1, HTA-2, HTA-3. (b) X-band EPR spectra of FR, HTA-1, HTA-2 and HTA-3 samples. Insets show ratios of total EPR signal relative to FR and high field region of HTA-3. (c) N₂O byproduct formation during SCR.

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% H₂O (typical of diesel exhaust conditions). HTA-2 also shows similar EPR patterns but with $\sim 24\%$ decreased EPR signal, confirming that high H₂O 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 CuAl₂O₄ species.²³ Since H₂ is oxidized over Cu sites (Fig. S5†), the ensued exothermicity may lead to a reaction between Cu and Al to form CuAl₂O₄-type species. This indicates that the presence of H₂ and high H₂O content, typical of H₂-ICE exhaust conditions during hydrothermal aging, leads to a significant loss of isolated Cu ($\sim 72\%$ based on Fig. S8†). Some of the lost Cu exits the zeolite framework, interacts with Al, and causes dealumination, leading to the formation of CuAl₂O₄. While CuO_x particles could still assist low-temperature SCR activity by oxidizing NO to form NO₂ *in situ*, facilitating the fast-SCR reaction, CuAl₂O₄ does not, resulting in a significant decrease in low-temperature SCR activity on HTA-3.

The detrimental impact of H₂-ICE exhaust goes beyond decreased SCR activity and the loss of active Cu sites; it also affects N₂O formation. As shown in Fig. 3c, HTA-3 generates significantly more N₂O compared to the other samples. The exact cause of N₂O formation remains unclear, whether it stems from reduced OHC efficacy or the formation of CuO_x or CuAl₂O₄ species. Nevertheless, it is evident that HTA-3 degradation due to high H₂O content and H₂ increases harmful N₂O emissions at both low and high temperatures.

In summary, this study evaluates the feasibility of Cu-SSZ-13 as an NH₃-SCR deNO_x catalyst under in H₂-ICE exhaust conditions. The high H₂O concentration typical of H₂-ICE exhaust reduces low-temperature SCR activity by hindering Cu migration and limiting the oxidation half-cycle efficacy. Additionally, H₂ 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 H₂O and unburned H₂ significantly decreases the SCR performance of Cu-SSZ-13 across the entire temperature range when compared to diesel exhaust. Hydrothermal aging under high H₂O results in a noticeable decrease in isolated Cu sites due to increased CuO_x formation. Moreover, the co-presence of high H₂O and H₂ causes severe deterioration of Cu-SSZ-13, including dealumination and the formation of inactive CuO_x and CuAl₂O₄ species. This evidence suggests that Cu-SSZ-13 may not be a suitable SCR catalyst for H₂-ICE applications. Molecular level understanding of these observations will be key to developing the next generation of SCR catalysts optimized for H₂-ICE applications. Reducibility of different isolated Cu species (Z₁CuOH *vs.* Z₂Cu) 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 H₂-ICE technology, with variables like NO_x levels, unburned H₂, and exhaust temperature still largely undefined. Therefore, maintaining open communication between catalyst developers and OEMs will be crucial for the successful deployment of H₂-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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