

Hydrothermal Aging Mechanism on Cu-CHA Type SCR Catalysts Assumed for the Use in H₂-engines

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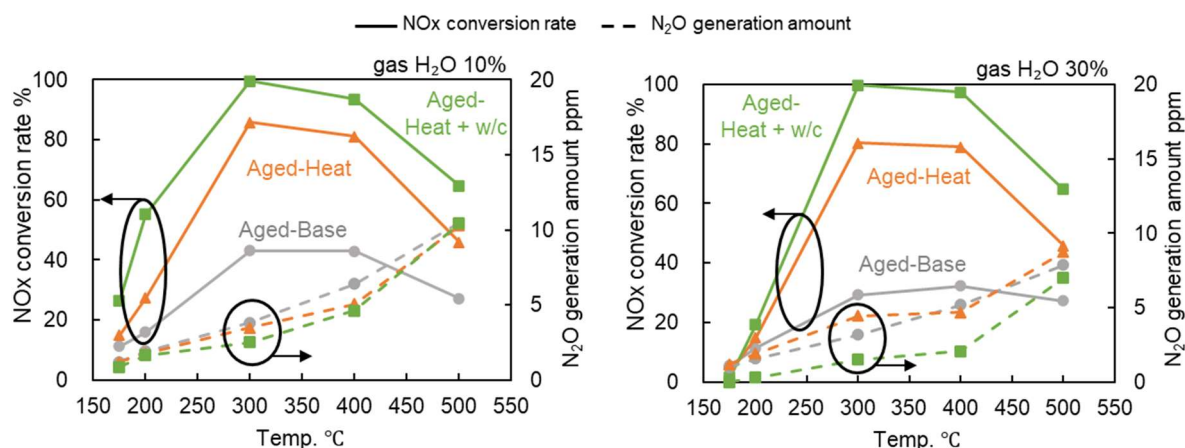
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In recent years, hydrogen engines, which emit no CO₂ in their exhaust, have attracted attention as a means to achieve carbon neutrality in heavy-duty vehicles. Compared to conventional diesel engines, hydrogen engine exhaust contains higher concentrations of NO_x (a regulated pollutant) and H₂O. To remove NO_x, after-treatment systems employ Cu-CHA type SCR catalysts that use urea as a reducing agent. However, these catalysts face the challenge of reduced NO_x purification efficiency caused by hydrothermal aging. In this study, we investigated the hydrothermal aging mechanism of Cu-CHA type SCR catalysts and the impact of exhaust H₂O concentration through experiments using model exhaust gas and numerical simulations.

We evaluated three types of catalysts under various hydrothermal aging conditions: a baseline catalyst (Baseline); a heat-resistant catalyst treated to retain Cu within the zeolite structure after hydrothermal aging (Heat); and a catalyst featuring both improved heat resistance and double the wash-coat loading (Heat+W/C). Steady-state NO_x purification efficiency was measured under Standard SCR conditions (300 ppm each of NO and NH₃) and Fast SCR conditions (300 ppm NH₃; 150 ppm each of NO and NO₂).

Figure 1 compares the NO_x purification efficiency (left axis, solid lines) and N₂O formation (right axis, dashed lines) for Aged-Base, Aged-Heat, and Aged-Heat+W/C—all exposed to identical hydrothermal aging conditions (800°C, 30% H₂O)—at gas-phase H₂O concentrations of (a) 10% and (b) 30%. Under Standard SCR conditions, Aged-Heat+W/C exhibited higher NO_x purification efficiency than the Baseline catalyst or the catalyst with only improved heat resistance; however, a significant drop in NO_x purification efficiency was observed under test conditions characterized by low temperatures and high H₂O concentrations. Similar to the "Aged-Heat+W/C" sample, N₂O formation decreased as the gas-phase H₂O concentration increased under severe hydrothermal aging conditions for both "Aged-Base" and "Aged-Heat" samples; this revealed a negative correlation between exhaust H₂O concentration and N₂O formation. Under Fast SCR conditions, the "Aged-Heat+W/C" catalyst demonstrated purification performance comparable to that of a fresh catalyst, even under the most severe hydrothermal aging conditions. At the same time, the formation of N₂O—which tends to occur under Fast SCR conditions—was suppressed.

To evaluate the purification performance of Cu-CHA type SCR catalysts, a quasi-two-dimensional computational fluid dynamics model accounting for surface reactions was employed. Experimental data for each catalyst were reproduced by adjusting the active site density and the pre-exponential factor in the Arrhenius equation. This study examined catalytic reactions closely approximating actual phenomena by incorporating the formation of Cu dimers—particularly in the high-temperature range—and the NH₃ oxidation reactions involving them. Under Standard SCR conditions, it was shown that catalysts with lower purification efficiency exhibited higher peak values for Cu⁺–H⁺ surface coverage; this is attributed to the inhibition of re-oxidation to Cu²⁺ caused by hydrothermal aging. Experimental values were also reproduced for Fast SCR conditions, and an analysis of reaction rates revealed that lower catalyst purification efficiency corresponded to higher selectivity for the ammonium nitrate formation reaction.



(a) Inlet H₂O gas: 10 %

(b) Inlet H₂O gas: 30 %

Fig 1 Comparison of NO_x conversion rate and N₂O generation amount with various catalysts
(Aged-Base, Aged-Heat, Aged-Heat+W/C, Aging temp: 800 °C-H₂O: 30 %, Experiment)