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Active and Stable PtPd Diesel Oxidation Catalysts under Industry-Defined Test Protocols

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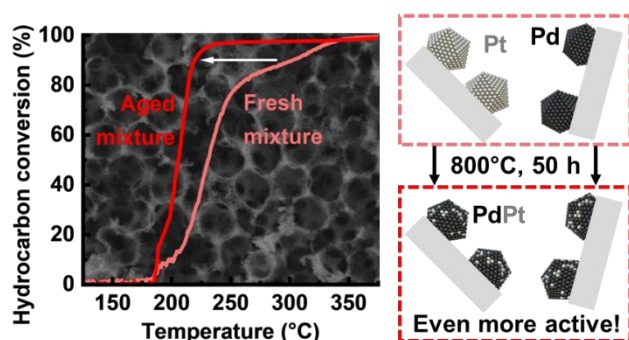
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ABSTRACT

Nanoparticle-supported Pt and Pd catalysts are employed industrially to convert CO and hydrocarbon residue from incomplete diesel fuel combustion. However, these catalysts deactivate over time due to sintering, especially for Pt nanoparticles which readily generate volatile species under high operating temperatures. Here, we turned the detrimental vapor-mediated sintering of Pt into an advantage by using a physical mixture of Pt and Pd catalysts prepared using a raspberry-colloid-templating (RCT) method. The RCT method produced Pt/Al₂O₃ and Pd/Al₂O₃ catalysts with partially embedded NPs to inhibit surface-mediated sintering pathways. As validated using an industry-defined emission control test protocol, aging a physical mixture of Pt/Al₂O₃ and Pd/Al₂O₃ at high temperature produced an alloyed PtPd/Al₂O₃ catalyst that outperformed the fresh catalyst mixture and both individual catalysts for hydrocarbon conversion, while exhibiting high catalytic stability and resistance to sintering and to SO₂ poisoning. X-ray photoelectron spectroscopy revealed that in the aged catalyst mixture, half of the Pd content existed in their more active metallic state, compared to the less active oxide forms in the fresh mixture and both individual catalysts, explaining the unusual activity enhancement. Our results represent a practical approach to producing active and stable PtPd/Al₂O₃ diesel oxidation catalysts for emission control applications.

KEYWORDS: diesel oxidation catalyst, palladium, platinum, alloys, catalyst stability, Ostwald ripening, emission control

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To resist nanoparticle sintering in diesel oxidation catalysts, a raspberry-colloid-templating method was employed to partially entrench nanoparticles into its support. Aging a physical mixture of Pt/Al₂O₃ and Pd/Al₂O₃ under an industry-defined protocol produced a highly stable and alloyed PtPd/Al₂O₃ catalyst that outperformed the fresh catalyst mixture and both individual catalysts.

INTRODUCTION

Diesel oxidation catalysts are critical to our automobile emission control strategy for the abatement of pollutants such as CO, hydrocarbons, and NO.¹ These catalysts are typically prepared by impregnation, forming Pt and/or Pd nanoparticles (NPs) surface-attached to Al₂O₃ support.² In emission control, a long-standing challenge is catalyst deactivation due to substantial NP sintering.¹ This problem is especially prevalent for Pt, which readily forms volatile species (*e.g.*, PtO₂) under high temperature oxidative gas streams (*e.g.*, automobile exhaust), leading to severe vapor- and surface-mediated Ostwald ripening.^{3–8} While Pd is relatively more stable due to the lower volatility of PdO,⁹ it remains susceptible to surface-diffusion-mediated sintering pathways.¹⁰ Thus, to compensate for the anticipated catalytic deactivation, automobile catalyst manufacturers often overload Pt and Pd NPs into their systems, further exacerbating the scarce supply and increasing cost of these precious metals.²

Here, we used a physical mixture of Pt and Pd catalysts prepared by a raspberry-colloid-templating (RCT) approach^{11–14} to address the catalyst deactivation challenge. The RCT method produces highly stable catalysts due to its unique feature of having catalytic NPs partially embedded within its support (**Fig. 1a**),^{15–21} which we anticipate will reduce surface-mediated sintering and related catalytic deactivation. Indeed, as validated using an industry-defined simulated exhaust and test protocol, we report that the high volatility of Pt species at elevated temperatures, when in the presence of Pd NPs in close vicinity, results in the formation of alloyed PtPd NPs with arrested sintering. Interestingly, thermal treatment not only yielded *more stable* catalysts, but also *more active* catalysts that recorded higher hydrocarbon conversion activities than the individual catalysts or fresh un-aged mixture. We discuss the mechanism behind this unusual reversal of the activity trend and argue that our approach turns an otherwise detrimental vapor-mediated sintering phenomenon of Pt catalysts into an unexpected practical advantage.

RESULTS AND DISCUSSION

Pt/Al₂O₃ and Pd/Al₂O₃ catalysts were prepared using the RCT method (**Fig. 1a**).^{10,11} Briefly, Pt or Pd NPs were attached to polymeric templates that were self-assembled into a colloidal crystal. A boehmite [AlO(OH)] suspension was infiltrated into the colloidal crystal, following which the infiltrated composite was calcined to remove the templates and convert boehmite to γ -Al₂O₃. Electron microscopy confirmed the macroporous and interconnected catalyst structure (**Fig. S1a–b**) essential for facilitating efficient mass transport,^{10,11} and the partial embedding of NPs in the support (**Fig. 1d inset, 1g inset**), corroborating with previous characterization.¹⁵ In the fresh catalysts, Pt NPs are slightly larger than Pd NPs (**Fig. 1d top, 1g top**), likely due to differences in the nucleation rates of Pt and Pd NPs.²³ During synthesis, we intentionally preset the metal loading in each catalyst to 0.1 atom % (corresponding to 0.6 wt % Pd/Al₂O₃ and 1.0 wt% Pt/Al₂O₃), which we verified in the catalysts produced by elemental analysis (**Table S1**). By fixing the metal loading in both catalysts, we preemptively eliminated metal loading-related effects in our catalytic analyses.²² Together with the comparable diffraction (**Fig. S1c–d**) and physisorption (**Table S2**) data, physical characterization established no notable differences in overall morphology, support phase, metal loading, or surface area between the fresh Pt/Al₂O₃ and Pd/Al₂O₃ catalysts.

We evaluated Pt/Al₂O₃ and Pd/Al₂O₃ separately following an industry-defined diesel combustion test protocol.²⁴ The simulated exhaust stream comprised of O₂, H₂O, CO, CO₂, NO, and a mixture of hydrocarbons (see **Methods** section). We center our discussion on CO and hydrocarbon activity as Pt and Pd are specifically used for these two reactants industrially, and that other metals (*e.g.*, Rh) are included in catalytic converters to manage NO exhaust;² however, for completeness, we provide NO and NO_x data in **Fig. S2–3**. In a typical test, 100 mg catalyst was subjected to three heating-cooling cycles in its freshly prepared, degreened, or aged state. Catalytic performance was assessed for fresh catalysts and then compared to catalysts that were degreened (700 °C, 4 h) or aged (800 °C, 50 h) in the reactant stream immediately before catalytic evaluation.²⁴ As a control, NP-free γ -Al₂O₃ exhibited no appreciable CO or hydrocarbon activity under similar conditions. Hence, we attribute all observed catalytic activity to the presence of Pt and Pd species.

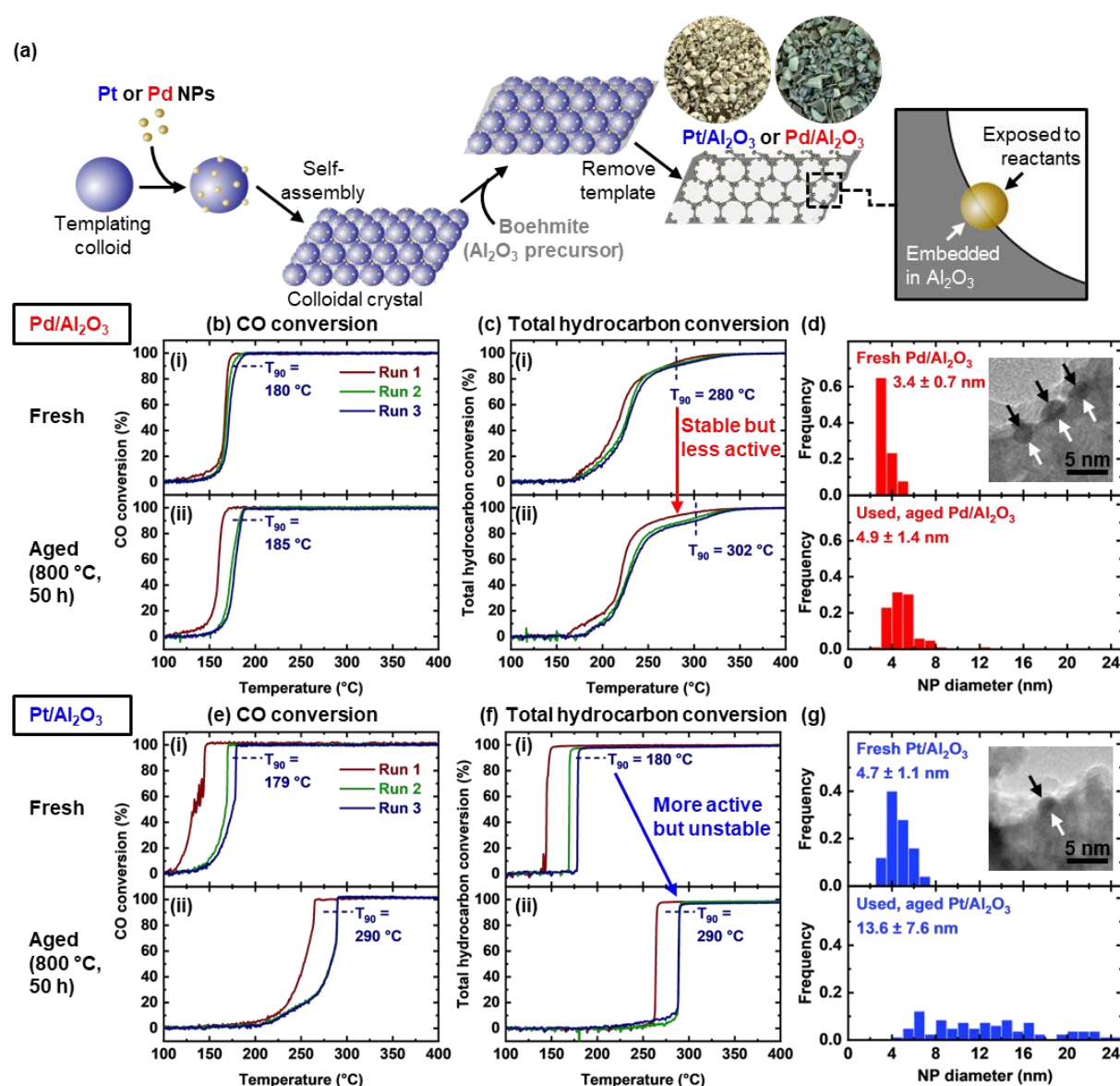


Fig. 1: Pt/Al₂O₃ and Pd/Al₂O₃ catalysts. (a) RCT method. Insets show optical photographs of fresh Pt/Al₂O₃ (left) and Pd/Al₂O₃ (right). (b–d) Results for Pd/Al₂O₃: (b) CO and (c) total hydrocarbon light-off curves, and (d) the NP size distribution. (e–g) Results for Pt/Al₂O₃: (e) CO and (f) total hydrocarbon light-off curves, and (g) the NP size distribution. In (b), (c), (e), (f) catalytic measurements were repeated thrice for each condition:

(i) freshly prepared or (ii) after aging. Navy dashed line indicates, in each case, T_{90} from the third run. In (d) and (g), inset show NPs partially embedded in γ - Al_2O_3 (white arrow); black arrow indicates unembedded regions of the NP surface.

$\text{Pd}/\text{Al}_2\text{O}_3$ was stable, evident from the relatively unchanged light-off curves with successive runs of the fresh [Fig. 1b(i), 1c(i)], degreened (Fig. S2), and aged catalysts [Fig. 1b(ii), 1c(ii)]. A slight increase in the Pd NP size after catalytic testing (Fig. 1d, S4a) suggests that surface-mediated ripening and coalescence mechanisms were largely inhibited, which we ascribe to the partial NP embedding feature in the RCT catalysts.¹⁰

$\text{Pt}/\text{Al}_2\text{O}_3$ was more active (Fig. 1e–f), especially for hydrocarbon conversion. (Note that the hydrocarbon light-off curves follow a step function with its temperature onset right after full CO conversion, implying strong competitive adsorption of CO on Pt.^{25–27}) However, $\text{Pt}/\text{Al}_2\text{O}_3$ was unstable, as its light-off curves shifted to higher temperatures with successive runs of the fresh [Fig. 1e(i), 1f(i)], degreened (Fig. S3), and aged catalysts [Fig. 1e(ii), 1f(ii)]. The temperature required to achieve 90% conversion (T_{90}) of CO and hydrocarbons after aging increased considerably from 179–180 °C to 290 °C, clearly indicative of catalyst deactivation. This deactivation was due to severe Pt NP sintering (Fig. 1g, S4b), suggesting that vapor-mediated Pt NP ripening was not arrested by partial NP embedment into Al_2O_3 .

Our catalytic results established that *$\text{Pd}/\text{Al}_2\text{O}_3$ was stable but less active for hydrocarbon conversion, whereas $\text{Pt}/\text{Al}_2\text{O}_3$ was more active but unstable*. Considering these results, we tested a 1:1 *physical mixture* (by mass) of both catalysts to investigate if we could take advantage of the higher activity of $\text{Pt}/\text{Al}_2\text{O}_3$ and the higher stability of $\text{Pd}/\text{Al}_2\text{O}_3$.

The physically mixed catalysts exhibited *high stability*, evident from the near-overlapping light-off curves with successive runs of the degreened (Fig. S5) and aged catalysts [Fig. 2a(ii), 2b(ii)]. A small ≈ 15 °C shift (to higher temperatures) in the light-off curve in the fresh catalyst from the first to subsequent runs [Fig. 2a(i), 2b(i)] is possibly due to some initial surface restructuring in the first temperature ramp. As an additional test, we pre-treated the aged mixture with SO_2 , a chemical poison produced during fuel combustion that rapidly deactivates Pd and Pt at a few parts per million (ppm) levels.^{1,28–31} T_{90} for both CO and hydrocarbon conversion was unaffected after SO_2 pre-treatment [Fig. 2a(iii), 2b(iii)], demonstrating the catalyst mixture's resistance against sulfur poisoning. We posit that the 3D macroporous RCT structure provided a high support surface area to increase the density of exposed surface hydroxyl groups on the Al_2O_3 support for SO_2 adsorption (Fig. S6).³²

For CO conversion (Fig. 2a), the mixture retained its originally low T_{90} (185 °C) after aging (184 °C), reflecting high Pt-like activity and Pd-like stability. Interestingly, for hydrocarbon conversion (Fig. 2b), the aged mixture recorded an appreciably lower T_{90} (218 °C) than the fresh mixture (302 °C), indicating that *hydrocarbon conversion activity was enhanced after aging the mixture*. Analysis of each hydrocarbon constituent in the reactant stream further revealed that the aged mixture accelerated the conversion of both alkanes and alkenes of various carbon chain lengths (Fig. S7). As the NP size distribution was largely unaltered after aging and catalytic testing (Fig. 2c, S4c), we excluded the possibility that more of the same active sites was created by redispersion into smaller NPs. Instead, elemental mapping of the aged and used catalyst mixture depicted appreciable Pt traces (≈ 10 –20 atomic

%) on Pd NPs as a newly alloyed PtPd phase (**Fig. 2d, S4d**). This result implies the vapor-mediated diffusion of Pt species from Pt/Al₂O₃ grains to Pd NPs on distinctly separate Pd/Al₂O₃ grains during the 800 °C aging step, consistent with other works reporting the facile generation and emission of highly volatile and mobile Pt species at $\approx 600\text{--}700$ °C.^{4,33,34}

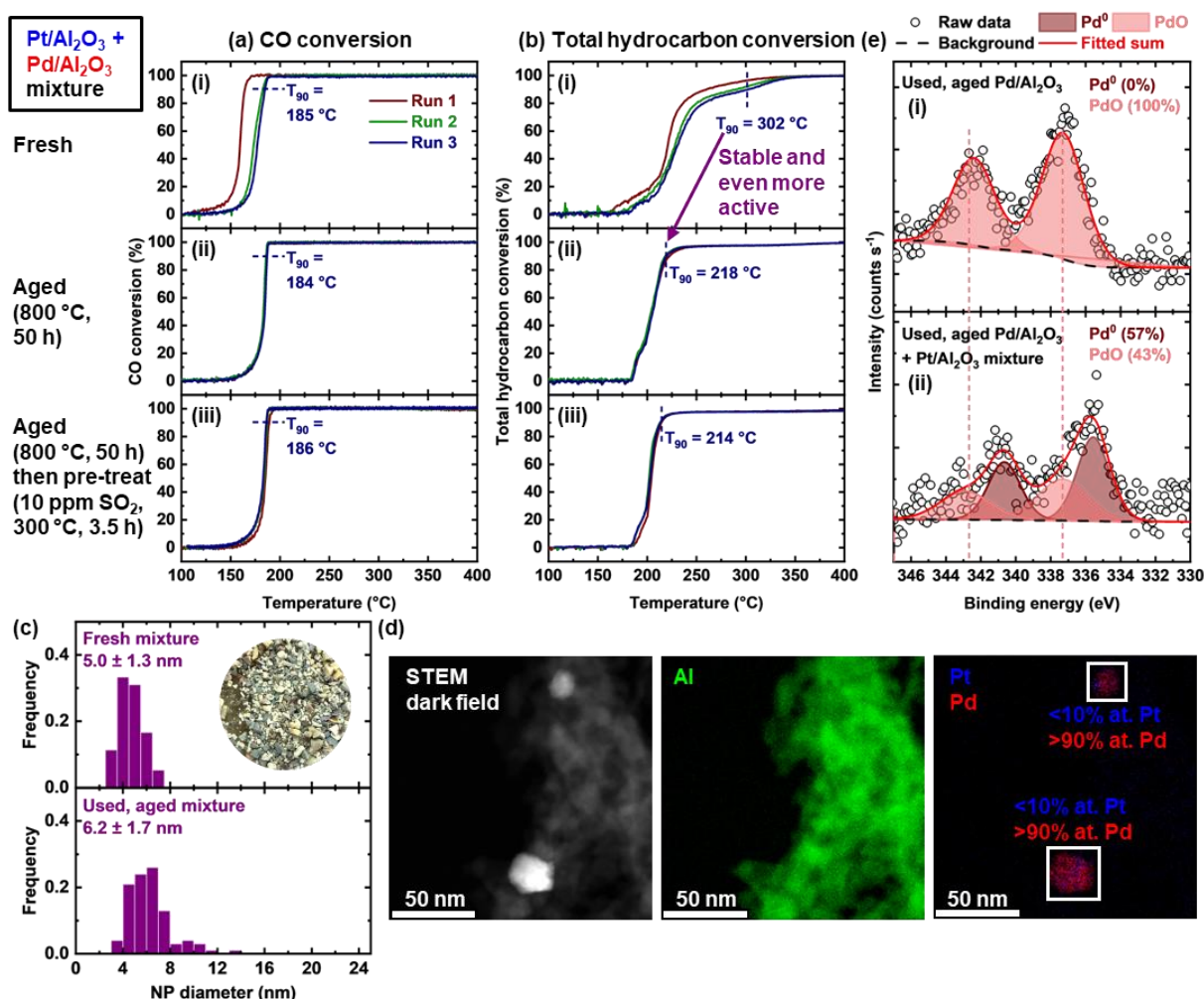


Fig. 2: Physical mixture of catalysts. (a) CO and (b) total hydrocarbon light-off curves. NO data is provided in **Fig. S5**. In (a)–(b), catalytic measurements are repeated thrice for each condition: (i) freshly prepared, (ii) after aging, (iii) after SO₂ pre-treatment following aging. Navy dashed line indicates, in each case, T₉₀ from the third run. (c) NP size distribution of the catalyst mixture. Inset shows an optical photograph of the fresh catalyst mixture. (d) Scanning transmission electron microscopy (STEM) dark field images and their corresponding energy dispersive X-ray spectroscopy (EDX) elemental maps of the aged and used catalyst mixture. Elemental composition of each NP was quantified by EDX (white boxes). (e) Pd 3d XPS spectra of aged and used catalysts: (i) Pd/Al₂O₃ and (ii) the catalyst mixture. Vertical dashed lines indicate PdO peak positions.

To explain the unusual increased activity of thermally treated mixture, we examined the alloyed PtPd phase with X-ray photoelectron spectroscopy (XPS). As Pt 4f and Al 2p XPS peaks overlap, we focused our analysis on the Pd 3d region (XPS data of the fresh catalysts are shown in **Fig. S8**). In the individual catalysts, Pd was fully oxidized to PdO after aging and catalytic testing as expected [**Fig. 2e(i)**].⁵ In contrast, for the aged catalyst mixture, 57% of Pd was detected in their metallic state [**Fig. 2e(ii)**], indicative of co-existing PdO and metallic Pd phases.^{6,35} Notably, metallic Pd is known to be intrinsically more active than PdO under oxidative conditions (*e.g.*, diesel exhaust).^{25,28,36,37} Thus, the high metallic Pd content in

the aged mixture explains their enhanced catalytic activity compared to the fresh mixture, or to the individual aged catalysts, that instead exist as less active PdO. Moreover, the higher stability of the mixture, compared to Pt/Al₂O₃, is due to the presence of stable surface-entrenched Pd NPs in the mixture that interrupted vapor-phase transport of mobile Pt species and trapped them to form metallic PtPd domains, in line with other works reporting that PtPd alloyed catalysts exhibited higher stability than Pt catalysts.^{4,6,35,38} We also point out that the small (but highly active) Pt domains on PtPd alloyed NPs could have also contributed to the overall enhanced catalytic performance in the aged catalyst mixture.³⁹

We compiled the hydrocarbon conversion results in **Fig. 3a** (CO results in **Fig. S9**, full dataset in **Table S3**). We focused on T₉₀ values as near-complete conversion levels are typically required for industrial applications.² Both the aged Pt (290 °C) and Pd (302 °C) catalysts recorded considerably higher T₉₀ values than the aged mixture (218 °C). Critically, the enhancement in hydrocarbon conversion activity of the catalyst mixture post-aging was not observed in the separate catalysts and thus, is *not a simple additive effect from both individual catalysts but instead arising from the formation of a more active PtPd phase*.

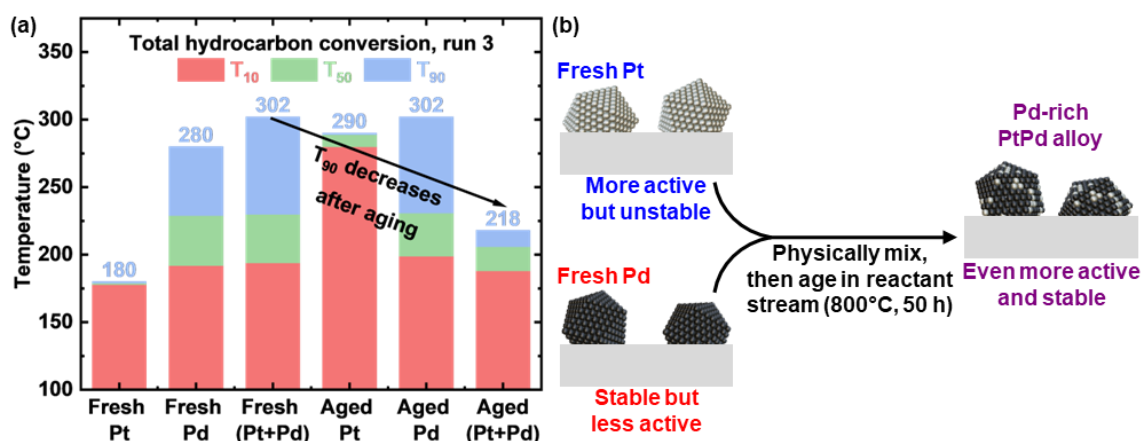


Fig. 3: Summary of catalytic results. (a) Temperature required to achieve 10% (T₁₀), 50% (T₅₀), and 90% (T₉₀) conversion of total hydrocarbons, using data from the third catalytic run. Pt/Al₂O₃, Pd/Al₂O₃, and the catalyst mixture are denoted as Pt, Pd, and (Pt+Pd), respectively. T₉₀ values are labelled in blue above each stacked bar. (b) A Pd-rich PtPd alloyed phase is formed after aging the catalyst mixture, leading to an appreciably lower T₉₀.

CONCLUSIONS

In summary, we employed the RCT method to produce partially embedded catalysts to inhibit surface-mediated NP sintering. Using a simple physical mixture of Pt/Al₂O₃ and Pd/Al₂O₃ RCT catalysts, we illustrate how the long-standing problem of Pt volatilization can be exploited to beneficially produce highly active and stable PtPd/Al₂O₃ catalysts (**Fig. 3b**), as validated using an industry-defined emission control test protocol. The alloyed PtPd/Al₂O₃ catalyst outperformed the fresh catalyst mixture and both individual catalysts for hydrocarbon conversion, while exhibiting high catalytic stability and SO₂ poisoning resistance. XPS revealed that the aging-induced alloying of the catalyst mixture preserved 50–60% of Pd in the more reactive metallic state, in contrast to the aged individual catalysts or fresh catalyst mixture that existed almost entirely in the less active PdO form. To further demonstrate the RCT method's flexibility and scalability,^{13,14} we also synthesized Pd/Al₂O₃ on cordierite monoliths used industrially (**Fig. S10**) through a modified RCT method.⁴⁰ We envision future

efforts to manipulate the catalyst mixing ratio or the alloying homogeneity to augment catalytic performance.^{25,26,37,39,41} Other opportunities include incorporating Pt, Pd, and Rh in a single RCT structure for three-way catalytic applications.

ASSOCIATED CONTENT

Supporting Information. Experimental section and additional experimental results.

DATA AVAILABILITY

Data from this study are available from the authors upon reasonable request.

AUTHOR CONTRIBUTIONS

K.R.G.L. and T.S. contributed equally to this work. K.R.G.L. and T.S. designed the experiments. T.S. and J.Alv designed and synthesized the materials. K.R.G.L. and T.S. characterized and analyzed the materials. T.J.T. designed and performed the catalytic tests. T.J.T. and K.R.G.L. analyzed the catalytic data. K.R.G.L. analyzed the entire set of results and wrote the manuscript with input from all authors. M.A. and J.Aiz supervised the entire work. All authors have given approval to the final version of the manuscript.

COMPETING INTERESTS

The authors declare no competing financial interests.

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