

Research Highlight

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Nano shielder of rare-earth metal oxide overlay promotes ultra-stable H₂ production on Pt/ γ -Mo₂N

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The utilization of highly reactive supports in constructing supported-metal catalysts is a promising choice for achieving efficient heterogeneous catalysis in chemical industries^[1], including the H₂ production from the methanol-reforming reaction (MRR), the water-gas shift (WGS), *etc.* Specifically, the support with a high reactivity could promote reactants adsorption-activation by offering additional catalytic sites, and shift the catalysis from a competitive adsorption-activation mechanism over supported-metal catalysts to a non-competitive model owing to the formation of the metal-support interfacial sites^[2]. This substantial alteration in catalytic pathways could unlock unparalleled reactivity with a superior catalytic performance^[3]. For example, as for Pt/ α -MoC proposed by Lin *et al.* in MRR, the reactive α -MoC support shows high water-dissociation activity, and could produce abundant surface -OH groups for the MRR^[4]. In comparison to the common Pt/ β -MoC (i.e., a competitive adsorption-activation between methanol and water on the Pt site), Pt/ α -MoC has two types of reactive site for the adsorption-activation of methanol and water, respectively (i.e., Pt is for the methanol adsorption/activation, while α -MoC is for the water dissociation). It induces an MRR at the interfacial sites of Pt/ α -MoC, offering an average turnover frequency (average TOF, ATOF) of $1.805 \times 10^4 \text{ h}^{-1}$ to the H₂ productivity over 0.2 wt% Pt/ α -MoC at 150-190 °C.



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Beyond achieving superior activity with excellent selectivity, enhancing the durability of a catalyst is one of the most challenging and crucial objectives in catalyst design, especially for supported-metal catalysts with highly reactive support, as the possible metal sintering and reactive support deterioration intensively shorten their lifespan^[5,6]. Currently, the problem of metal sintering can be well-solved by introducing a strong metal-support interaction effect that stabilizes metal species on the surface of support^[7,8]. However, it is worth noting that the deterioration of reactive support has not been well-resolved. It seriously damages the active metal-support interfacial sites, leading to a reversion from the previously constructed non-competitive mechanism to a competitive adsorption-activation model. For example, highly dispersed Pt on α -MoC and/or γ -Mo₂N catalysts are well-known for their exceptional activities in the field of H₂ production from low-temperature MRR and WGS reaction, owing to the excellent H₂O dissociation activity of α -MoC and γ -Mo₂N^[4]. However, the methanol conversion over Pt/ α -MoC dramatically declines by 62% within 11 h, which is caused by a damage of α -MoC crystal structure from the deep oxidation during water dissociation^[4]. It indicates that the protection of vulnerable crystal structure of highly reactivity supports (e.g., α -MoC) is significant. Even though Zhang *et al.* proposed a strategy of crowding Pt on α -MoC to keep partial H₂O reactant away from the surface of α -MoC and obtained improved catalytic stability remaining ~70% in about 260 h of reaction, the deactivation of Pt/ α -MoC reveals that such strategy cannot eliminate the decomposition of highly reactive α -MoC support^[9]. Therefore, a new strategy that enhances the stability of highly reactive support towards a practical application of such catalysts, while maintaining their superior activity and selectivity, is highly desired, however, with a great challenge and rare exploration.

Recently, Gao *et al.* filled some of these gaps by proposing a novel and universal strategy, which shields a partial surface of reactive support by constructing an inert nano-overlays that acts as a “nano shielder” to keep the reactive support away from deterioration, without a negative effect on the catalytic activity of metal/support interfaces^[10]. The superiority of this new strategy was fully displayed by using an interfacial catalyst of Pt/ γ -Mo₂N in the H₂ production from the probe reaction of MRR, which performs a non-competitive adsorption-activation between water and methanol over Pt/ γ -Mo₂N [Figure 1A]. In detail, a lanthanum (La) oxide nano-overlay was immobilized on γ -Mo₂N by the following procedure: (1) La₂O₃ and MoO₃ are mechanically mixed and calcined in a muffle furnace at 500 °C for 10 h; (2) a nitridation treatment is performed on the obtained sample in NH₃ (flow rate: 200 mL·min⁻¹) under a temperature program from room temperature to 350 °C (rate: 10 °C·min⁻¹), then to 450 °C (rate: 0.5 °C·min⁻¹), then to 785 °C (rate: 2 °C·min⁻¹) and staying at 785 °C for 4 h, finally cooling down to room temperature with a passivation in 0.5% O₂/Ar (flow rate: 60 mL·min⁻¹) overnight to obtain La- γ -Mo₂N (labeled as La-Mo₂N). After that, Pt was loaded on to La-Mo₂N by a simple impregnation method (Pt/La-Mo₂N). They reported that the “nano shielder” of La oxide promotes an efficient and robust performance for H₂ production over Pt/La-Mo₂N, with an ATOF of 1 wt% Pt / 2 wt% La-MoN (1Pt/2La-Mo₂N) maintaining above $7 \times 10^3 \text{ mol}_{\text{H}_2} \cdot \text{mol}_{\text{metal}}^{-1} \cdot \text{h}^{-1}$ (i.e., turnover number, TON, of $1.028 \times 10^7 \text{ mol}_{\text{H}_2} \cdot \text{mol}_{\text{metal}}^{-1}$) at 200 °C after above 1,300 h of reaction, 5 times higher than that of 1 wt% Pt/ γ -Mo₂N [Figure 1B]. Remarkably, lowering Pt to mere 0.26 wt% with a 5 wt% of La, 0.26Pt/5La-Mo₂N shows a record-high TOF of $2.45 \times 10^5 \text{ mol}_{\text{H}_2} \cdot \text{mol}_{\text{metal}}^{-1} \cdot \text{h}^{-1}$ (i.e., TON of $1.53 \times 10^7 \text{ mol}_{\text{H}_2} \cdot \text{mol}_{\text{metal}}^{-1}$). The superior H₂ producibility with an excellent long-term stability over Pt/La-Mo₂N reveals the success of such nano shielding strategy.

A key finding of this work is the identification of the significant role of rare-earth La oxide nano-overlays that act as a shielder for protecting Pt/ γ -Mo₂N^[10]. They conclude three main functions: (1) partially cover the surface sites of γ -Mo₂N and prevent the crystal structure of γ -Mo₂N from the deterioration caused by the adsorption of excessive water, without a negative effect on the instinct water dissociation activity of the residual surface sites on γ -Mo₂N [Figure 1C]; (2) separate the γ -Mo₂N surface into isolated areas that settle the interface between Pt and γ -Mo₂N [Figure 1A]; and (3) prevent the platinum aggregation during catalytic

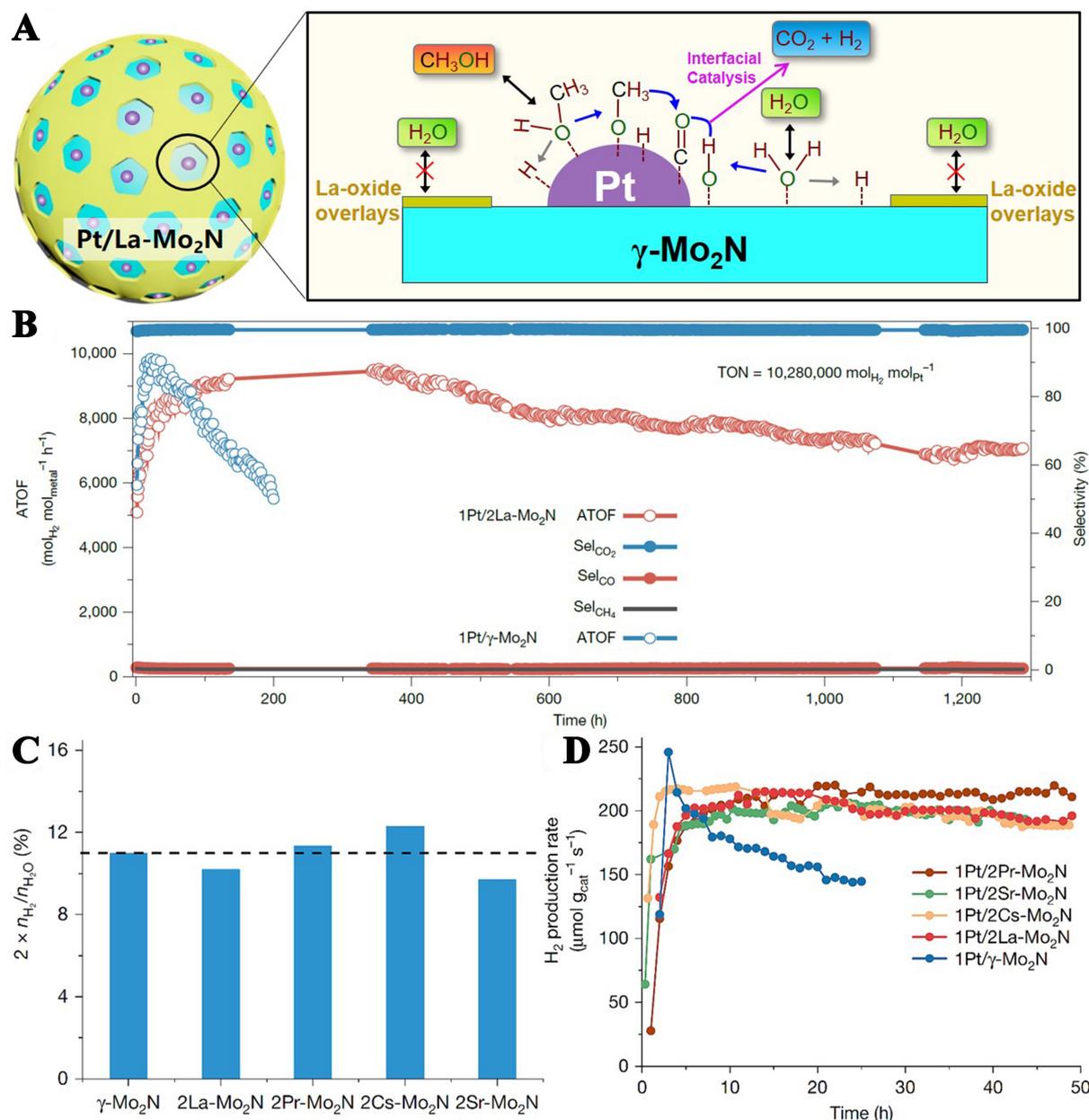


Figure 1. (A) Schematic diagram of the non-competitive adsorption-activation mechanism in the MRR over Pt/La-Mo₂N; (B) Catalytic stability test of the 1Pt/γ-Mo₂N and 1Pt/2La-Mo₂N catalysts under 200 °C, 5 bar and WHSV of 12.87 h⁻¹[10]; (C) Twice the ratio of H₂ production/H₂O consumption acquired in H₂O TKA experiments at 100 °C and (D) MRR catalytic activity under 250 °C, 10 bar and WHSV of 25.74 h⁻¹ over the γ-Mo₂N and 2M-Mo₂N (M = La, Pr, Cs and Sr) catalysts[10]. MRR: Methanol-reforming reaction; WHSV: weight-hourly space velocity.

reaction. More importantly, the wide suitability of the proposed strategy by constructing “nano shielder” for enhancing the catalytic performance of Pt/γ-Mo₂N was also verified by using various catalytically inert elements (i.e., Y, Pr, Ho, Ca, Sr, and Cs). All the catalysts with various of additives (i.e., 1Pt/2Pr-Mo₂N, 1Pt/2Sr-Mo₂N, 1Pt/2Cs-Mo₂N) have a similar H₂ production rate as that of 1Pt/2La-Mo₂N and 1Pt/γ-Mo₂N (~200 μmol·g_{cat}⁻¹·s⁻¹ in Figure 1D). However, they both show a constant H₂ production rate (i.e., ~200 μmol·g_{cat}⁻¹·s⁻¹) after over 50 h of reaction, similar to that of Pt/La-Mo₂N, but much superior to that of 1Pt/γ-Mo₂N (i.e., below 150 μmol·g_{cat}⁻¹·s⁻¹ after 25 h of reaction).

As conclusions and perspectives, Gao *et al.* innovate a powerful and universal strategy of “nano shielder” for stabilizing the active metal-support interfacial sites in Pt/ γ -Mo₂N catalyst by introducing rare-earth La oxide overlays, reaching a record-high catalytic activity owing to the substantial alteration in reaction pathways following a non-competitive mechanism model^[10]. However, several questions remain open. A key area for further investigation is elucidating the universality of such “nano shielder” in alternative highly reactive supports, other than MoC and Mo₂N. Besides that, the metal-support interfacial sites need to be deeply explored, such as (1) the practical dimension of the isolated area segmented by the dispersion of La oxides nano-overlays on γ -Mo₂N; (2) no electronic interaction between Pt and La species is simply concluded from the Pt4f XPS analysis, exploration on the state Pt in Pt/La-Mo₂N (e.g., the X-ray absorption spectroscopy, CO-DRIFT), and on the mechanism of such no electronic interaction behavior on La-Mo₂N surface (e.g., selectively electrostatic adsorption of Pt onto Mo₂N, rather than La oxides nano-overlays, during impregnation synthesis) may show a great attractive in future study. More interestingly, the proposed non-competitive mechanism model may also be suitable for the catalyst design in catalysis involving multi-molecule reactions, such as butadiene semi-hydrogenation. All these questions are required to be addressed in future studies to set up the way for its further application to design effective and stable heterogeneous catalysts.

DECLARATIONS

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Authors' contributions

Made contributions to the conception and design of the study: Wang, Z.; Su, B. L.

Data acquisition and administrative, technical, and material support are equally provided by: Hong, Y.; Cheng, B. C.; Liu, S. L.; Wang, Z.

Availability of data and materials

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Conflicts of interest

Su, B. L. is Editor in Chief of the journal *Chemical Synthesis*. Su, B. L. was not involved in any steps of editorial processing, notably including reviewers' selection, manuscript handling, or decision-making. The other authors declare that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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