

Research Highlight

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# Nano shielder of rare-earth metal oxide overlay promotes ultra-stable H<sub>2</sub> production on Pt/ $\gamma$ -Mo<sub>2</sub>N

Zhao Wang<sup>1,\*</sup> , Ying Hong<sup>1</sup>, Bin-Can Cheng<sup>1</sup>, Shu-Lin Liu<sup>1</sup>, Bao-Lian Su<sup>1,2,\*</sup>

<sup>1</sup>The State Key Laboratory of Advanced Technology for Material Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, China.

<sup>2</sup>Laboratory of Inorganic Materials Chemistry (CMI), University of Namur, Namur B-5000, Belgium.

**\*Correspondence to:** Prof. Zhao Wang, the State Key Laboratory of Advanced Technology for Material Synthesis and Processing, Wuhan University of Technology, NO. 122, Luoshi Road, Hongshan District, Wuhan 430070, Hubei, China. E-mail: zhao.wang@whut.edu.cn; Prof. Bao-Lian Su, Laboratory of Inorganic Materials Chemistry (CMI), University of Namur, NO. 61, Rue de Bruxelles, Namur B-5000, Belgium. E-mail: bao-lian.su@unamur.be

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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<sup>[1]</sup>, including the H<sub>2</sub> 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<sup>[2]</sup>. This substantial alteration in catalytic pathways could unlock unparalleled reactivity with a superior catalytic performance<sup>[3]</sup>. For example, as for Pt/ $\alpha$ -MoC proposed by Lin *et al.* in MRR, the reactive  $\alpha$ -MoC support shows high water-dissociation activity, and could produce abundant surface -OH groups for the MRR<sup>[4]</sup>. In comparison to the common Pt/ $\beta$ -MoC (i.e., a competitive adsorption-activation between methanol and water on the Pt site), Pt/ $\alpha$ -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  $\alpha$ -MoC is for the water dissociation). It induces an MRR at the interfacial sites of Pt/ $\alpha$ -MoC, offering an average turnover frequency (average TOF, ATOF) of  $1.805 \times 10^4 \text{ h}^{-1}$  to the H<sub>2</sub> productivity over 0.2 wt% Pt/ $\alpha$ -MoC at 150-190 °C.



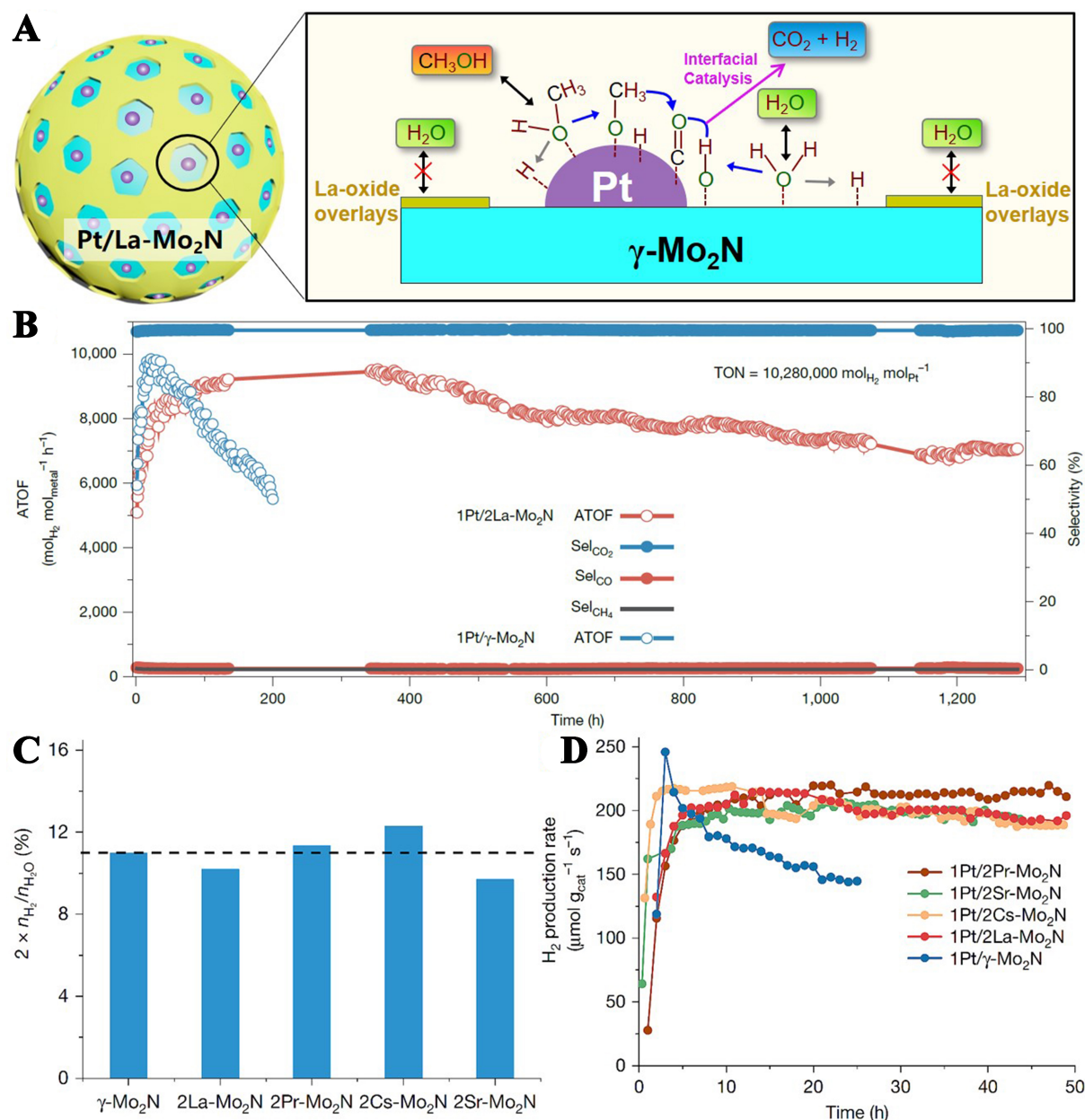
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Beyond achieving superior activity with excellent selectivity, enhancing the durability of a catalyst is one of the most challenging and crucial objectives in catalyst design, especially for supported-metal catalysts with highly reactive support, as the possible metal sintering and reactive support deterioration intensively shorten their lifespan<sup>[5,6]</sup>. 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<sup>[7,8]</sup>. 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  $\alpha$ -MoC and/or  $\gamma$ -Mo<sub>2</sub>N catalysts are well-known for their exceptional activities in the field of H<sub>2</sub> production from low-temperature MRR and WGS reaction, owing to the excellent H<sub>2</sub>O dissociation activity of  $\alpha$ -MoC and  $\gamma$ -Mo<sub>2</sub>N<sup>[4]</sup>. However, the methanol conversion over Pt/ $\alpha$ -MoC dramatically declines by 62% within 11 h, which is caused by a damage of  $\alpha$ -MoC crystal structure from the deep oxidation during water dissociation<sup>[4]</sup>. It indicates that the protection of vulnerable crystal structure of highly reactivity supports (e.g.,  $\alpha$ -MoC) is significant. Even though Zhang *et al.* proposed a strategy of crowding Pt on  $\alpha$ -MoC to keep partial H<sub>2</sub>O reactant away from the surface of  $\alpha$ -MoC and obtained improved catalytic stability remaining ~70% in about 260 h of reaction, the deactivation of Pt/ $\alpha$ -MoC reveals that such strategy cannot eliminate the decomposition of highly reactive  $\alpha$ -MoC support<sup>[9]</sup>. 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<sup>[10]</sup>. The superiority of this new strategy was fully displayed by using an interfacial catalyst of Pt/ $\gamma$ -Mo<sub>2</sub>N in the H<sub>2</sub> production from the probe reaction of MRR, which performs a non-competitive adsorption-activation between water and methanol over Pt/ $\gamma$ -Mo<sub>2</sub>N [Figure 1A]. In detail, a lanthanum (La) oxide nano-overlay was immobilized on  $\gamma$ -Mo<sub>2</sub>N by the following procedure: (1) La<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub> 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 NH<sub>3</sub> (flow rate: 200 mL·min<sup>-1</sup>) under a temperature program from room temperature to 350 °C (rate: 10 °C·min<sup>-1</sup>), then to 450 °C (rate: 0.5 °C·min<sup>-1</sup>), then to 785 °C (rate: 2 °C·min<sup>-1</sup>) and staying at 785 °C for 4 h, finally cooling down to room temperature with a passivation in 0.5% O<sub>2</sub>/Ar (flow rate: 60 mL·min<sup>-1</sup>) overnight to obtain La- $\gamma$ -Mo<sub>2</sub>N (labeled as La-Mo<sub>2</sub>N). After that, Pt was loaded on to La-Mo<sub>2</sub>N by a simple impregnation method (Pt/La-Mo<sub>2</sub>N). They reported that the “nano shielder” of La oxide promotes an efficient and robust performance for H<sub>2</sub> production over Pt/La-Mo<sub>2</sub>N, with an ATOF of 1 wt% Pt / 2 wt% La-MoN (1Pt/2La-Mo<sub>2</sub>N) 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/ $\gamma$ -Mo<sub>2</sub>N [Figure 1B]. Remarkably, lowering Pt to mere 0.26 wt% with a 5 wt% of La, 0.26Pt/5La-Mo<sub>2</sub>N 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 H<sub>2</sub> producibility with an excellent long-term stability over Pt/La-Mo<sub>2</sub>N 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/ $\gamma$ -Mo<sub>2</sub>N<sup>[10]</sup>. They conclude three main functions: (1) partially cover the surface sites of  $\gamma$ -Mo<sub>2</sub>N and prevent the crystal structure of  $\gamma$ -Mo<sub>2</sub>N 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  $\gamma$ -Mo<sub>2</sub>N [Figure 1C]; (2) separate the  $\gamma$ -Mo<sub>2</sub>N surface into isolated areas that settle the interface between Pt and  $\gamma$ -Mo<sub>2</sub>N [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-Mo<sub>2</sub>N; (B) Catalytic stability test of the 1Pt/γ-Mo<sub>2</sub>N and 1Pt/2La-Mo<sub>2</sub>N catalysts under 200 °C, 5 bar and WHSV of 12.87 h<sup>-1</sup><sup>[10]</sup>; (C) Twice the ratio of H<sub>2</sub> production/H<sub>2</sub>O consumption acquired in H<sub>2</sub>O TKA experiments at 100 °C and (D) MRR catalytic activity under 250 °C, 10 bar and WHSV of 25.74 h<sup>-1</sup> over the γ-Mo<sub>2</sub>N and 2M-Mo<sub>2</sub>N (M = La, Pr, Cs and Sr) catalysts<sup>[10]</sup>. 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-Mo<sub>2</sub>N 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-Mo<sub>2</sub>N, 1Pt/2Sr-Mo<sub>2</sub>N, 1Pt/2Cs-Mo<sub>2</sub>N) have a similar H<sub>2</sub> production rate as that of 1Pt/2La-Mo<sub>2</sub>N and 1Pt/γ-Mo<sub>2</sub>N (~200 μmol·g<sub>cat</sub><sup>-1</sup>·s<sup>-1</sup> in Figure 1D). However, they both show a constant H<sub>2</sub> production rate (i.e., ~200 μmol·g<sub>cat</sub><sup>-1</sup>·s<sup>-1</sup>) after over 50 h of reaction, similar to that of Pt/La-Mo<sub>2</sub>N, but much superior to that of 1Pt/γ-Mo<sub>2</sub>N (i.e., below 150 μmol·g<sub>cat</sub><sup>-1</sup>·s<sup>-1</sup> 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/ $\gamma$ -Mo<sub>2</sub>N 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<sup>[10]</sup>. 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 Mo<sub>2</sub>N. 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  $\gamma$ -Mo<sub>2</sub>N; (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-Mo<sub>2</sub>N (e.g., the X-ray absorption spectroscopy, CO-DRIFT), and on the mechanism of such no electronic interaction behavior on La-Mo<sub>2</sub>N surface (e.g., selectively electrostatic adsorption of Pt onto Mo<sub>2</sub>N, 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

Not applicable.

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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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Zhao Wang

Zhao Wang received his B.S. degree from Anhui University of Science and Technology in 2010 and earned his Ph.D. from Université Pierre et Marie Curie (Paris, France) in 2017. From 2018 to 2019, he conducted postdoctoral research with Professor Bao-Lian Su, focusing on hierarchically porous materials. Since 2020, he has been serving as an Associate Professor at the State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology. His research interests include the development of hierarchically porous materials, catalysis, and energy conversion technologies.



Ying Hong

Ying Hong obtained her B.Sc. from China Three Gorges University in 2023 and is currently pursuing postgraduate studies under the supervision of Dr. Wang. Her research centers on the design and fabrication of hierarchically porous metal catalysts.

**Bin-Can Cheng**

Bin-Can Cheng received his B.Sc. from Hubei University in 2024. He is currently a postgraduate student in Dr. Wang's research group, with a focus on photocatalytic selective hydrogenation.

**Shu-Lin Liu**

Shu-Lin Liu earned her Bachelor of Engineering degree from Jilin Normal University of Engineering and Technology in 2019. In 2023, she joined Dr. Wang's research team, where she is engaged in the design and construction of single-atom alloy catalysts for hydrogenation processes relevant to the petrochemical industry.

**Bao-Lian Su**

Bao-Lian Su is a distinguished member of the European Academy of Sciences and the Royal Academy of Belgium, a Fellow of the Royal Society of Chemistry, and a life member of Clare Hall, University of Cambridge. He holds the prestigious "Chaire Francqui au titre Belge". Professor Su is a full professor and Director of the Laboratory of Inorganic Materials Chemistry (CMI) at the University of Namur, Belgium. He also serves as a "Strategical Scientist" at Wuhan University of Technology. His multidisciplinary research covers the synthesis, characterization, and molecular engineering of organized, hierarchically porous, and bioinspired materials. His expertise spans biomaterials, living and leaflike materials, nanostructures, and the immobilization of living organisms for applications in artificial photosynthesis, nanotechnology, biotechnology, cell therapy, and biomedicine.