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A Smart Design of Non-Noble Catalysts for Sustainable Propane Dehydrogenation

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Abstract: Propane dehydrogenation (PDH), an important process for propylene synthesis, relies on expensive noble metals or highly toxic oxides as catalysts. In a recent publication in Science, Gong and coworkers report a breakthrough discovery for PDH by introducing a sustainable catalyst composed of titanium oxide overlayers encapsulating nickel nanoparticles, termed Ni@TiO_x. This innovative catalyst showcases exceptional performance in PDH, exhibiting high propylene selectivity and stability under industrially relevant conditions. The study elucidates the role of defective TiO_x overlayers and the electronic promotional effect of subsurface Ni in enhancing catalytic activity, translating a traditional model catalyst system into a sustainable industrial catalyst for low-carbon energy and the chemical industry.

Introduction

Propane dehydrogenation (PDH) is a crucial process in the production of propylene, an essential building block for the petrochemical industry^[1]. This endothermic reaction typically occurs in the presence of a catalyst at high temperatures ranging from 500 to 700 °C. Traditional catalysts for PDH primarily involve noble metals, such as platinum (Pt)^[2] and highly toxic chromium oxides (CrO_x)^[3], which, despite their effectiveness, are associated with high costs and environmental concerns. Additionally, the use of these systems is often compromised by issues such as carbon deposition and catalyst deactivation. Achieving a balance between catalytic efficiency, cost-effectiveness, and environmental sustainability remains a significant challenge^[4].

In a recent cover story published in Science, Gong and coworkers^[5] made a breakthrough in sustainable catalysis for PDH. An ordinarily less-active oxide, titanium oxide (TiO₂) can be assembled with earth-abundant metallic nickel (Ni) to form an extraordinary Ni@TiO_x catalyst with enhanced performance (Figure 1). Metallic Ni-based catalysts show a high C-C cleavage capability, which is tendentious to induce methane production and coke deposition^[6]. This leads to poor selectivity and rapid deactivation. Compared to conventional systems, the Ni@TiO_x catalyst demonstrated a high initial selectivity for propylene and maintained near 94% selectivity with a high propane conversion rate. Long-term stability tests confirmed the durability of Ni@TiO_x, with consistent propylene selectivity over extended periods.

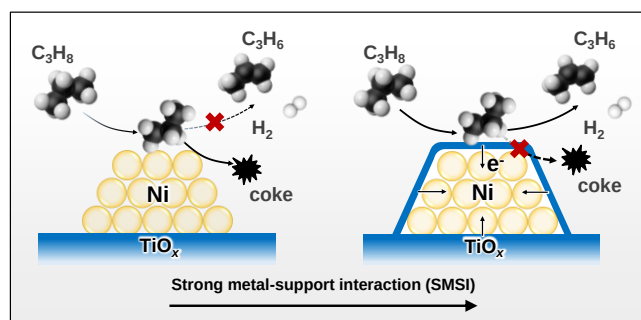


Figure 1. Schematic illustration of Ni/TiO_x and Ni@TiO_x for PDH.

Characterization using in situ CO-DRIFTS, environmental transmission electron microscopy (ETEM), and electron energy loss spectroscopy (EELS) confirmed the formation of TiO_x overlayers encapsulating Ni nanoparticles (NPs). Specifically, the coverage degree of TiO_x on Ni NPs can be gradually increased by increasing the hydrogen reduction temperatures, attributed to the enhanced metal-support interaction under elevated temperatures. Temperatures in excess of 550 °C were required to achieve complete encapsulation of Ni NPs. Additionally, Gong and coworkers demonstrated the generality of this strategy for other catalytic systems by replacing Ni with copper (Cu) or TiO_x with zinc oxide (ZnO). These analogues exhibited similar encapsulation behavior and improved catalytic performance, inspiring the possibility of utilizing this design strategy for PDH along with other industrially relevant catalytic processes.

Furthermore, Gong and coworkers have provided mechanistic insights into the role of TiO_x overlayers and subsurface Ni NPs. In situ Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and extended X-ray absorption fine structure (EXAFS) analyses revealed that the TiO_x overlayer underwent significant electronic modifications upon reduction at different temperatures. The TiO_x overlayer, characterized by tetracoordinated Ti₄C sites with oxygen vacancies (O_v), was identified as the active site for PDH, while the subsurface Ni NPs served as electronic promoters, facilitating C–H bond activation and H₂ desorption on the TiO_x overlayer. Furthermore, the density functional theory (DFT) calculations also verified the superior activity of Ni@TiO_x in C–H bond activation, attributed to the demonstrated upshift of the projected density of states for d-bands of surface Ti and p-bands of surface O atoms relative to fermi level.

We propose that through the precise design and fine-tuning of catalysts, it is possible to achieve remarkable and unexpected

improvements in performance^[7]. For instance, we recently reported a novel strategy to overcome the limitations of traditional bimetallic alloy catalysts in alcohol oxidation^[8]. By spatially separating gold and palladium components in carbon-supported catalysts, significantly increased reaction rates were achieved compared with those observed with alloyed catalysts. This enhancement is driven by a cooperative redox effect, where isolated gold and palladium sites engage in synergistic redox process. Similarly, the discovery by Gong and coworkers is conceptually novel, not only enhancing our understanding of catalyst behavior but also paving the way for designing more efficient catalysts for a wide range of chemical reactions.

In summary, the study from Gong and coworkers opens the way for sustainable catalysis by combining conventionally less-active titanium oxide with metallic nickel to form a defective TiO_x overlayer encapsulated Ni@TiO_x catalyst for industrial catalysis. Compared with current commercial PDH catalysts, the Ni@TiO_x catalyst exhibits lower deactivation rates, and also benefits from reduced costs and decreased environmental impacts. This strategy represents a significant advancement in developing sustainable catalysts and poses an effective low-carbon pathway for olefin synthesis. The potential impact of this breakthrough could inspire further research and innovation in the field of sustainable catalyst design, ultimately leading to a more sustainable chemical industry. Future research could build on these findings to assess the broader applications of metal@oxide catalysts in industrial settings.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgements

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Keywords: Propane dehydrogenation • Hydrogen induction • Defective TiO_x overlayers • Ni@TiO_x catalyst

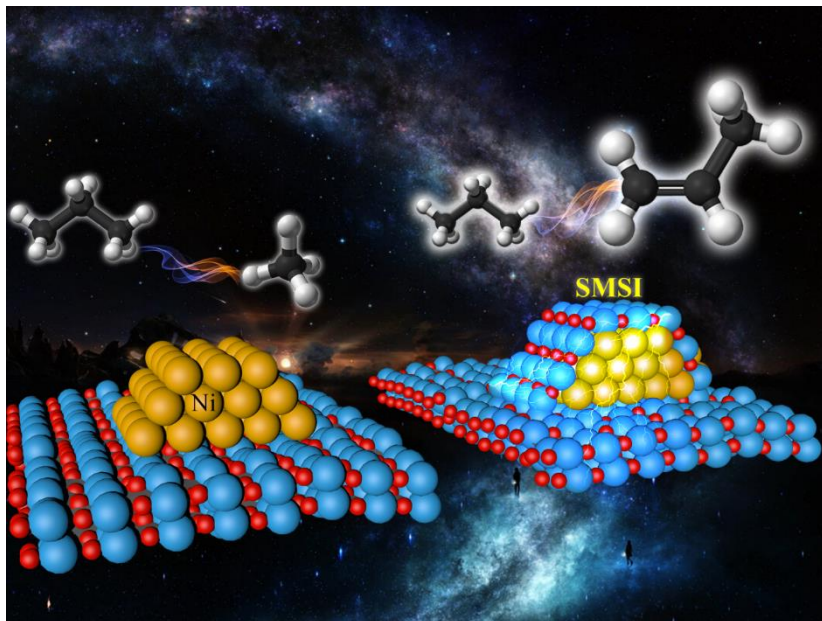
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This paper highlights a smart sustainable Ni@TiO_x catalyst, Ni encapsulated in TiO_x, for propane dehydrogenation (PDH), as reported by Gong and coworkers. The catalyst demonstrates exceptional performance in PDH, achieving 94% propylene selectivity and high stability. This design offers a cost-effective and environmentally friendly alternative to traditional noble metal-based catalysts, with potential for broader industrial applications.