ABSTRACT:

Synergistic Active Centres in Ru–Pyrochlore Catalysts for Highly Efficient COx-free H_2 Production from Ammonia Decomposition: From Catalyst Design to Performance in Structured Catalytic Architectures

C. Italiano, D. Maccarrone, M. Thomas, G. Marino, A. Vita
Institute of Advanced Energy Technologies" Nicola Giordano"
(CNR-ITAE), 98126, Messina, Italy.

Ammonia is widely recognized as a carbon-free, high-density H2 carrier, offering an effective route for the storage and long-distance transport of renewable hydrogen. However, ammonia synthesis and cracking are the main cost drivers of the NH3-based H2 value chain, and large-scale NH_3 decomposition still requires significant process intensification. In this context, the present study investigates Ru/pyrochlore-type oxides (A2B2O7) as promising catalysts for ammonia decomposition and explores their integration into Periodic Open Cellular Structured (POCS), aiming to enhance heat and mass transfer and improve the overall efficiency of the ammonia cracking process in compact reactors. A series of La2CexZr1-xO7 pyrochlores ($0 \leq x \leq 1.5$) were synthesized via a sol–gel combustion method and subsequently loaded with 2 wt% Ru by wetness impregnation. Comprehensive characterisation by N2 physisorption, XRD, H2-TPR, CO_2-TPD, CO chemisorption, TEM, and in situ DRIFTS revealed that the adaptable crystal framework, high thermal stability, tunable redox and acid–base properties, and strong metal–support interactions of pyrochlores synergistically contribute to enhancing key surface reactions. The Catalytic activity (P = 1 atm, T = 300 – 500 °C, NH3 Feed = 25%, WSV = 60,000 $NmL^3 g^{-1} h^{-1}$) demonstrates that the Ce-Zr combination (1:1) in the structure outperforms other compositions, achieving a total NH3 conversion at 475°C. The most promising catalyst (2wt.%Ru/La2CeZrO7) was subsequently integrated into POCS with a gyroid architecture via a tailored coating procedure. The resulting structured catalysts exhibited improved heat distribution and enhanced gas–solid contact, enabling stable operation at higher WSV and significantly increasing hydrogen productivity within a relatively compact catalytic volume.

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