

Rational Design of Ni-Mo₂N Nitrogen Carriers for Chemical Looping Ammonia Synthesis

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Abstract

Chemical looping ammonia synthesis (CLAS) has emerged as a promising green ammonia production technology, demonstrating significant potential in the field of decentralized ammonia synthesis. Although early transition metal-based nitrogen carriers have shown encouraging prospects in CLAS, their practical application has been persistently constrained by the inherent limitations of lattice nitrogen conversion and insufficient NH₃ selectivity. Herein, we design an efficient Ni-Mo₂N composite nitrogen carrier synthesized via a one-step pyrolysis strategy. The optimized 25% Ni-Mo₂N (molar ratio) system achieves an outstanding lattice nitrogen conversion of 76%. Ni-Mo₂N exhibits a remarkable initial ammonia yield of 9,050 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, three times higher than that of pristine Mo₂N. Critically, the incorporation of Ni effectively suppresses the formation of the inactive Mo₂C phase during pyrolysis, ensuring that the Mo species exist exclusively as metallic Mo and the active Mo₂N phase. This structural integrity endows the catalyst with excellent stability over 10 consecutive cycles, delivering an average ammonia production rate of 451 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, a 4.5-fold enhancement compared with pristine Mo₂N. Systematic characterization combined with density functional theory (DFT) calculations elucidates the CLAS reaction pathway on the Ni-Mo₂N surface and reveals a pronounced synergistic interaction between Ni clusters and Mo₂N. Specifically, Ni sites act as hydrogen activation centers, adsorbing and dissociating H₂ into reactive H* species, which subsequently undergo spontaneous spillover onto adjacent Mo₂N surfaces and cooperatively activate lattice nitrogen species for efficient ammonia formation. Collectively, this work establishes a solid foundation for the rational design of advanced transition-metal nitrogen carriers and offers fresh theoretical and methodological perspectives for developing high-performance CLAS systems.

Keywords

Chemical Looping, Ni-Mo₂N, Nitrogen Carrier, Lattice Nitrogen Conversion, Ammonia Synthesis, Transition Metal Nitride