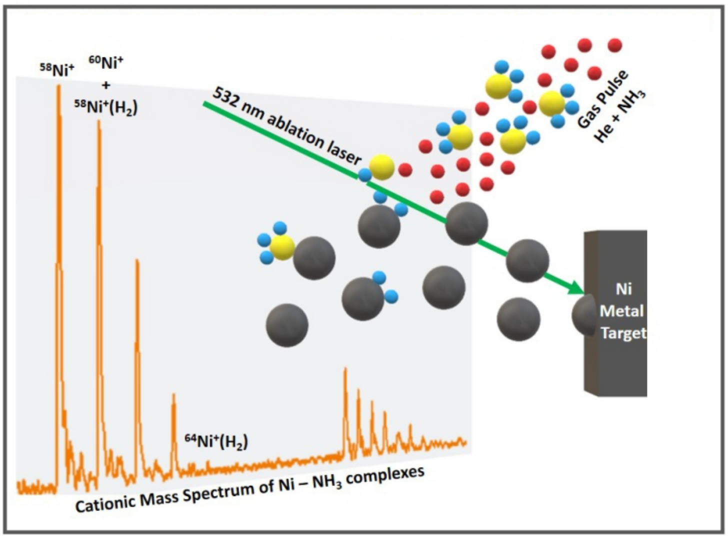
Designing of Efficient Catalysts

Ammonia Activation and Nitride Formation Pathways in Transition Metal Clusters



Ammonia activation by transition metal clusters, linking chemistry to hydrogen energy.

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This study provides new mechanistic insights into the pathways of ammonia activation and transition metal nitride formation at the nanoscale. The results not only enhance fundamental understanding of cluster reactivity but also offer guiding principles for the rational design of efficient catalysts for hydrogen production and nitrogen cycle processes.

The figure displayed at the top depicts the reaction products of a few transition metal clusters (V, Ti, Ni, Co, & Fe) with NH_3 gas in a laser vaporization source.

Ammonia (NH_3) is a key hydrogen carrier and a vital feedstock for fertilizers, yet its decomposition and activation pathways remain challenging in catalysis. Transition metal (TM) nitrides have recently emerged as promising alternatives to noble-metal catalysts, offering high activity, stability, and lower cost. To gain atomistic insights into ammonia activation, a combined experimental and theoretical study was carried out at the Atomic and Molecular Physics Division, BARC.

In this work, laser-vaporized clusters of Ti, V, Fe, Co, and Ni were generated and their reactions with ammonia were investigated using reflectron time-of-flight mass spectrometry (ReTOFMS). Complementary density functional theory (DFT) calculations were employed to unravel the underlying reaction pathways.

Distinct metal-specific trends were observed. Titanium clusters readily form extended nitride series $(TiN)_n$, whereas vanadium and iron clusters predominantly yield mononitrides, with size-dependent efficiency of NH_3 dehydrogenation. Cobalt clusters exhibit limited reactivity, primarily through ammonia adsorption and partial dehydrogenation. In contrast, nickel clusters show unique behavior—forming stable solvated nitride/imide complexes and even releasing molecular hydrogen (H_2) via Ni^+ hydrogenation pathways. Theoretical calculations validated the experimental findings, highlighting the role of cluster size, charge state, and electronic structure in governing N–H bond activation and hydrogen evolution.

Reference:

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