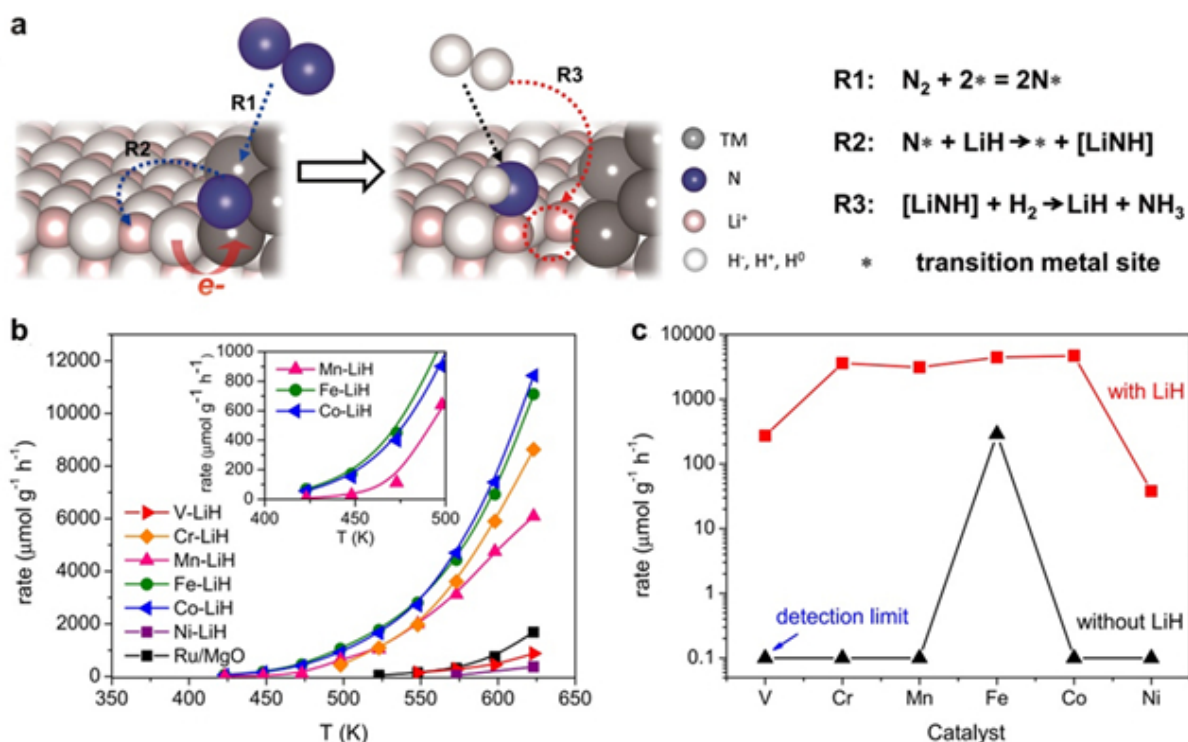


LiH mediates low-temperature ammonia synthesis

August 24 2016



Mechanistic proposal for the relayed two-active center catalysis of the TM-LiH system (a) and the catalytic performances of 3d TM-LiH composite catalysts (b and c). Credit: Guo Jianping, Chen Ping

Nearly half of the world's population is fed by industrial N₂ fixation, i. e., the Harbor-Bosch process. Although exergonic in nature, NH₃ synthesis from N₂ and H₂ catalyzed by the fused Fe has to be conducted

at elevated temperatures and high pressures. It consumes over 1 percent of the world's annual energy supply. Developing efficient catalysts that enable NH_3 synthesis under mild conditions is a grand scientific challenge and is of great practical need.

The ideal catalyst for NH_3 [synthesis](#) should have strong activation to N_2 (small activation energy E_a) but relatively weak binding to the activated N species (small E_N), which is, unfortunately, unattainable by transition metals (TM) themselves because of the linear scaling relations between E_a and E_N , i.e., a transition metal catalyst having strong activation to N_2 will have strong binding to the activated N, and vice versa. Such relations determine the rate of NH_3 synthesis over the TM catalyst, and therefore, although tremendous research efforts have been applied, the industrial catalyst used today is essentially the same as the original one developed by Mittasch in 1909.

The Dalian Institute of Chemical Physics (DICP) research group led by Prof. CHEN Ping demonstrates, for the first time, that the scaling relations on catalytic NH_3 synthesis can be broken. Thus, NH_3 synthesis under mild reaction conditions can be achieved at an unprecedentedly high rate over a new set of catalysts.

The key element leading to this change is the employment of ionic hydride LiH . Distinctly different from proton or atomic H applied in biochemical, organometallic, and heterogeneous NH_3 formation, H in LiH bears a negative charge that ensures that LiH is a strong reducing agent breaking the TM-N bond, and an immediate H source abstracting N to Li to form LiNH_2 . LiNH_2 can further split H_2 , heterolytically giving off NH_3 and regenerating LiH . Through this mechanism (See Figure a), the activation of N_2 and the subsequent hydrogenation of N are carried out separately over the two reactive centers, i.e., TM and LiH , respectively, so that the direct influence of TM on the NH_3 formation rate is broken.

Such a "relayed" two-active center catalysis enables the 3d TM(N)-LiH composites (3d TM spread from V to Ni) universal and unprecedentedly high NH₃ synthesis activities. The DICP researchers found that, at 573 K, their activities are at least four (Cr-, Mn- and Co-LiH), three (V-LiH), two (Ni-LiH), and one (Fe-LiH) order of magnitude higher than the corresponding neat or supported TM(N) (See Fig. b and c), respectively.

Of equivalent importance are the superior low-temperature activities that have been achieved. The composites mentioned above perform extraordinarily well at lower temperatures, i.e., below 600 K (See Figure b). In particular, Fe-LiH and Co-LiH show constant activities of ca. 69 and 56 $\mu\text{mol g}^{-1} \text{h}^{-1}$ at 423 K, respectively. Also notable is that the Cr-, Mn-, Fe- and Co-LiH composite catalysts outperform the Cs-promoted Ru catalyst, one of the most active NH₃ synthesis catalysts, by two to three times at 573 K and 12-20 times at 523 K.

The dissociative activation of N₂ on transition metals has long been regarded as the rate-determining step in NH₃ synthesis. For TM-LiH composites, however, the rate-determining step is found to be the hydrogenation of LiNH_x species, showing remarkable changes in the energetics of catalysis.

NH₃ synthesis is regarded as a bellwether reaction in heterogeneous catalysis. The strategy in the circumvention of the scaling relations, the employment of ionic hydride in hydrogenation, and the abnormal behavior of early transition metal nitrides etc., shown in this work should be highly relevant to other catalytic processes.

The DICP group has been engaged in hydrogen storage over alkali hydrides, amides and imides for 14 years (Nature 2002). An accidental finding in the year 2009 stimulated the researchers to investigate the interaction of [transition metals](#) with those alkali compounds. The

continuous research efforts over the years led them from hydrogen storage to NH₃ decomposition and now to NH₃ synthesis.

More information: Peikun Wang et al, Breaking scaling relations to achieve low-temperature ammonia synthesis through LiH-mediated nitrogen transfer and hydrogenation, *Nature Chemistry* (2016). [DOI: 10.1038/nchem.2595](https://doi.org/10.1038/nchem.2595)

Provided by Chinese Academy of Sciences

Citation: LiH mediates low-temperature ammonia synthesis (2016, August 24) retrieved 27 April 2024 from <https://phys.org/news/2016-08-lih-low-temperature-ammonia-synthesis.html>

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