Historical perspective on: The role of potassium in the catalytic synthesis of ammonia [Volume 60, Issue 3, 15 January 1979, Pages 391–394]

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The industrial synthesis of ammonia (Haber–Bosch process) is performed with iron-based catalysts in which small amounts of potassium act as an ‘electronic’ promoter [1]. In the course of our studies on the mechanism of this reaction, along the surface science approach [2], the effect of coadsorbed K on a Fe (100) single crystal surface on the kinetics of dissociative nitrogen adsorption (which is the rate-determining step of the reaction) was investigated. The observed strong enhancement of the rate of this step was attributed to a local increase of the adsorption energy of N₂, whereby the activation energy for dissociation of this species is also lowered.

As is reflected in the strong decrease of the work function, K adsorption is associated with a pronounced transfer of electronic charge to the substrate, and a neighbouring N₂ molecule will experience a stronger ‘backbonding’ effect from the metal to its π*-orbitals, whereby the M–N₂ bond will be strengthened and the N–N bond weakened. This electrostatic model was later confirmed by further experiments [3], as well as by theory [4].

References