**Introduction**

As said by the chairman and the previous speaker, only three chemical systems catalyze \( \text{N}_2 \) to \( \text{NH}_3 \) conversion: Haber-Bosch solids (heterogeneous system)[1], nitrogenase enzymes (biochemical system)[2], and molybdenum soluble molecules (homogeneous system)[3][4]. The structural and chemical differences between these systems have already been discussed. These systems also use different sources of hydrogen (gas phase molecular dihydrogen (\( \text{H}_2 \)), cellular medium protons (\( \text{H}^+ \)), or inorganic acids in solution) and different surrounding “cofactors” (such as inorganic promoters, coenzymes or organometallic redox systems), suggesting that they rely on very different mechanisms to circumvent dinitrogen inertness.

Here, we will try to compare and contrast these mechanisms, and in particular we will propose how dihydrogen can be a chemical key to allow lower-energy proton- and electron-transfer steps in light of a novel dinitrogen activation system that we have uncovered.

**Results**

We have observed the unprecedented cleavage of dinitrogen by dihydrogen at 250°C and atmospheric pressure on isolated silica surface–supported \( \text{Ta}^{\text{III}} \) and \( \text{Ta}^{\text{V}} \) hydride centers \([\equiv\text{SiO})_2\text{TaH}]\) and \([\equiv\text{SiO})_2\text{TaH}_3]\), leading to the \( \text{Ta}^{\text{V}} \) amido imido product \([\equiv\text{SiO})_2\text{Ta}(\equiv\text{NH})(\equiv\text{NH}_2)]\) reported in reaction 1 [5].

We assigned the product structure based on extensive characterization by infrared (IR) solid-state nuclear magnetic resonance (NMR) and extended X-Ray absorption fine structure (EXAFS) spectroscopies, isotopic labeling studies, supporting data from theoretical simulations, and by comparison with the product directly obtained from ammonia [6].
Reaction intermediates revealed by in situ IR monitoring of reaction 1 and reactivity of \( [(\omega\text{SiO}_2)\text{Ta}(\text{NH})(\text{NH}_2)] \) with \( \text{H}_2 \) [7] support a mechanism highly distinct from those previously observed in enzymatic, organometallic, and heterogeneous \( \text{N}_2 \) activating systems.

Computational density functional theory (DFT) studies performed on the model cluster \( \{[(\mu-\text{O})(\text{HO})_2\text{SiO}]_2\text{TaH}_3\} \) for the silica supported tantalum trishydride complex with B3PW91 functional and the SDD effective core potential show that a straightforward mechanism relying on hydride, \( \text{H}^- \), insertion in successive M-N\(_2\) bonds [8] is not the most energy-efficient pathway: lower energy steps are achieved by successive \( \text{H}^+ \) and \( 2e^- \) transfer step originating directly from the dihydrogen molecule, in a series of uncommon molecular steps in dinitrogen chemistry (see scheme 1).

**Conclusions**

In the three catalytic systems for ammonia production, activation of dinitrogen was known to be activated either by acid/electron couples or by \( \text{H}_2 \). We have shown here a stoichiometric example of \( \text{N}_2 \) activation where \( \text{H}_2 \) is the acid/electron source. We propose that such proposed elementary steps might have interesting overlaps with some aspects of nitrogenase mechanism(s) linked to dinitrogen inertness [2], among which the unavoidable production of one mole of \( \text{H}_2 \) for every mole of ammonia produced by nitrogenases.

**References**