

RATIONAL DESIGN OF TETRADENTATE TRANSITION METAL LIGANDS FOR ATMOSPHERIC PRESSURE AMMONIA SYNTHESIS

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Ammonia (NH₃) is one of the most important compounds produced in industry. NH₃ production adds up to approximately 140 million tons per year. Still, the production in its present form is not efficient. Converting N₂ to NH₃ via the Haber-Bosch process accounts for about 3% of the world's greenhouse gas emission and more than 1% of the world's annual energy consumption due to the high pressure and temperature (150-300 atm, 400-500°C). In order to produce ammonia in a more environment-friendly and energy efficient way, one should find a method that could operate at room temperature and atmospheric pressure.

Interestingly, microorganisms in nature can fix dinitrogen and produce ammonia at ambient conditions. Thus, it would be reasonable to mimic the active site of nitrogenase enzymes and design artificial catalysts that could be competitive alternatives to the Haber-Bosch process. In this work we investigate recently synthesized biomimetic catalysts¹⁻³ with DFT methods to understand their catalytic activity. These complexes contain a central metal atom surrounded by tetradentate trisphosphino scorpionate ligands (Figure 1). In recent years numerous similar complexes have been successfully synthesized that reduce dinitrogen into ammonia in the presence of proton and electron sources at atmospheric pressure. Since the experimental characterization of the intermediates is challenging, the exact steps of the catalytic cycle are not clear yet. By studying the Gibbs free enthalpy profile, we determine the exact reaction paths of these catalysts and identify the critical steps. Our results indicate that the reduction of N₂ most likely proceeds via the so-called hybrid pathway (-N₂ → -NNH₂ → -NH₂NH₂ → 2 NH₃) and that the thermodynamical driving force disappears in the last steps of the cycle (-NH₂NH₂ → 2 NH₃). These observations enable the rational re-design of the tetradentate ligands based on the destabilization of the intermediates located in the energy valleys of the obtained profile.

The exploration of the catalytic mechanism requires careful examination of the spin states of all intermediates as the molecular spin quantum number of the experimentally characterized structures ranges from 0 to 2. Thus, we computed all (theoretically) possible spin states of a given intermediate in order to find the thermodynamically most stable species. This process was preceded by extensive test calculations based on experimental data (e.g. Mössbauer spectra) to confirm the reliability of the chosen density functional.

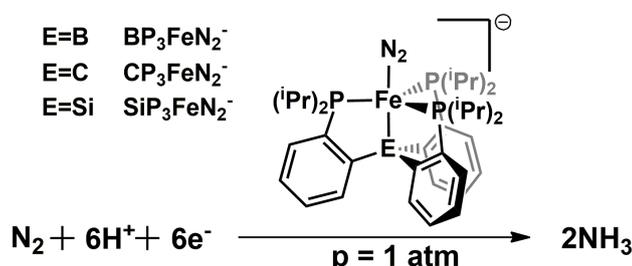


Figure 1. Reduction of dinitrogen to ammonia by EPPP scorpionate complexes at atmospheric pressure.

References:

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