


Development of transformations of dinitrogen based on highly active nitrogen-fixing catalysts

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Project Information	Project Number	24H00049	
	Project Period (FY)	2024-2028	
	Keywords	ammonia, dinitrogen, energy conversion, fuel cell, organonitrogen compounds	

Purpose and Background of the Research

● Outline of the Research

The culmination of research over the past approximately 15 years on catalytic nitrogen fixation has resulted in the successful development of efficiently catalytic ammonia formation from nitrogen gas and water under ambient reaction conditions. Additionally, significant progress has been made in elucidating the reaction mechanism, leading to remarkable improvement in catalytic activity. Building on the insights gained during the development process, the primary objective of this study is to develop catalytic transformations for nitrogen molecules with new value and potential, enabling the resource utilization of nitrogen molecules using previously developed highly active nitrogen fixation catalysts.

● Background and Objectives of the Study

Ammonia is an essential compound for human survival. Ammonia serves as a precursor for nitrogen fertilizers necessary for food production. Without nitrogen fertilizers, food production would be impossible, and without obtaining food, the body cannot produce essential components for sustaining life. The Haber-Bosch process, developed in the early 20th century, has been used for over 100 years as an industrial method for synthesizing ammonia from nitrogen gas and hydrogen gas under harsh conditions. However, this process is energy-intensive and relies on vast amounts of hydrogen gas derived from fossil fuels, contributing to significant carbon dioxide emissions and thus negatively impacting the Earth's environment. There is a need for the development of a next-generation ammonia synthesis method.

Given this research background, the researchers of this study have been developing ammonia synthesis reactions using transition metal nitrogen complexes as molecular catalysts, aiming to achieve the development of next-generation ammonia synthesis reactions. Particularly recently, they succeeded in developing a catalytic ammonia synthesis reaction using samarium dibromide as a reducing agent and water as a proton source. Furthermore, they successfully elucidated the reaction mechanism in the newly developed reaction system. By introducing substituents that accelerate the rate-determining step of the catalytic reaction into molybdenum complexes with PCP-type pincer ligands, designed via DFT theoretical calculations, they achieved a significant improvement in catalytic activity (Figure 1).

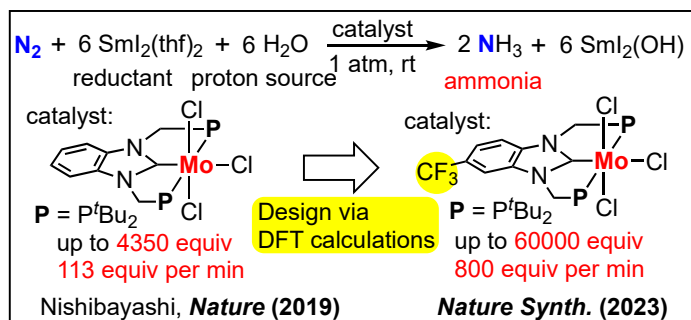


Figure 1. Catalytic ammonia formation from nitrogen gas and water

Expected Research Achievements

Based on the research achievements, the primary objective of this study is to develop versatile transformations for nitrogen molecules that embodies new values and possibilities, aiming to realize the resource utilization of nitrogen molecules abundant in the atmosphere. Furthermore, this study also focuses on the development of direct ammonia fuel cells utilizing techniques.

● Project 1: Development of Versatile Transformations for Nitrogen Molecules

Building upon insights gained from the development process of catalytic ammonia formation, we are engaged in developing catalytic reactions for the direct synthesis of nitrogen-containing organic compounds by reacting carbon nucleophiles with nitride complexes. Specifically, in a catalytic reaction utilizing carbonate ester derivatives as carbon nucleophiles, we have demonstrated the production of isocyanates at a rate of 9 equivalents per molybdenum catalyst. Based on this insight, we aim to enhance catalytic activity and explore the development of novel catalytic reactions utilizing various carbon nucleophiles other than carbonate esters.

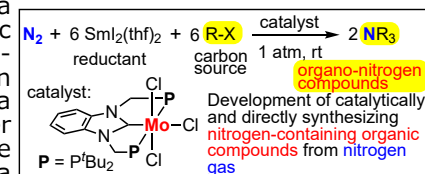


Figure 2. Project 1

● Project 2: Development of Nitrogen Fixation for Energy Conversion

We are working on the development of ammonia formation that converts externally derived energy, such as renewable energy, into chemical energy in the form of ammonia. With the ultimate goal of utilizing renewable energy, we are undertaking the challenge of developing catalytic ammonia formation using photoinduced electron transfer complexes capable of harnessing energy from visible light. As a preliminary investigation, we successfully developed catalytic ammonia formation using dihydroacridine as a sacrificial reducing agent and proton source under visible light irradiation. Building on preliminary findings, we aim to achieve significant improvements in quantum yield and ultimately, develop an ideal catalytic reaction using water as a sacrificial reducing agent and proton source.

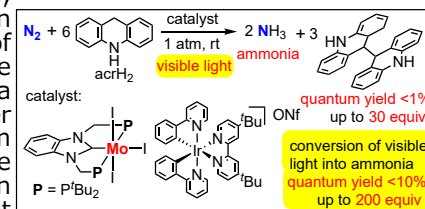


Figure 3. Project 2

● Project 3: Development of Ammonia Fuel Cells

In our laboratory, we have demonstrated that ruthenium complexes act as effective catalysts in the catalytic ammonia decomposition. To develop a more active reaction system, we have conducted detailed investigations into the reaction mechanism, revealing that the dissociation of the axial ligands of ruthenium complexes promotes catalyst deactivation. Building upon these previous research findings, we aim to utilize the ruthenium complexes developed successfully in the decomposition reaction of ammonia as the anode electrode reaction and the reduction reaction of oxygen as the cathode electrode reaction in the development of direct ammonia fuel cells.

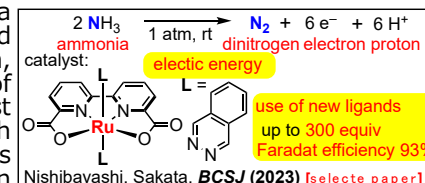


Figure 4. Project 3