

Elucidating key parameter of electrochemical N₂ reduction on metal sulfide to ammonia

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The chemical evolution hypothesis for the origin of life requires that compounds important for life's metabolism be synthesized from simple molecules. Among those molecules, ammonia, NH₃/NH₄⁺, is one of the important molecules as a building block of nitrogen-containing biomolecules like nucleic acid. Because metal sulfide minerals are widely distributed at the deep-sea floors, they could have worked as reaction sites/catalysts for nitrogen conversion, which contributed to the emergence of life. Especially, based on the knowledge that electrical power is generated at the hydrothermal vent (R. Nakamura et al., *Angew. Chem.*, **2010**, 122, 7858), it is important to investigate electrochemical nitrogen conversion activity of metal sulfide minerals to get insight about how chemical evolution has been proceeded.

Here in this work, we examined electrochemical N₂ reduction activity of metal sulfide minerals for NH₃ synthesis. Furthermore, we adapted machine-learning technique to clarify which physicochemical properties of metal sulfides are key parameter to achieve high NH₃ synthesis activity.

We synthesized 18 kinds of metal sulfides (Ag₂S, CdS, CoS₂, CuS, Cu₂S, FeS₂ (Marcasite and Pyrite), In₂S₃, MnS, MoS₂, NiS₂, NiS, PbS, SnS, SnS₂, WS₂, and ZnS (Sphalerite and Wurtzite)) using hydrothermal method and characterized them with X-ray diffraction, Scanning Electron Microscopy observation, and elemental analysis. The characterization results indicated that all the samples were single phase. Those samples were subjected to electrochemical test using flow reactor under N₂ flow.

As for the NH₃ generation activity, metal sulfide with layered structure such as SnS₂ and WS₂ demonstrated higher activity, while other layered metal sulfides like SnS and MoS₂ exhibited lower activity.

To clarify the relationship between physicochemical properties of metal sulfides and observed NH₃ generation rate, multi-regression analysis was conducted using Gradient-Boosted Decision Tree model. Among 15 parameters considered, it revealed that absolute electron negativity and maximum metal-sulfur-metal bonding angle largely affected the NH₃ generation rate. Namely, to achieve high NH₃ generation rate, larger absolute electron negativity and smaller maximum meta-sulfur-metal bonding angle are necessary.

In summary, higher electrochemical N₂ reduction activity to NH₃ was observed on SnS₂ and WS₂. Machine learning technique revealed that absolute electron negativity and maximum metal-sulfur-metal bonding angle were key parameters to achieve higher NH₃ generation rate. Results in this work show the possibility that N₂ was electrochemically reduced to ammonia on metal sulfide minerals and it contributed to the emergence of life.