

Project Title: Direct Conversion of Methane to Ammonia and Ethylene by a Three-Step Thermochemical Cyclic Process: Reduction, Nitridation, and Protonation

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1. The Progress of the Research

During the period of September 1, 2017 - August 31, 2018, we focused our effort on the selective oxidation of methane to ethylene over various metal oxide catalysts and the atmospheric ammonia synthesis over a ruthenium mayenite electride $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) catalyst.

1.1 Selective Oxidation of Methane to Ethylene

a) Selection and Synthesis of Potential Metal Oxides.

The single metal oxides of SnO_2 , MnO_2 , Cr_2O_3 , Fe_2O_3 , CoO , and NiO without additional purification were purchased and evaluated without additional purification. The mixed metal oxides of phase-pure perovskite oxide $\text{BaCe}_{0.5}\text{Co}_{0.5}\text{O}_3$ (BCC) and dual-phase perovskite oxide composite of $\text{BaCe}_{0.5}\text{Fe}_{0.5}\text{O}_3$ (BCF) and $\text{BaCe}_{0.4}\text{Fe}_{0.4}\text{Co}_{0.2}\text{O}_3$ (BCFC), which showed well-mixed conductivities, were synthesized by the polymeric gelation method. The MnO_2 loaded proton conducting perovskite oxide $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ (BZY) with the MnO_2 molar percentage of 5-20% were also synthesized by the polymeric gelation method. In the polymeric gelation, the desired metal cations were chelated by organic ligands (EDTA acid and citric acid), which allowed for the homogeneous formation of polymerized metal salts in the form of a sticky gel. After vaporizing water, the gel changed into black charcoal-like powders, which were further calcined at 900-1400°C. The desired phase-pure perovskite and dual perovskite phases were obtained for BCC, BCF and BCFC respectively. The MnO_2 loaded BZY powders only showed the pure BZY perovskite phase, which revealed the excellent dispersion of MnO_2 nanoparticles on BZY surface.

b) Evaluation of Reaction Performance

All the oxide powders were pressed, crushed, and sieved and the particles with sizes between 40 and 60 mesh were used for evaluating the performance of methane to ethylene. Around 0.3g samples were put into a house-made plug-flow reactor based on a quartz tube in a tubular furnace. The gases with a flow rate of 50ml/min were fed through MFC. The exit gas composition was analyzed online by mass spectroscopy (MS). After loading the oxide samples at room temperature, the inert gas of dry Ar was fed into the reactor and held for 1h before heating up. After the temperature reached at 600°C in dry Ar and held for 1h, the reaction gas of diluted methane CH_4 (balanced by helium) was introduced and reacted for 20min. After that, the inert dry Ar was switched back and held for 10min for removing residual reactant gas. Then the Air (or humidified Ar) flow was introduced for 20min for oxidation. The steps of methane reduction, dry Ar sweeping, and air or water oxidation were defined as one redox cycle. It was found that all the metal oxides showed unstable cycles between methane reduction and water oxidation since water didn't show enough reoxidation capability. When air was used as the oxidant, all the metal oxides showed very stable redox cycles.

Fig. 1 shows eight stable redox cycles for 10mol% MnO_2/BZY catalyst. During the methane reduction half cycle, the signals of water (18), C_2H_4 and/or CO (28), and carbon dioxide (44) were observed.

The production of CO_2 and H_2O shows that the complete combustion of methane occurred, while the CO or C_2H_4 means that the partial or selective oxidation occurred. A further experiment is ongoing to distinguish C_2H_4 from CO .

1.2 Atmospheric Ammonia Synthesis

We also studied atmospheric ammonia synthesis, which will finally be used for direct synthesis of ethylene and ammonia from methane and nitrogen. Currently, we focused our effort on a promising Ru loaded mayenite electride $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) catalyst for ammonia synthesis from nitrogen and hydrogen under mild conditions (atmospheric pressure and low temperature). The traditional synthesis of the electride is so complicated that related research has been significantly obstructed. Herein, a simple massive production of C12A7:e⁻ was achieved using one-step moderate aluminothermic process (i.e., 1100°C, 8h) directly from a mixture of commercial powders (i.e., CaO , Al_2O_3 , and Al), avoiding conventional high-temperature (1350°C) crystallization, severe reduction (700-1300°C, up to 240h) and post-purification steps. Controllable electron densities (N_e) up to $1.23 \times 10^{21} \text{ cm}^{-3}$ were obtained by only

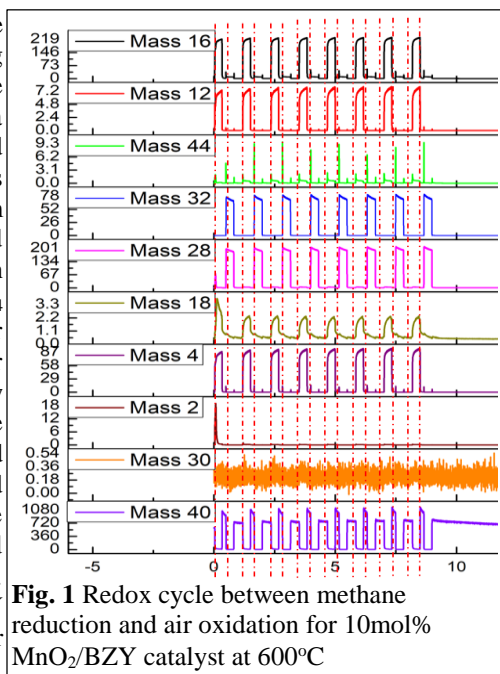
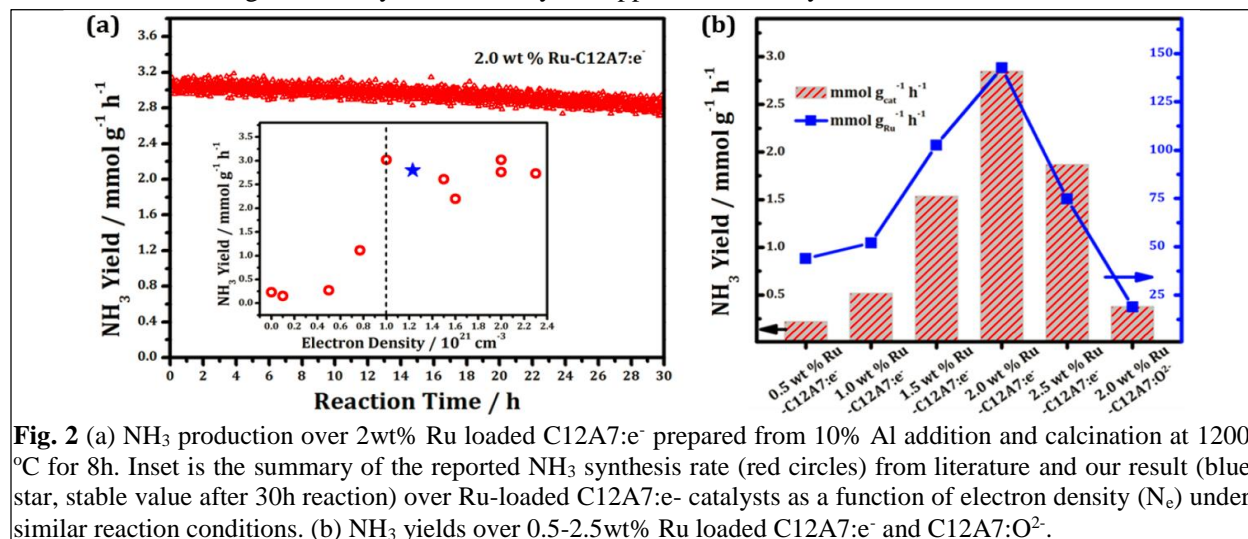


Fig. 1 Redox cycle between methane reduction and air oxidation for 10mol% MnO_2/BZY catalyst at 600°C

adjusting the amount of Al, covering the insulator-metal transition (MIT). Mechanistic studies revealed the dual-functional roles of Al that it not only performed as an *in-situ* reducing agent during the electride formation but also significantly enhanced the construction of mayenite skeleton.

Fig. 2a indicates that the NH_3 formation rate over 2wt % Ru loaded C12A7:e^- reached $3.66 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ at 400°C and still retained $3.20 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ after the 10h continuous reaction, the highest value ever reported for C12A7:e^- . The NH_3 synthesis further tended to be stable after 30h with a yield around 2.8-3.0 $\text{mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$. This outstanding performance should be attributed to the high N_e ($1.23 \times 10^{21} \text{ cm}^{-3}$) of the massively produced C12A7:e^- support, clearly above the MIT point ($1 \times 10^{21} \text{ cm}^{-3}$) of mayenite. Besides, the effect of Ru loading amount and substrate was also studied. **Fig. 2b** shows that, with the increase of Ru from 0.5 to 2.5wt%, NH_3 yield presents volcano-trend with the maximum at 2wt%. The yield over 2wt% Ru loaded C12A7:e^- is still the highest ($183 \text{ mmol g}_{\text{Ru}}^{-1} \text{ h}^{-1}$) after being normalized by the Ru loading amount, while the yield in the case of 2.5wt% Ru loading is even lower than that in the case of 1.5wt%. The much-suppressed activity upon excess Ru loading is probably due to the overgrowth of Ru NPs with degraded surface dispersion on the low-BET C12A7:e^- support. Enhanced performance, as well as improved sustainability, can be expected by further optimizing the dispersion and morphology of Ru. Notably in **Fig. 2b**, when the electron-free C12A7:O^{2-} was used as the substrate in place of C12A7:e^- , the NH_3 yield is only $19 \text{ mmol g}_{\text{Ru}}^{-1} \text{ h}^{-1}$, almost one order of magnitude lower than that over C12A7:e^- , further demonstrating the crucial role of a high- N_e substrate for boosting the NH_3 synthesis ability of supported Ru catalysts.



2. The Impact of the Research on My Career

The two research achievements on the selective oxidation of methane to ethylene and the atmospheric ammonia synthesis helped the PI to open up two new research directions. The newly mixed metal oxides can also work as mixed conducting materials for PI's other researches such as solid oxide fuel cells and electrolysis cells. The new C12A7 mayenite material has the form of oxide, electride, and can also accommodate other anions, which will be excellent anion conductors. It can further be used for fuel cells, hydrogen permeation membranes, and electrochemical sensors. It is clear that the research not only directly introduced the methane to ethylene research and atmospheric ammonia synthesis but also open up a lot of other research potentials, which helped the PI to establish his research career on Sustainable Clean Energy. In fact, the atmospheric ammonia synthesis based on the $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C12A7) electrides has attracted considerable attention. The close collaboration with Oak Ridge National Laboratory (ORNL) has been established for performing atmospheric ammonia synthesis. The preliminary results has been submitted to a journal paper and are enough for writing proposals for more external funds.

3. The Impact of the Research on Students

The research was directly performed by one graduate student with the help of one postdoc. Five undergraduate student researchers were also hired to work on this project. The research helped to educate the students to work on scientific research, writing, and presentation. They all learned the natural gas conversion, gas to liquid (GTL), is an important process for efficient and clean use of fossil energy. They also learned that the ammonia is a kind of fertilizer and energy carrier, which should be synthesized under a milder condition. They learned a lot of material synthesis and characterization techniques and how to operate modern equipment such as mass spectroscopy to analyze gas composition. One manuscript is under reviewing with ACS-PRF as first acknowledgment.