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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, 2018 - August 31, 2019, we focused our effort on the further study of the mayenite electride $12CaO{\cdot}7Al_2O_3$ (C12A7) for ammonia synthesis. The C12A7 was successfully doped with silicon for improving electron density. We collaborated with Oak Ridge National Laboratory for neutron characterization. We also established a specific experimental setup for evaluating the thermochemical performance of oxide materials.

1.1 Synthesis of C12A7 Electrides

In previous work, we have developed the aluminothermic method to synthesize C12A7 electride powders in one thermal treatment step in the inert atmosphere. In order to achieve better ammonia synthesis performance, the electron density in the C12A7 should be improved. Here, we successfully synthesized $12CaO{\cdot}5Al_2O_3{\cdot}4SiO_2$ (C12A5S4) from the raw materials of CaO, Al_2O_3, SiO_2, Aluminum, and Silicon. The XRD results (**Fig. 1**) indicated that the C12A7 mayenite structure was formed and the iodine titration experiment indicated that electron density is much higher than the C12A7 electride.

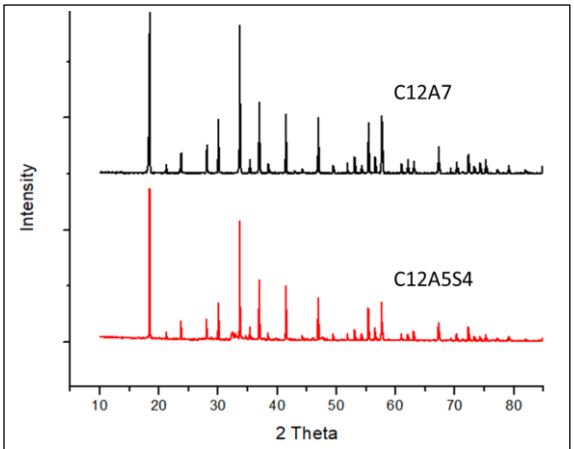

Fig. 1 XRD patterns of C12A7 and Si-doped C12A7 powders by one-step reduction method.

1.2 Mixed conductivity of C12A7 oxide

Novel structures with mixed ionic and electronic conduction (MIEC) are beautiful for their versatility in energy and sustainable technologies. Sub-nanoporous mayenite ($12CaO{\cdot}7Al_2O_3$, C12A7) presents a unique cage structure, which can accommodate a series of anions, including O^{2-}, O^-, OH^-, H^- and even e^- (electride). Conduction behavior of C12A7 in reducing conditions (H_2) is attractive due to the coexistence of various cage species. Herein, to get in-depth insights into the H^- incorporation, dynamic C12A7 hydrogenation was studied by in-situ electrical conductivity tests up to 800 ^oC, concerning the mixed conduction of O^{2-}, H^-, and e^- within the sub-nano cages. It was found H^- injection was accompanied by the production of electronic conduction, which can be retained even by slow cooling. MIEC was further confirmed by an electromotive force (emf) tests over the range of 500-800 ^oC. Systematic studies indicated that bulk injection of H^- probably proceeded via an indirect approach, the simultaneous transport of e^- and H^+. Conductive competition between O^{2-} and H^+ within the cages were also suggested by +/- switching of the open-circuit voltage (OCV) at different temperature zones. Furthermore, based on the high sensitivity of the MIEC

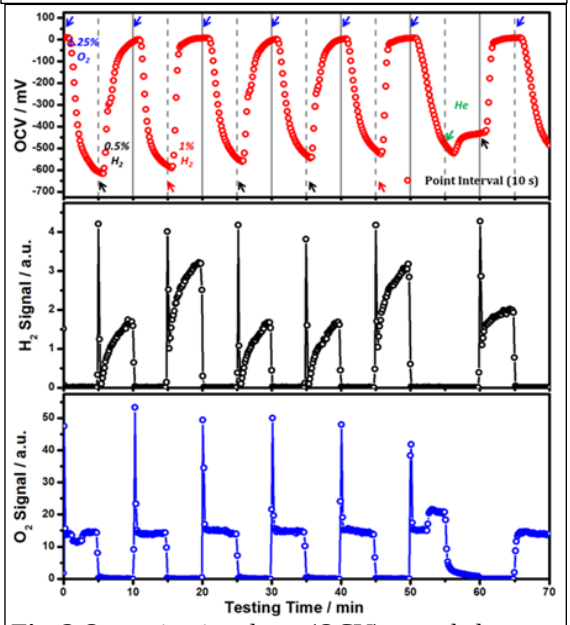

Fig. 2 Open-circuit voltage (OCV) recorded over C12A7 pellets after activation at 800^oC. The upper chamber was filled with 5 % H_2, and the lower chamber was filled with O_2 with various concentrations. On-line MS signal of H_2/O_2 of sweep gas from the lower chamber are shown as well.

equilibrium in hydrogenated C12A7 to the environment, the prototype of high-temperature ceramic sensors for H_2 and O_2 were also presented (**Fig.2**).

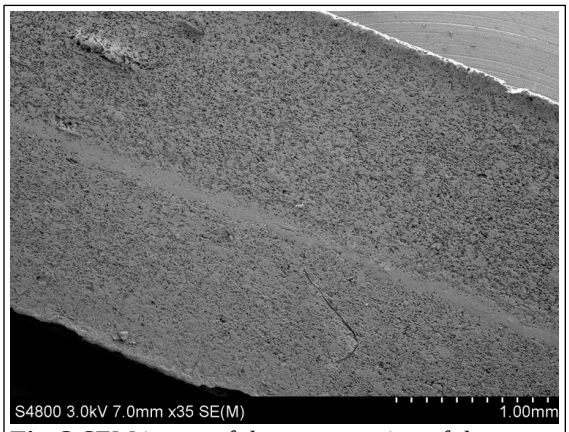

Fig. 3 SEM image of the cross-section of the C12A7 sandwiched structure.

1.3 C12A7 used for energy conversion devices

Based on the results obtained for the conductivities measurement under different temperatures and atmospheres. The C12A7 can potentially be used as the main component for hydrogen anion conductor for ammonia synthesis electrocatalytic reactor, hydrogen-permeable membrane reactors, and fuel cells. We have tried to fabricate sandwiched structure with thin dense C12A7 and porous C12A7 on both sides for working as hydrogen-permeable membrane and button cells. Although we haven't achieved the device performance yet. We made significant progress in the fabrication of single cells. **Fig. 3** provides the SEM image of the sandwiched structure, which indicates that the dense C12A7 thin film can be obtained. The hydrogen permeation test has been tested, and very promising hydrogen permeation flux was obtained. We are doing further repeating work and characterization for confirming these results and will publish this result soon.

1.4 Collaboration with ORNL

We have prepared C12A7 powder samples with high electron density for ORNL to carry neutron characterization to figure out the functions of hydrogen anion and electron for the high-performance of ammonia synthesis performance. The results will be shared with us soon.

1.5 Other research work during this period

The automatic and programmable tubular reactor was designed and manufactured for doing thermochemical redox experiments, which allows the rapid temperature switching between 1400^{o}C to 500^{o}C. This can be used for the oxidation coupling of methane using the redox cycles of the mixed oxides.

2. The Impact of the Research on My Career

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 $12CaO{\cdot}7Al_2O_3$ (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 have 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 several undergraduate students. 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 essential 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. Three papers have been published with ACS-PRF as the main acknowledgment.