Progress of "Artificial Photosynthesis (ARPChem)" Project

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Abstract: Six years or more have passed since "Artificial Photosynthesis" project started in 2012 as a 10-year program. There are three key subjects in this project, which are photo semiconductor catalysts that actualize water splitting under sunlight irradiation, selective separation of hydrogen and oxygen from an explosive gas mixture by ceramic membrane, and an innovative olefin production process derived from CO_2 and hydrogen. We would like to demonstrate the progress of catalyst research in ARPChem project from a view point of technology and to argue our strategy for the mitigation of CO_2 emissions.
Keywords: CO_2 utilization, water splitting, solar hydrogen

1. Introduction of ARPChem Project

Drastic reduction of anthropogenic CO_2 emissions is one of the most important issues in the 21st century to mitigate climate change. In the current chemical industry, various fossil resources are used to emit huge amount of CO_2. We believe that chemical industry can greatly contribute to curbing CO_2 emissions by changing its resources to more environmentally benign ones.

Solar hydrogen (hydrogen obtained by catalytic water splitting under sunlight) is an ideal sustainable resource and can be utilized as a chemical resource in the combination with CO_2. In Japan, the 10-year program named "Artificial Photosynthetic Chemical Process (ARPChem)" has been in progress under the support of New Energy and Industrial Technology Development Organization (NEDO) since 2012. There are three key subjects in this project, which are catalysts that actualize water splitting under sunlight irradiation, selective separation of hydrogen and oxygen from an explosive gas mixture, and an innovative olefin production process.

The most important and difficult subject among them is to establish water splitting catalyst technology that satisfies both high activity (sunlight conversion to hydrogen (STH)) and low manufacturing cost per unit irradiation area. We set the target so that solar hydrogen can rival the ones derived from fossil resources (e.g. natural gas) in terms of production cost, and we are mainly developing photo semiconductor catalysts and modules.

Several processes are possible to provide olefins from CO_2 and solar hydrogen as raw materials. Since CO_2 can easily be converted to CO by reverse water gas shift reaction, those processes will be compatible with such conventional processes as methane reforming, methanol synthesis, and methanol conversion to olefins (MTO). Considering that these conventional processes are commercially viable now, novel processes based on CO_2 and solar hydrogen must be economical enough to be competitive with conventional processes by introducing some innovations that have not been realized so far. Interestingly, such innovations can be applied to the conventional processes to improve their yield and/or energy consumption. For this purpose, we propose two innovative technologies: reactive separation for methanol synthesis, which can break the limitation in the thermodynamic equilibrium, and immortal zeolite catalysts having a remarkably high steam resistance at high temperatures that are generally used in MTO reaction.

2. Progress of the Project

2.1 Photo Semiconductor Catalyst for Water Splitting

For water splitting catalysts, various hydrogen evolving catalysts (HEC) and oxygen evolving catalysts (OEC) have been proposed. Two-step type catalyst combining HEC and OEC on the same contact layer can be designed like a semiconductor device, where one high performance catalyst can compensate the other poor performance counter catalyst. Furthermore, this type of catalyst allows so called "Photo catalyst

sheet" that are prepared through thin film formation by casting/printing. It will be very attractive to reduce the manufacturing cost of the catalyst modules. Several chalcogenide materials and some oxysulfides are promising candidates for HEC. On the other hand, $BiVO_4$, Ta_3N_5, and some oxynitrides are the candidates for OEC. As shown in Figure 1, water splitting takes place at the crossing point of the I-V curves for the two types of catalysts. We have achieved more than 3% of STH using a tandem type photo catalyst sheet.

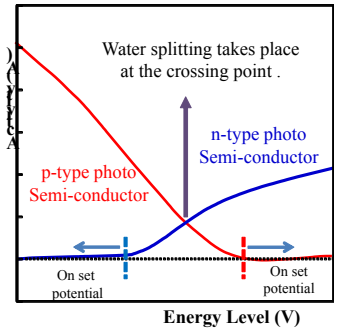

Figure 1. Conceptual Design of Photo catalyst Sheet.

2.2 Reactive Separation for Methanol Synthesis Using Zeolite Membrane

A typical operating conditions for industrial methanol production process is ca. 250°C and ca. 8 MPa. Methanol yield is strictly controlled by the thermodynamic equilibrium between CO, H_2 and methanol. Installation of zeolite membranes in such a process allows methanol to leave the reaction system to shift the equilibrium (reactive separation of methanol). We have been successful in operating such a reactive separation process at bench-scale. The overall yield of methanol has been kept around 90% for 500 hours at 230°C and 3 MPa as shown in Figure 2. Notably our reactive separation technology enabled us to surpass the thermodynamic equilibrium in the methanol synthesis. It is also noteworthy that we were able to confirm the stability of zeolite membrane under the severe conditions required for methanol synthesis.

2.3 Novel zeolite catalyst of MTO reaction

Conversion of methanol to olefins involves formation of water, resulting in a significant de-alumination from zeolite especially at high reaction temperatures. Even with a well-modified Al-MFI type zeolite, there is a clear limitation about the reaction temperature to suppress such de-alumination though a higher reaction temperature is desired for a higher productivity. We found that a modified CON type zeolite does not show any de-alumination even though it is exposed to a very severe steaming condition as shown in Figure 3. In our bench-scale plant, our catalyst showed excellent stability even in the steam carrier at 500°C for 500 hours. In other words, it is almost an immortal MTO catalyst having an extraordinary steam resistance.

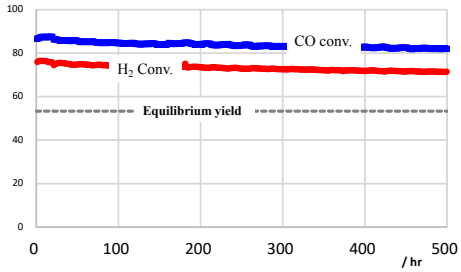

Figure 2. Reactive Separation of Methanol Synthesis (Conditions: 230°C, 3 MPa).

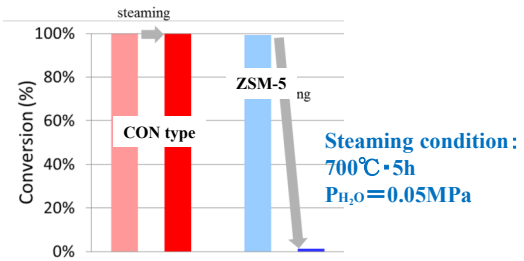

Figure 3. Comparison of Steam Resistance for Zeolites Both zeolites were modified independently to maximize steam resistance properties with various treatment methods.

3. Conclusions

In order to realize the "artificial photosynthesis" for olefin production, photo catalyst sheets for water splitting, reactive separation for methanol synthesis, and a novel MTO zeolite having remarkable steam resistance have been developed. With the combination of these innovative technologies, it is expected that CO_2 will be a sustainable feedstock for chemicals, not a notorious Green House Gas (GHG).

References

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