Catalyst Laboratory of National Taiwan University- 2011 graduate

W. F. Tsai

Thesis: Photocatalytic CO₂ hydrogenation in a Novel photo-reactor

Global warming and energy shortage raising the concern about green house gases reducing and energy recovery. One of the best routes to covert CO₂ into renewable energy and reduce the concentration of CO₂ in atmosphere is artificial photosynthesis. The first key step may rely on the hydrogenation of CO₂ to organic compounds. This study explored the photocatalytic hydrogenation of CO₂ under light irradiation. A series of sol-gel prepared InTaO₅ were loaded with different metal oxide such as NiO, RuO₂, Cu(OH)₂ and Pt were as co-catalysts. The UV-VIS spectra of this series catalysts indicated that the photocatalysts could absorb visible light. The maximum yields of acetaldehyde and methyl formate were 0.25 and 0.16 μmol/g⋅hr, respectively. The results were from irradiation by AM 1.5G sunlight on the series InTaO₅ catalysts when system introduced with CO₂ and water vapor at 25°C. When inlet changed to CO₂ and H₂, the products became acetaldehyde, formic acid and ethanol, and the maximum yields are 0.16μmol/g⋅hr, 0.23μmol/g⋅hr and 0.22μmol/g⋅hr, respectively. Then the CO₂ hydrogenation catalysts were applied into a novel twin photoreactor, which can separate H₂ and O₂ during water splitting. Methanol yield was 0.03μmol/g⋅hr in gas phase of twin photoreactor, and in slurry system the maximum yields of methanol and acetaldehyde were 9.27μmol/g⋅hr and 11.30μmol/g⋅hr at 25°C. The twin photoreactor increased the photoconversion of CO₂ into fuel.

X. M. Lin

Thesis: Biodiesel Synthesis by Esterification/Transesterification Using Solid Catalysts

Biodiesel is an alternative fuel for traditional fossil fuel. It can be produced by transesterification from triglyceride. In this study, we use solid catalysts to catalyze esterification and transesterification in order to solve the problems of free fatty acid (FFA) in the feedstock oil.

The first method: Both esterification and transesterification were catalyzed simultaneously by solid acid catalyst. In experiment, we used commercial lard as feedstock oil, and SZA(Sulfated Zirconia Alumina) solid acid catalyst to catalyze both reactions. We studied different reaction parameters, the catalyst amount, the methanol/oil molar ratio, and reaction temperature. We also chose waste cooking oils (WCO) which contained FFA as feedstock oil. Under methanol/oil molar ratio 12/1, catalyst amount 1wt%, reaction temperature 150°C, and reaction time 2hr, the biodiesel yield reached 80%. Moreover, the biodiesel yield of WCO showed that different feedstock oils did not influence the efficiency of catalyst. So we could use the low quality WCO as the feedstock oil to decrease cost of oil.

The second method: The second method was two sequence reactions. Under mild reaction temperature 60°C, use SZA solid acid catalyst to catalyze esterification first. The objective was to convert FFA into ester. Then used calcium diglyceride Ca(C₃H₅O₂)₂ solid base catalyst to catalyze transesterification. We added 5wt% and 20wt% palmic acid into soybean oil to simulate the feedstock oil which contained FFA. The research result showed that it was necessary to esterify FFA in oil in the first step, and the overall yield was 80% after this two sequence reactions.

Z. W. Chang

Thesis: Photocatalytic water splitting using sol-gel prepared Pt/SrTiO₃:Rh in twin membrane reactor via

Ce ions mediator by visible light irradiation with the increasing demand for energy in the industrial society, using solar energy to produce hydrogen by water splitting is an alternative clean and pollution-free way to produce energy. Z-scheme system is the use of two different kinds of photocatalysts to do half-reaction of water splitting, respectively, and the use of different transmission medias to transmit electrons and holes, and finally completes the whole reaction. Previous studies in our laboratory point out that the use of pretreated Nafion membrane to separate the different reaction catalyst systems, not only to pass through ion transfer mediator by diffusion effect, but also to separate hydrogen and oxygen, and thus enhance the production. In this study, first we use sol-gel method to produce Pt/SrTiO₃:Rh catalyst as hydrogen production, then put it in 10vol% methanol aqueous solution to do the test of hydrogen production activity in visible light, and hydrogen production can reach 10 μmol/gcat within 6 hours. We found that at pH 1.5 the catalytic activity is the best. Producing SrTiO₃ by sol-gel method can get higher activity than using solid-state method and hydrothermal method. Secondly, we add BiVO₄ as oxygen production into the twin membrane reactor, and Ce⁴⁺/Ce³⁺ as ion transfer mediators in the aqueous solution, and use Nafion cation exchange membrane to separate the two catalysts to do water decomposition in visible light. Besides, the membrane can separate hydrogen and oxygen. In our study we use 300W xenon lamp as the visible light source and Ce⁴⁺ pre-treated Nafion membrane to separate two sides of half-reaction. The result is that the hydrogen production can be achieved certain level, and that in line with H₂/O₂ = 2 stoichiometric decomposition of water. Pt/SrTiO₃:Rh is prepared by Sol-gel method with light deposition method, and BiVO₄ is produced by liquid phase synthesis. The use of double-membrane reactor can reduce the chance of reversing reaction of hydrogen and oxygen, therefore it enhance hydrogen production rate. Separating two
sides of the catalysts can also solve the problem of competitive absorption of light. We expect to test the best reaction conditions in the presence of cerium ions in order to improve the hydrogen production performance.