



UNIVERSITÀ DEGLI STUDI DI MILANO

DIPARTIMENTO DI
SCIENZE FARMACEUTICHE

AVVISO DI SEMINARIO:

Prof. Ken Sakai

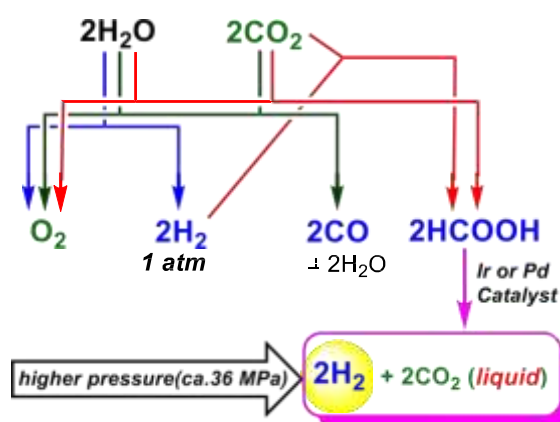
Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, Giappone

Mercoledì 7 Settembre 2022

Ore 11:00, Aula G22 (Via Golgi, 19)

Mechanistic Studies on Water Splitting and CO₂ Reduction Towards Solar Fuels Production

Among various approaches attempting to develop renewable energy sources, solar hydrogen production via water splitting has received an increasing attention in relation to the recent advancement in the hydrogen fuel cell technology. The combustion energy after storing two reductive equivalents decreases in the order of H₂ (**he**) > CO (0.99**he**), HCHO (0.99**he**) > HCOOH (0.89**he**) > CH₃OH (0.85**he**) > CH₄ (0.78**he**) (**he**=286 kcal/mol). The source of electrons and protons can be produced in the artificial photosynthetic water oxidation process ($2\text{H}_2\text{O} + 4\text{h}\nu \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$). Among these fuels, only formic acid and methanol are liquid and possess superior characteristics from a viewpoint of energy density together with the feasibility in refueling and transportation in ambient conditions. Further, formic acid has a remarkable potential as a source of **high-pressure H₂** because of its reversible conversion capability: $\text{HCOOH} \leftrightarrow \text{H}_2 + \text{CO}_2$ ($\Delta G = -12$ kcal/mol; see figure, right). The production of {O₂+2HCOOH} is advantageous owing to the spontaneous separation of the two products into the gas and aqueous phases, while the production of {2H₂+O₂} or {2CO+O₂} yields a flammable gas mixture. With these perspectives in mind, our recent interests still concentrate on the basic studies towards the improvement of our understanding on the mechanisms of water reduction and CO₂ reduction on various transition metal molecular to heterogeneous catalysts.¹⁻⁵ We succeeded to develop and investigate the environmentally friendly photocatalytic CO₂ reduction in fully aqueous media.^{1,2} We have advanced our understanding on the mechanisms of catalytic CO₂ reduction by DFT.^{2,3} We have also advanced our studies on two-electrode solar water splitting systems which permit H₂ separation at a dark cathode.⁴ A quite new topic in our group is the project on the mechanistic studies of electrocatalytic hydrogen evolution reaction by platinum subnanoclusters.⁵ Some of these topics are to be discussed in Ottawa.





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1. A. Call, M. Cibian, K. Sakai, et al., *ACS Catal.* **2019**, *9*, 4867-4874.
2. X. Zhang, K. Yamauchi, and K. Sakai, *ACS Catal.* **2021**, *11*, 10436-10449.
3. Y. Sakaguchi, A. Call, K. Yamauchi, and K. Sakai, *Dalton Trans.* **2021**, *50*, 15983-15995.
4. H. Ozawa and K. Sakai, *AsiaChem* **2021**, *2*, 80-87.
5. K. Kuge, K. Yamauchi and K. Sakai, *ChemRxiv*, April 1, **2022**.

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