

Hydrogen Generation: Catalytic Acceleration and Control by Light

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Contents:

experimental methods
spectrum of sunlight
spectrum of the light source, transmission of the filter
typical gas evolution curves for some catalyst systems

General methods:

All catalytic experiments were carried out under an inert gas atmosphere (argon) with exclusion of air. Formic acid and triethylamine were distilled prior to use and stored under argon. The formic acid to amine ratio was determined by ^1H NMR on a Bruker Avance 300 spectrometer. The catalyst precursors and phosphine ligands have been purchased from commercial suppliers and stored under argon. $[\text{RuH}_4(\text{PPh}_3)_3]$ was prepared according to literature procedures.¹

The amount of gas evolved is measured by a gas burette. In addition, a GC for analyzing gases is applied (gas chromatograph HP 6890N, permanent gases: Carboxen 1000, TCD, external calibration. The equipment used has been described in detail elsewhere.²

The light source used for irradiation is a 300 W PerkinElmer Cermax PE300BF Xenon Arc lamp. An A2-005 hot mirror was employed as filter.³

Typical procedure for the decomposition of formic acid/amine adducts

For in situ catalysts, 28.6 μmol (14.3 mg) of $[\text{RuCl}_2(\text{benzene})]_2$ were dissolved in 3 mL DMF and stirred overnight. 1 mL of this stock solution was then transferred to a Schlenk tube containing 114.4 μmol (30.0 mg) triphenylphosphine. The resulting solution was then stirred at 80 $^\circ\text{C}$ for 2 h and then let cool down to room temperature.

A premixed solution of 59.5 mmol $\text{HCO}_2\text{H} \cdot 2 \text{NEt}_3$ (5.0 mL) was warmed to 40 $^\circ\text{C}$ in a double walled thermostated reaction vessel. The vessel is purged with argon to remove any other gas before the reaction is started by addition of the catalyst either as powder in a Teflon crucible (hydride complex) or as a solution in DMF via septa and a small polyethylene tube. The reproducibility of gas evolution is typically 5-10%.

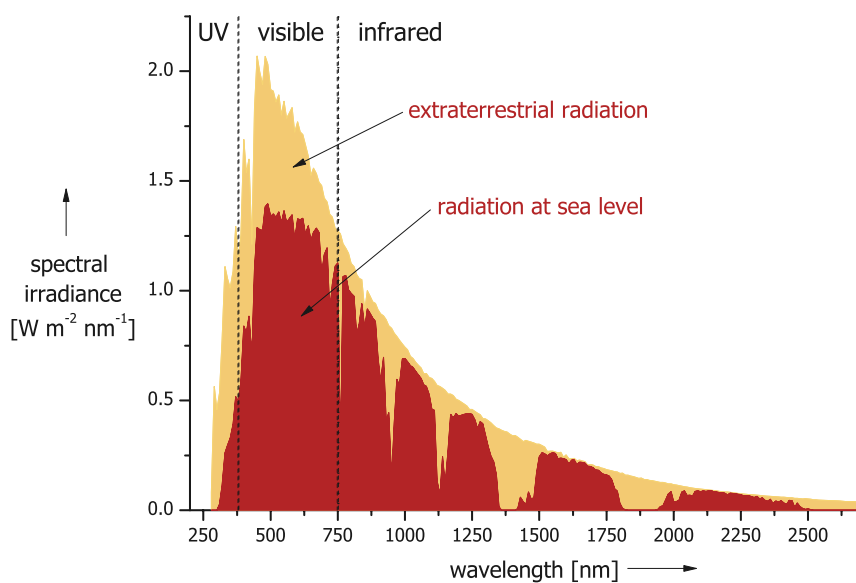


Figure 1: spectrum of sunlight

The spectra are derived from the standard reference table for solar irradiance ASTM G173 of the American Society for Testing and Materials. Data available from the Renewable Energy Resource Center of National Renewable Energy Laboratory of the U.S. Department of Energy: <http://rredc.nrel.gov/solar/spectra/am1.5/>

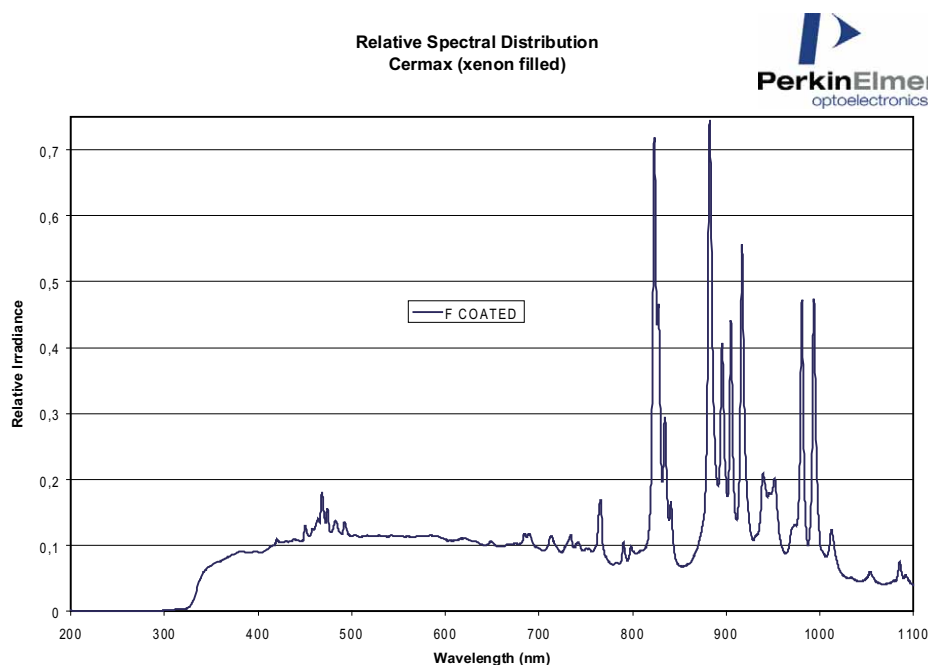


Figure 2: Typical emission of Perkin Elmer Cermox F lamp (data courtesy of PerkinElmer Optoelectronics)

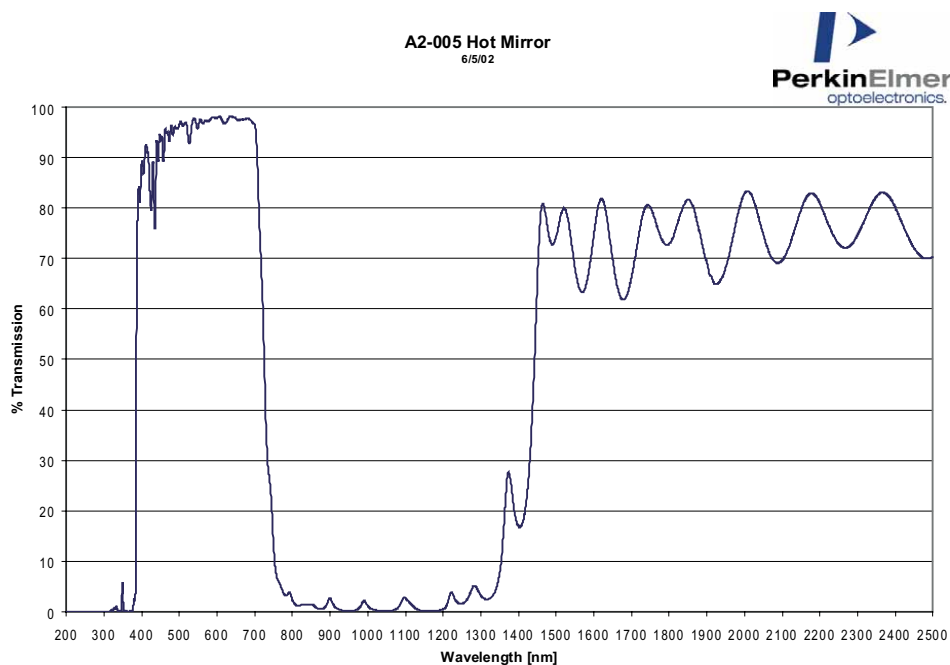


Figure 3: Transmission of the PerkinElmer hot mirror A2-005 (data courtesy of PerkinElmer Optoelectronics)

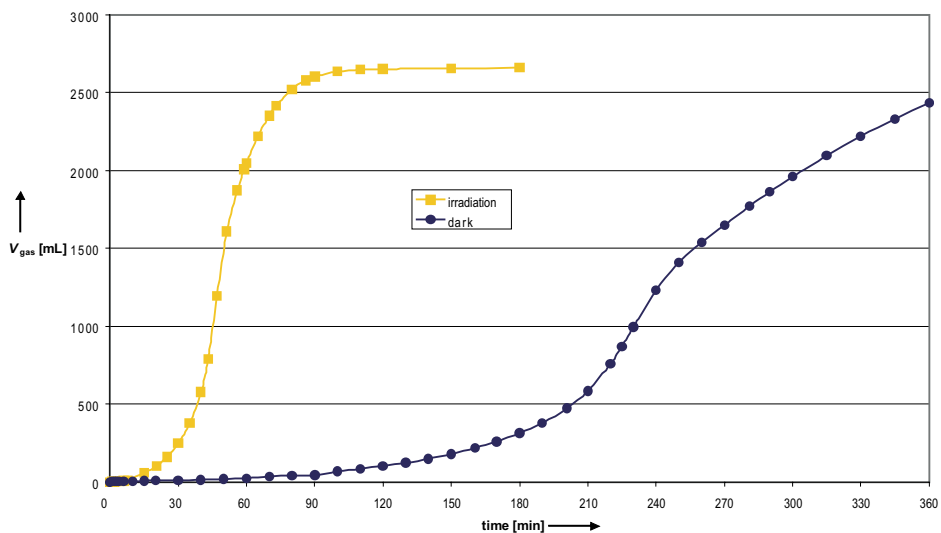


Figure 4: Typical gas evolution from 5 mL 5 HCO₂H · 2 NEt₃ with 19.1 μmol 1/2 [RuCl₂(benzene)₂] / 3 dppe at 40 °C; H₂ : CO₂ = 1:1

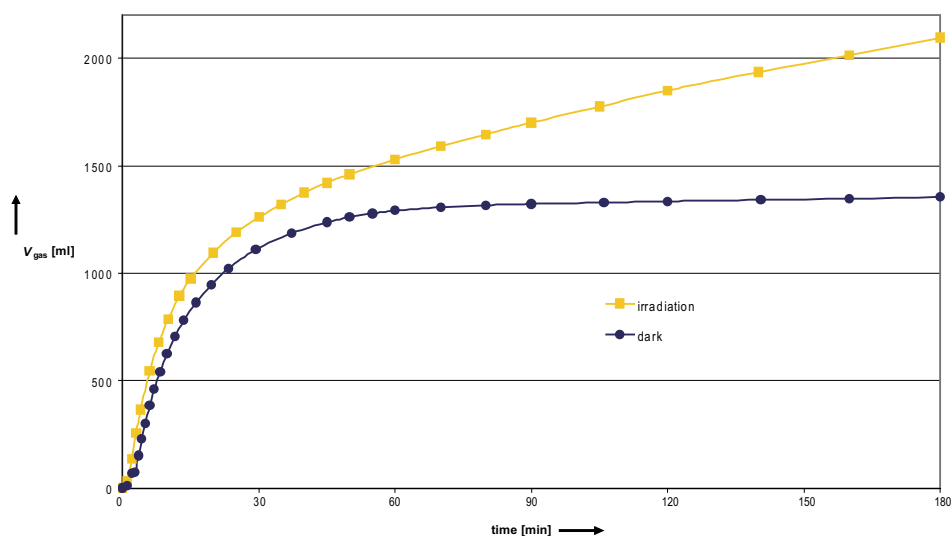


Figure 5: Typical gas evolution from 5 mL 5 HCO₂H · 2 NEt₃ with 19.1 μmol RuCl₃ · x H₂O / 6 PPh₃ at 40 °C; H₂ : CO₂ = 1:1

Notes and references

- 1 a) R. O. Harris, N. K. Hota, L. Sadavoy, J. M. C. Yuen, *J. Organomet. Chem.* 1973, **54**, 259-264; b) D. G. Hamilton, R. H. Crabtree, *J. Am. Chem. Soc.* 1988, **110**, 4126-4133; c) L. S. Van der Sluys, G. J. Kubas and K. G. Caulton, *Organometallics*, 1991, **10**, 1033-1038.
- 2 a) B. Loges, H. Junge, B. Spilker, C. Fischer, M. Beller, *Chem. Ing. Tech.* 2007, **79**, 741-753; b) A. Boddien, B. Loges, H. Junge, M. Beller, *ChemSusChem* 2008, **1**, 751-758.
- 3 For further details, please see the product specifications and the Cermax Engineering Guide on <http://optoelectronics.perkinelmer.com/>.