

Bimetallic Doping of Titanium Dioxide for Use in Photocatalytic Splitting of Water

Akawat Sirisuk^{1,*}, Eakachai Manatiwson¹, and Piyasan Praserttham¹

¹ Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University, Bangkok, 10330, Thailand

*Akawat.s@eng.chula.ac.th

Introduction

Presently, photocatalytic splitting of water using titanium dioxide has great potential because it is cheap and environmentally friendly. Nevertheless, the efficiency of the process is too low for the technology to be economically sound. One of the barriers of this process is the rapid recombination of photo-generated electron/hole pairs. To alleviate these deficiencies, titanium dioxide is modified by means of addition of metal or anion [1].

The photo-excited electrons can be transferred from conduction band of titanium dioxide to metal particles deposited on the surface of titanium dioxide, while photo-generated holes in the valence band remain on the titanium dioxide. These activities greatly reduce the possibility of electron-hole recombination, resulting in efficient separation of charge carriers and better photocatalytic reactions. In this work, we synthesized titanium dioxide via a sol-gel method and loaded a combination of two metals. The catalysts were employed in photocatalytic splitting of water.

Materials and Methods

Titanium dioxide was synthesized a sol-gel method [2]. First, titanium isopropoxide was mixed with ethanol, water, and nitric acid at room temperature while being stirred. The resulting titanium dioxide sol was dried at 100 °C for 24 hours and was calcined at 350 °C for one hour. After the calcination, chromium was deposited by incipient wetness impregnation technique along with either platinum or rhodium. The precursors used for Cr, Rh, and Pt were $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Na}_3\text{RhCl}_6 \cdot 2\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$, respectively. The catalysts were dried at 100 °C for 24 hours and were calcined under air flow at the rate of 6 mL/min at 300 °C for two hours.

The photocatalytic activity measurement was performed over 0.3 g of catalyst. The catalyst was suspended in a solution of water and methanol in the 50 mL vertical tubular batch reactor made of Pyrex glass. The volume ratio of water to methanol is 4:1. Ultra high purity argon was used to purge the reactor for two hours so as to remove hydrogen from inside the reactor prior to each run. The reactor was irradiated by eight black light bulbs (Philips Actinic blue 20W). The samples were taken from void space above the solution every 30 minutes until the experimental time reached five hours.

Results and Discussion

XRD results indicate that TiO_2 composed of primarily anatase phase with a small amount of brookite and rutile present in some cases. The average crystallite size was approximately 6.2 nm. The crystallite size grew slightly upon the loading of the metals, probably due to the calcination performed after metal deposition.

Photocatalytic activities of doped titanium dioxide were quantified by the amount of hydrogen gas produced in the photoreactor. From Fig. 1, titanium dioxide loaded with 0.05 wt% Cr possessed the highest activity. This result agreed with result from photoluminescence measurement. The photocatalysts with high activities had low photoluminescence signals (i.e. slow recombination rate of the photogenerated electron-hole pair). For TiO_2 that was loaded with two metals, the highest photocatalytic activities was obtained with TiO_2 with 0.01 wt% Cr and 1 wt% Pt (or Rh). These samples also had the lowest photoluminescence signals among the catalysts in the same series. These results suggest photocatalytic activity of the catalyst is influenced by the recombination rate of electron/hole pair [1,3-4].

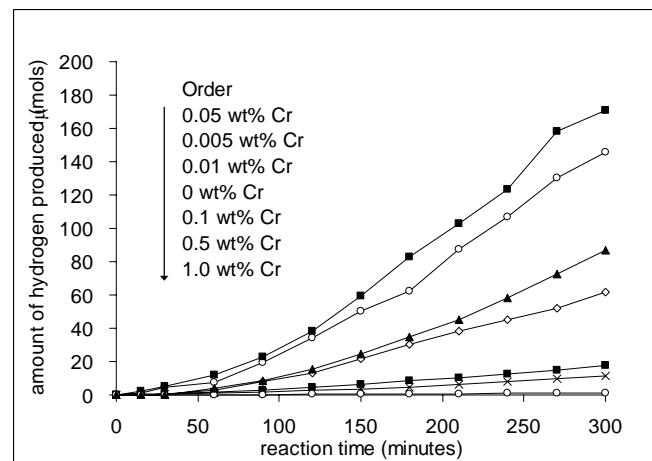


Figure 1. Evolution rate of hydrogen gas from photocatalytic water splitting over TiO_2 with various Cr loading

Significance

The activity of TiO_2 in photocatalytic water splitting can be enhanced by addition of Cr and Pt (or Rh).

References

1. Ni, M., Leung, M.K.H., Leung, D.Y.C. and Sumathy, K. *Renew. Sust. Energ. Rev.* 11, 401 (2007).
2. Dagan, G. and Tomkiewicz, M. *J. Phys. Chem.* 97, 12651 (1993).
3. Zhu, J., Deng, Z., Chen, F., Zhang, J., Chen, H., Anpo, M., Huang, J. and Zhang, L. *Appl. Catal. B-Environ.* 62, 329 (2006).
4. Sreethawong, T., Suzuki, Y. and Yoshikawa, S. *Int. J. Hydrogen Energ.* 30, 1053 (2005).