IN SITU TIME RESOLVED SPECTROSCOPIC STUDIES OF METAL OXIDE PHOTOCATALYSTS FOR WATER SPLITTING

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Summary

Photocatalysis involves phenomena occurring at high time resolutions under unique conditions. Studies probing these time scales under relevant *in situ* conditions will lead to improved photocatalysts. Thus, catalysts containing 1-60 wt% TiO_2/SiO_2 were dehydrated under flowing 10% O_2 at 400 ^oC. Laser excitation was used and the lifetime of catalysts' excited states was determined *in situ*. H_2 production was monitored for the water splitting reaction in a UV-irradiated reactor. This methodology will be applied to novel bulk metal catalysts (TaON, $SrTiO_3$, GaN:ZnO). Intermediate and product formation during water splitting will be monitored using ATR FT-IR during transient UV irradiation.

Keywords

Hydrogen Production, Rational Design of Catalysts

Introduction

The goal of this study was to examine the photocatalysis of well-defined TiO_2 nanodomains supported on SiO_2 and to determine their structure-photocatalytic relationships. This methodology will then be extended to the state-of-the-art, novel bulk metal catalysts that are currently the yielding the best results for hydrogen production during photocatalytic splitting of H_2O. Understanding how catalytic structure relates to photocatalytic properties (photoluminescence, electron excitation, intermediate and product formation) in the TiO_2/SiO_2 catalysts of known structure will lead to more rapid development in the understanding of the novel catalysts. Furthermore, the ability to probe reactions *in situ* and at time resolutions relevant to the photo-excitation process will yield deeper insight into the reaction mechanism and ultimately allow for improved rational design of future photocatalysts for water splitting.

Experimental and Results

1-60% TiO_2/SiO_2 (x% TiO_2/SiO_2) catalysts were synthesized by incipient wetness impregnation of Ti-isopropoxide into the SiO_2 support (Cab-O-Sil), with drying followed by calcination at 500 ^oC. The molecular and electronic structures of the TiO_2 nanodomains were determined with *in-situ* Raman, UV-vis spectroscopy, EXAFS, and atomic absorption spectroscopy. The nature of the TiO_2 nandomain was found to change in the following manner as a function of the titania loading: isolated site (1% TiO_2/SiO_2) < polymeric chain (12% TiO_2/SiO_2) < 2D sheets (20-40% TiO_2/SiO_2) < 3D nanoclusters (60% TiO_2/SiO_2).[1,2]

Studies were conducted using *in-situ* photoluminescence (PL) spectroscopy to determine if the type of TiO_2 nanodomain present in the sample affects the emission spectrum. Samples were dehydrated under flowing 10% O_2 at 400 ^oC in order to avoid the quenching effect of water on PL emission. Spectra were collected on a Jobin-Yvon Fluorolog system which also allowed collection of PL maps. Studies were also conducted *in-situ* using a 76 MHz pulsed tunable laser, tuned to 400 nm excitation, and a gated Picostar detector with time resolution in picoseconds. The same dehydration procedure was used and the lifetime of excited states of the various nano-domain containing samples was determined by changing the delay time of the detector. Production of H_2 was monitored by gas chromatography for the water splitting reaction in a UV irradiated batch reactor at room temperature.

In situ attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy was down using a Thermo Nicolet 8700 equipped with a Harrick Horizon ATR cell with a ZnSe crystal. Thin films of catalysts were coated on the crystal and spectra were obtained under UV irradiation.

The results initially show several main trends. The PL spectra show that as the percent loading of titania increases, the peak emission occurs at higher wavelength excitation, meaning those samples are more easily excited with lower energy irradiation. However, the excitation lifetime measurements indicate that the lower percent loading samples (those containing isolated TiO_4 sites) have slower decay rates, meaning there is a greater opportunity for reactions to occur. This finding offers an explanation for the observed higher production of H_2 during water splitting by the lower titania loading catalysts when normalized by exposed Ti site (Figure 1).

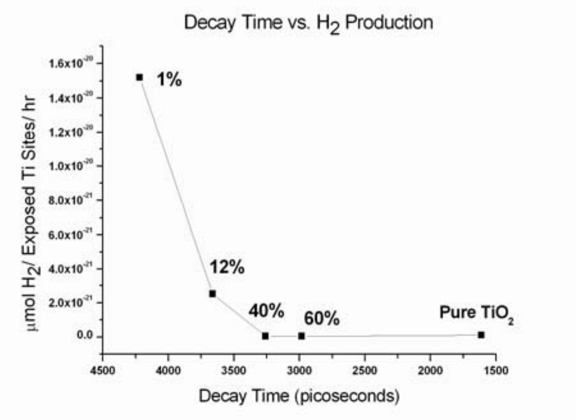

Figure 1: Hydrogen production rate for water splitting normalized by exposed Ti site as a function of the decay time for x% TiO_2/SiO_2

This methodology will be applied to novel bulk metal catalysts (TaON, $SrTiO_3$, GaN:ZnO). Intermediate and product formation during water splitting will be monitored using ATR FT-IR during transient UV irradiation in an attempt to further understand these superior water splitting catalysts

References

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