EFFECT OF METALLIC TYPES ON 2-PROPANOL PHOTOOXIDATION FOR PHOTOINDUCED HYDROGEN FORMATION

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Abstract

M/TiO_2 photocatalyts (M=Ag, Au, Cu, Ir, Ni, Pd, Pt, Ru and Rh), (metal content 0.0008 mmol/200mg TiO_2) were synthesized by a photodeposition method in the presence of sacrificial agent (2-propanol) under UV irradiation. Bare TiO_2 and M/TiO_2 anatase samples were subsequently used for photoinduced hydrogen (H_2) formation. The generation of propane and propene from the photoassisted dehydration of 2-propanol was studied over various metallic types to classify the metal behavior. The results show that H_2 chemisorptions energy (ΔE_H) of metal from Norskov principal has influence for H_2 production and propene hydrogenation. Pt, Pd, Rh and Ir revealed high amount of H_2 due to thermal-neutral energy. Propane was produced on Pt, Ru and Pd. On the other hand, propene was mainly generated from unreactive metals, with high ΔE_H , including Au, Cu, Ag.

Keywords

Photodeposition, Photo-oxidation, 2-propanol, Metal behavior , H_2 production, TiO_2 anatase

Introduction

The modification of TiO_2 with noble-metal cocatalyst can enhance the overall photocatalytic efficiency by acting like an electron sink to separate the electrons and holes, resulting in increasing the overall photoredox reaction (Yuan et al., 2014).

Therefore, the metal photodeposition is considered for preparing the heterogeneous catalyst. Metal-ions are reduced by photogenerated electrons on the semiconductor. This method can be enhanced by adding aqueous alcohol as sacrificial electron donor. Most of research have been focused on the net photoefficiency or the effect of physical properties for the photoactivity (Melián et al., 2013; Ohyama et al., 2011). However, the metal behavior for H_2 formation on alcohol photooxidation is less understood.

Here, a metal-photodeposition method was proposed to access the effective noble-metal nanoparticles through monitoring the amount of evolved H_2. Metal precursors including Ag, Au, Cu, Ir, Ni, Pd, Pt, Ru and Rh were applied on TiO_2 anatase to study photocatalytic H_2 generation in UV irradiation with 2-propanol as sacrificial agent. The generation of carbon products, such as propane and propene was evaluated to categorize the role of metals.

Experimental

Photodeposition of metal on TiO_2 anatase was performed on a photoreactor. $H_2Cl_6Pt.6H_2O$, $PdCl_2$, $RhCl_3$, $IrCl_3$, $HAuCl_4$, $Cu(NO_3)_2.3H_2O$, and $Ni(NO_3)_2.6H_2O$ were used as metal precursor of Pt, Pd, Ir, Rh, Au, Cu and Ni, respectively. 200 mg TiO_2 was dispersed in 50 mL of aqueous 2-propanol solution (50 vol%) in the reactor and purged with Ar. Addition of metal solution was gradually

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injected into catalyst suspension. Subsequently, the photocatalytic reaction was carried out by illuminating the suspension with a 125-W mercury lamp while continuous stirring. Analysis of the H_2 and oxidized products evolution were analyzed by Gas Chromatography with Thermal Conductivity Detector. The precipitate was centrifuged and washed repeatedly with distilled water and then dried at 110°C overnight under air.

Results and Discussions

Effect of metallic type-TiO_2 on photooxidation of 2-propanol

Fig. 1 shows the products, including H_2, propane and propene produced from the photoreaction. The results exhibit that Pt/TiO_2 produced the highest amount of H_2 rate following by Pd, Rh and Ir, respectively. Propane was produced only with Pt at about 1.0 µmol hr^{-1}. On the other hand, propene was mainly generated over Au, Cu and Ag. However, propane and propene were also observed in other metals with very small quantity. As Norskov principal, Pt, Pd, Rh and Ir have a thermal-neutral of H_2 chemisorption energy (ΔE_H), resulting in produce high amount of H_2 as shown in Fig. 2. The Classification of metal behavior was demonstrated in Table 1. Propene was produced over Ni with strong M-H bonding and Cu, Ag, Au as unreactive metals with weakness of M-H bonding (Nørskov et al., 2005).

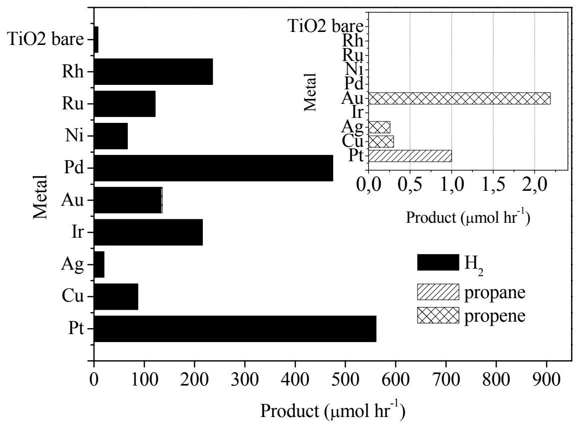

Figure 1. The metallic behavior on photo-oxidation of 2-propanol for H_2 generation

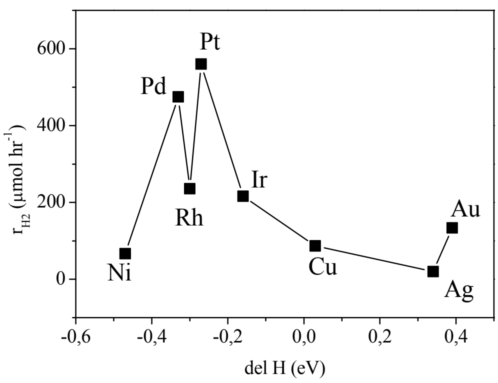

Figure 2. H_2 rate over different metals plotted as a function of ΔE_H

Table 1. Classification of metal behavior on photooxidation of 2-propanol for H_2 photogeneration

Classification	Metal
A) $CH_3-CHOH-CH_3 \xrightarrow{M/TiO_2} CH_3-CO-CH_3+H_2$	Sn, Ir
B) $CH_3-CHOH-CH_3 \xrightarrow{M/TiO_2} CH_3-CO-CH_3+H_2$; $\xrightarrow{M/TiO_2} CH_2=CH-CH_3+H_2O$	Cu, Ag, Au, Ni
C) $CH_3-CHOH-CH_3 \xrightarrow{M/TiO_2} CH_3-CO-CH_3+H_2$; $\xrightarrow{M/TiO_2} CH_2=CH-CH_3+H_2O$ $\downarrow +H_2$ $CH_3-CH_2-CH_3$	Pt, Ru, Pd

Conclusions

The H_2 chemisorption energy (ΔE_H) has influence in H_2 production and propene hydrogenation reaction. The metals with balancing of ΔE_H (Pt, Pd, Rh and Ir) reveal high amount of H_2. The photooxidation of 2-propanol for H_2 evolution over different metallic types can be classified for three proposed mechanism pathway. Propene generation was mainly found in unreactive metals, Au, Cu, Ag.

Acknowledgements

The authors would like to thank Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program (Grant no. PHD/0371/2552), The french government and Centre National de la Recherche Scientifique (CNRS), France for their financial supports.

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