Engineering Photocatalytic Reaction Tests in Liquid Media

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Abstract: Mass transfer limitations are frequently overlooked in liquid phase photocatalytic reactions. Due to the low temperatures involved in photocatalysis, the reaction kinetics are assumed to be slow enough not to be influenced by the diffusional and film mass transfer resistances. A systematic study presented here revealed mass transfer limitations during photocatalytic hydrogen production tests in the liquid phase. The influence of the parameters such as; temperature, stirring rate and residence time of the produced gas in solution were investigated for photocatalytic hydrogen evolution reaction in water/methanol mixture. Observed reverse relationship between the H_2 residence time and H_2 evolution rates reveal significant mass transfer limitation and back-oxidation effects.

Keywords: Photocatalysis, water splitting, TiO_2.

1. Introduction

Photocatalytic water splitting is receiving much attention because of its key role in artificial photosynthesis systems as well as its potential as a clean energy source. Photocatalytic water splitting is often studied in liquid H_2O media with a photocatalyst (that would utilize light to create electron/hole pairs and run photocatalytic reduction/oxidation reactions with addition of precious (Pt) and non precious (Cu) metals) and a sacrificial reagent (to promote charge separation). Ever since the photoelectrochemical water splitting by a TiO_2 electrode reported by Fujishima and Honda [1], TiO_2 photocatalyst is frequently used in photocatalytic water splitting reactions due to the low cost, low toxicity and chemical stability [2]. In order to improve photocatalytic hydrogen production of TiO_2 catalysts, sacrificial reagents such as methanol are also often used, which are believed to prevent charge recombination and complete the redox cycle by being oxidized by the photogenerated holes [3].

Unstandardized illumination intensities, catalyst concentration and reactor design renders proper comparison of photocatalytic rates impossible [4]. In order to understand effect of reaction conditions and be able to report activity test results without any limitations on kinetics, it is required to take a closer look into reaction media and transport phenomena realized in that media. In this report, a systematic study on photocatalytic hydrogen evolution from water/methanol mixture using Pt/TiO_2 is conducted to reveal mass transfer limitation effects on reaction rates. Reaction parameters such as stirring rates, H_2 residence times and temperature are investigated in liquid phase photocatalytic reaction tests.

2. Experimental

0.5 and 1 wt % Pt/TiO_2 were prepared by incipient wetness method using Degussa P25 and $Pt(NH_3)_4Cl_2 \cdot H_2O$ (Alfa Aesar) as the Pt source. Effect of stirring rate, H_2 residence time and temperature experiments were conducted in a batch Pyrex glass reactor (with a diameter of 5 cm and height of 18 cm) containing 250 ml de-ionized water and 2 ml methanol mixture with 0.25 g of catalyst. In H_2 residence time experiments, the volume of de-ionized water was changed to 62.5, 125 and 187.5 ml (while keeping the catalyst concentration as 1 g/L for each experiment [5]) in order to alter the residence time of the product H_2 in liquid media. 100 W UV lamp (365 nm) is used as the light source and batch testing of the catalysts were performed while the reaction mixture is stirred with a magnetic stirrer. The gas samples were withdrawn from the gas volume on top of the reaction mixture and analyzed using a gas chromator (HP 4890) with TCD and an Alltech Porapak Q column.

3. Results and discussion

Photocatalytic hydrogen evolution experiments with 0.5 wt % Pt / TiO_2 were performed at different stirring rates to investigate presence of mass transfer limitations in liquid media. 350 and 900 rpm stirring rates resulted in 620 and 870 µmol H_2 g_{cat}^{-1} h^{-1} H_2 evolution rates respectively, indicating reduction in the boundary layer thickness with increasing stirring rate (Figure 1.a). Residence (hold-up) times of H_2 product in liquid water and catalyst slurry was tested by changing the liquid volume while keeping the catalyst/water ratio constant. Figure 1.b shows the decreasing H_2 evolution rates on a per gram basis 2077 µmol H_2 g_{cat}^{-1} h^{-1} to 870 µmol H_2 g_{cat}^{-1} h^{-1} with increasing liquid volume (250 ml to 62.5 ml). When the H_2 evolution rates are not normalized with respect to the catalyst weight, evolved H_2 amounts into the gas phase were similar to each other, which indicates presence of mass transfer limitations at the gas-liquid interface. Decreasing H_2 evolution rates on a per gram basis, on the other hand, could be explained with increased back oxidation of H_2 (into H_2O) with increased interaction of H_2 with other catalyst particles.

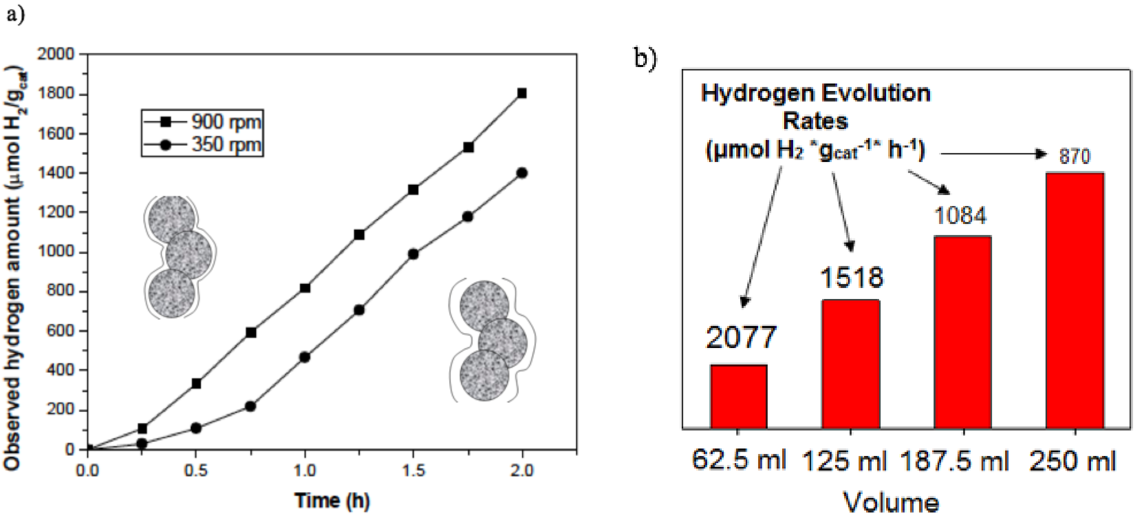

Figure 1. Effect of a) stirring rate and b) liquid volume on photocatalytic H_2 evolution rates using 0.5% Pt/ TiO_2

Finally, when the effect of temperature on reaction rates was studied with reaction temperatures of 32, 65, 77, 85 °C, a proportional increase in rates (782, 1058, 1241 and 1563 µmol H_2 $*g_{cat}^{-1}*h^{-1}$ respectively) was observed with increasing temperature. Apparent activation energy is calculated as 12 kJ/ mol, the magnitude of which also indicates presence of mass transfer limitations rather than catalytic effects.

4. Conclusions

Having a better insight into transport processes in liquid phase photocatalytic reactions does not only contribute to more accurate reaction rate mechanisms but also would promote systematic design of the processes when the photocatalytic systems are ultimately used in large scale. In this report, mass transfer limitations were observed to inhibit observation of kinetic rates in photocatalytic reaction tests performed in liquid media. It can be inferred from the results that the photocatalytic reactors should be designed to achieve minimum solid-liquid and liquid-gas boundary layer thicknesses and minimum path length for faster product diffusion to the gas volume. More effective ways of transferring reaction products away from the catalyst particles should be designed to minimize the back-oxidation reactions and maximize the photocatalytic rates.

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