

Photocatalytic Hydrogen Production using PD doped CDS

Thangam N¹, Lavanya C², Ezhilarasi E³, Ahila Devi E⁴

^{1, 2, 3}Assistant Professor, PERI Institute of Technology

⁴Assistant Professor, St. Joseph's College of Engineering

Abstract - We report on the photocatalytic hydrogen production of Pd/CdS photocatalyst using an unconventional batch process with passive mixing. The catalyst has been characterized using X-ray diffraction and Scanning electron microscope. The result reveals that particle size 3.7 μm . The feasibility studies were carried out by varying the treatability parameters and it was found that maximum hydrogen production occurs at their respective optimum values. The highest volume of hydrogen produced after optimization is 80 mL at 250 W/m² light intensity, 0.2 M sulphide concentration, 0.2 M sulphite concentration, 10 pH, 300 mL photolyte volume, 0.5g catalyst dosage and 30mL/hr recycle flow rate. Close investigation revealed that this high production is due to the optimization of parameters coupled with batch process with passive mixing. The catalyst also has proved to be photo stable for up to 5 trials

Index Terms - Batch process, Photocatalyst, Passive mixing, Photostable.

I. INTRODUCTION

Hydrogen has gained importance as a clean fuel in the energy economy recently. The idea is to obtain a renewable solution to supply this fuel in sufficient quantities and photocatalytic splitting of hydrogen sulphide waste stream have been garnering attention in this area. H₂, as an energy carrier with a high calorific value of 122 kJ g⁻¹ (2.75 times greater than hydrocarbon fuels) is clean and renewable [1]. Photocatalysis was carried out using Pd-Cr₂O₃ nanocomposite cocatalyst which has been reported earlier in achieving high photocatalytic efficiencies greatly due to the doping of CdS with Pd and Cr [2]. The rate of hydrogen production depends on the type of reactor used as its main purpose is to facilitate photocatalysis using a catalyst. Batch process with passive mixing was found out to have good

photocatalytic hydrogen production [3]. This method of batch process with passive mixing omits the need for a magnetic stirrer to circulate the catalyst that have settled at the bottom in conventional batch processes. There is no formation of dead zones where some amount of the catalyst settles down and remains stagnant.

II. MATERIALS AND METHOD

2.1 Preparation of photocatalyst

For the synthesis of the photocatalyst Palladium chloride (PdCl₂, 99.99% purity), Chromium nitrate (Cr (NO₃)₃.9H₂O, 98% purity), Sodium borohydride (NaBH₄, 98%) and Cadmium sulphide (CdS) were obtained from Merck. All chemicals were used as received without further purification. Then a calculated amount of CdS was added based on the experimental requirements and the solution is stirred vigorously for 20 minutes.

2.2 Photocatalytic reaction

For carrying out the reaction in a batch process with passive mixing, an airtight reactor made out of Borosilicate® glass was fabricated with a volume capacity of 500 mL (Fig. 1). The reactor has three openings, one for photolyte entry, photolyte exit and gas exit respectively. The photolyte exit is placed at the bottom of the reactor which is tapered so that the photocatalyst loaded into the reactor will also exit along with the photolyte and go into passive circulation. All of the openings have a valve attached and circulation is achieved using a peristaltic pump [3]. The gas is collected in an inverted water displacement apparatus where there is a septum through which the gas can be sampled. Gas chromatography analysis was carried out to test the presence of hydrogen in the gas sample.

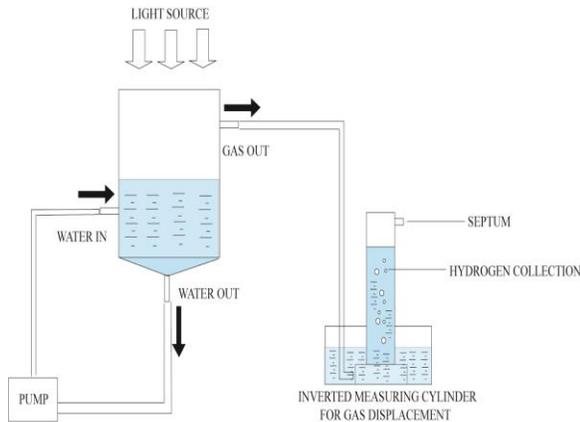


Fig. 1 - Schematic diagram showing photocatalytic hydrogen production from H₂S.

III. EXPERIMENTAL RESULTS

3.1 XRD analysis

The crystal structure of the catalyst was determined by the XRD analysis graph shown in Fig. 2. The three peaks correspond to Cd and Pd respectively. The particle size was determined using Scherrer's equation and was found to be 3.7 μm. The peaks occur at 23°, 45°, and 55° respectively.

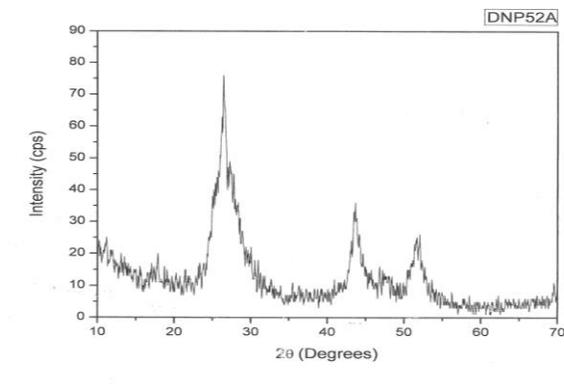


Fig. 2-XRD pattern

3.2 SEM analysis

To determine the surface morphology of the catalyst, SEM analysis was done (Fig. 3). From the image the aggregate of CdS particles can be seen along with Pd on their surface. The size of the particles is determined to be in the range of 4-5 μm coinciding with the XRD result. From this image, the colloidal nature of the catalyst co doped with Pd can be observed. Uniform particle size can be seen in the SEM image suggesting that contact surface for photocatalysis plays a very influential role.

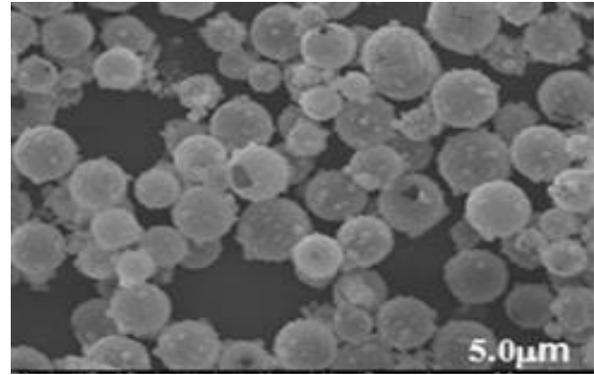


Fig. 3-SEM analysis

IV. PHOTOCATALYTIC HYDROGEN PRODUCTION

The whole setup is irradiated with 300W sodium halogen lamp and prior to the start of the experiment; nitrogen gas was purged into the photolyte solution in the absence of catalyst and light in order to create an inert atmosphere. The volume of hydrogen was measured at every 15-minute interval. The experimental procedure involves running a series of cycles in which one parameter is varied while the others are kept constant in order to determine its optimum value. The experiment was carried out by varying the treatability parameters and arriving at optimized values. In order to test the presence of hydrogen, the gas was sampled and gas chromatography analysis was carried out.

The photocatalytic hydrogen production of Pd-Cr₂O₃/CdS was first assessed by varying the catalyst dosage and keeping the pH, sulphide concentration, sulphite concentration, volume and flow rate at 10, 0.1M, 0.1M, 300mL and 30% respectively (Fig.4). The optimum catalyst dosage was found to be at 0.5g and above that the yield is low which is caused due to shadowing and screening effect of the catalyst [5][6].

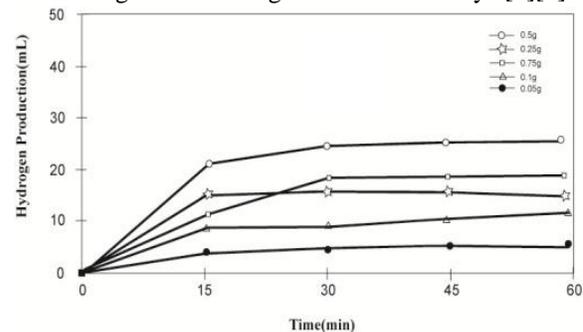


Fig. 4-Effect of catalyst dosage

The effect of sulfide ion concentration on the production of hydrogen was evaluated by varying the concentration of sulphide while the other parameters were fixed along with catalyst dosage at 0.5g indicated in Fig. 5. The pH, catalyst amount, sulphite concentration, volume and flow rate at 10, 0.5 g, 0.1M, 300mL and 30 L/h respectively. The maximum hydrogen yield was found to be at 0.2M and the decreasing trend in hydrogen volume was due to the fact that polysulfide ions were formed as the sulfite ion concentration increases and deactivate the active sites of the catalyst. Furthermore the number of active sites is constant whereas the number of absorbed sulfide ions increased and no possible increase in photocatalysis could be observed. Higher concentration of photolyte can cause increase in viscosity hence obstructing the detachment of hydrogen bubbles from the catalyst surface thereby lowering the hydrogen production [7][8][11].

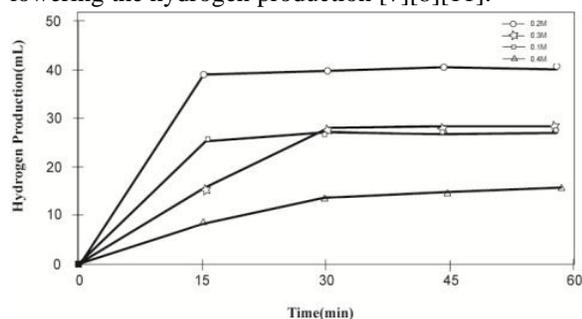


Fig. 5-Effect of sulphide concentration

In order to test the photolytic activity of the catalyst based on the sulphite concentration, the sulphite concentration was varied with the other parameters like pH, catalyst amount, sulphide concentration, volume and flow rate kept at 10, 0.5 g, 0.2M, 300mL and 30 L/h respectively indicated in Fig. 6. 0.2M concentration of Na₂S showed maximum hydrogen production and decreased activity was observed as the concentration of sulphite increases due to the change in the pH contributed by higher concentration of sulphite.

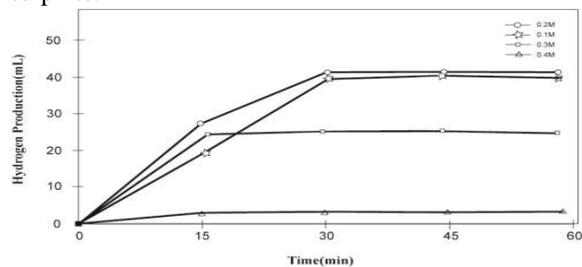


Fig. 6-Effect of sulphite concentration

The effect of pH was evaluated by varying the pH while keeping sulphide concentration, sulphite concentration, volume, flow rate and catalyst dosage constant at 0.2 M, 0.2 M, 300mL and 30 L/h respectively shown in Fig. 7. At pH 10, the optimum hydrogen production was observed. At higher pH, OH⁻ from the aqueous solution interrupt the photocatalytic activity and at lower pH the S²⁻ gets protonated and this is the reason for low hydrogen evolution[6]. The increase in hydrogen evolution was due to the increase in dissociation of HS⁻ to S²⁻. At a higher pH, more number of OH⁻ ions are produced which interact with photogenerated H⁺ to form water hence reducing the hydrogen production.[9]

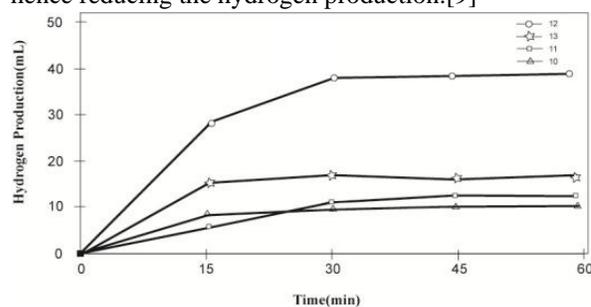


Fig. 7-Effect of pH

The photocatalytic activity of the catalyst was then assessed for volume variation and the working volumes of 200mL, 300mL and 400mL respectively. The pH, catalyst amount, sulphite concentration, sulfide concentration and flow rate were kept at 10, 0.5 g, 0.2 M, 0.2 M and 30 L/h respectively. The experimental conditions are indicated in Fig. 8. At 300 mL maximum hydrogen production was observed and beyond that it reduces due to increase in photolyte depth which reduces the penetrating power of the illuminating source.[10]

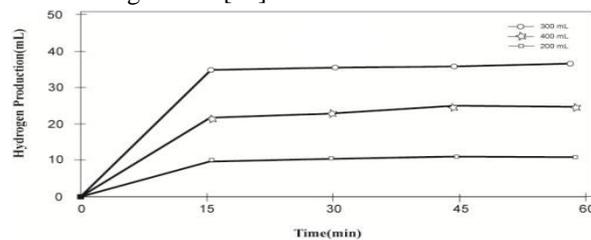


Fig. 8-Effect of volume

The photostability of the catalyst was then evaluated by filtering the catalyst followed by washing and air-drying it. This is done to remove the clogged sulfide ions on the active sites of the catalyst. The experiment was carried out seven times and there was no yield in the 6th and 7th trial (Fig. 9). This shows that there might

be some loss in the catalyst while washing and inability to clear the clogged active sites completely. The operating parameters like pH, catalyst amount, sulphite concentration, sulphide concentration, volume and flow rate were maintained at 10, 0.5 g, 0.2 M, 0.2 M, 300mL and 30 L/h respectively.

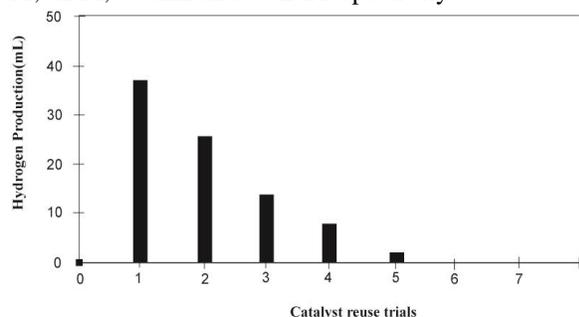


Fig. 9-Effect of catalyst reuse

V.CONCLUSIONS

Photocatalytic hydrogen production was carried out from H₂S and the operating parameters were varied to arrive at their optimum value. 80 mL of hydrogen was the optimized production capacity if the catalyst obtained at 250 W/m² light intensity. The presence of doping with Pd and CdS has greatly increased the efficiency of the catalyst. To ensure maximum employability of the catalyst, batch process with passive missing was used so that the catalyst was circulated evenly. The particle size of 3.7 μm inferred from XRD analysis also corroborates our result indicating the inverse proportionality of particle size and hydrogen production. Our results also highlight the importance of optimizing the operating variables in order to achieve higher H₂ production.

REFERENCE

[1] R.S. Besser, P.J. Lindner, Microplasma reforming of hydrocarbons for fuel cell power., *Journal of Power Sources*, Vol. 196 (2011) 9008-9012.

[2] W. Yao, C. Huang, N. Muradov, A. Raissi, A novel Pd-Cr₂O₃/CdS photocatalyst for solar hydrogen production using a regenerable sacrificial donor, *international journal of hydrogen energy*, Vol. 36 (2011) 4710-4715.

[3] C. Huang, W. Yao, A. Raissi, N. Muradov, Development of efficient photoreactors for solar hydrogen production, *Solar Energy*, Vol. 85 (2011) 19–27.

[4] S.W. Chen, K. Huang, J.A. Stearns, Alkane thiolate-protected palladium nanoparticles, *Chemical Mater*, Vol. 12 (2000) 540-547.

[5] A.Ueno, N. Kakuta, K.H. Park, M.F. Finlaysou, A.J. Bard, A. Campion, Silica supported ZnS-CdS mixed semiconductor catalyst for photo generation of hydrogen, *Journal of Physical Chemistry*, Vol. 89 (1985) 3828-3833.

[6] J. Bangun, A. A. Adesina, The Photodegradation Kinetics of Aqueous Sodium Oxalate Solution using TiO₂ Catalyst., *Applied Catalysis A-General*, Vol. 175 (1998) 221-235.

[7] N. Bao, L. Shen, T. Takata, K. Domen, Self-Templated Synthesis of Nanoporous CdS Nanostructures for Highly Efficient Photocatalytic Hydrogen Production under Visible Light, *Chemical Matter*, Vol. 20 (2008) 110–117.

[8] V.Preethi, S.Kanmani, Photocatalytic hydrogen production over CuGa₂-xFe_xO₄ spinel, *international journal of hydrogen energy*, Vol. 37 (2012) 18740-18746.

[9] N. Strataki, M. Antoniadou, V.Dracopoulos, P. Lianos, Visible-light photocatalytic hydrogen production from ethanol–water mixtures using a Pt–CdS–TiO₂ photocatalyst, *Catalysis Today*, Vol. 151(2010) 53–57.

[10] M. Faramarzpour, M.Vossoughi and M. Borghei, Photocatalytic degradation of furfural by titania nanoparticles in a floating-bed photoreactor, *Chemical Engineering Journal*, Vol. 146(2009) 79–85.

[11] R. Priya and S. Kanmani, Solar photocatalytic generation of hydrogen under ultraviolet-visible, light irradiation on (CdS/ZnS)/Ag₂S + (RuO₂/TiO₂) photocatalysts, *Bulletin of Materials Science*, Vol. 33(2010), 85-88.