

# Hydrogen generation by laser transformation of methanol using n-type WO<sub>3</sub> semiconductor catalyst

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## Abstract

A laser based method for photocatalytic reforming of methanol at ambient temperature using n-type WO<sub>3</sub> semiconductor catalyst has been investigated for the first time. A non-explosive mixture of gases containing hydrogen, carbon monoxide and methane with high concentration of hydrogen was observed. The amount of catalyst and laser energy was optimized for maximum yield of hydrogen. The effect of aging of the catalyst proved that there was no deactivation of catalyst; instead, an increase in the activity of the catalyst was observed. The effect of addition of water to methanol in various proportions as feedstock on the hydrogen yield during this laser induced photocatalytic process was also studied.

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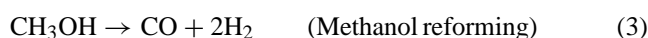
**Keywords:** Photocatalysis; Methanol; Hydrogen; WO<sub>3</sub>; Clean fuels; Fuel cells; Lasers; Laser applications; Renewable energy sources

## 1. Introduction

Hydrogen is considered to be as an ideal and clean fuel for power generation systems with virtually zero emissions of air pollutants. It is the best candidate for replacement of conventional fossil fuels [1]. When reacted with oxygen, hydrogen produces only water as a by-product. Hence, hydrogen is an environmentally friendly fuel and can be used in fuel cells to power automobiles or to provide electricity and thermal energy. Research in the Hydrogen Generation and Utilization is important in order to reduce the greenhouse gas emissions. This is done by developing new ways to produce hydrogen and by enhancing its utilization in fuel cells.

Presently, the major processes for hydrogen production are steam reforming of natural gas, steam reforming of methanol, hydrogen from chemical industry sources (ammonia plants), direct methanol base fuel cells, gasification of coal, biomass and electrolysis of water [2–19].

Steam reforming of natural gas and methanol are the most widely used industrial procedures for the production of hydrogen at large scale. Following are the important processes for production of hydrogen on large scale:



The natural gas and methanol reformers currently in use are usually fixed-bed catalytic reactors [4] that suffer from a number of inherent problems. They operate at extreme conditions of temperature and pressure, with the requirement of special catalysts. Hot and cold spots are commonly encountered in the catalyst bed that results in poor performance over longer period of time [5,6]. These types of reactors typically have poor response to transients and require a prolonged time to reach working temperature from cold start-up.

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Fuel cells are being developed for applications in the transportation and the distributed power generation sectors due to energy, security, environmental and economical benefits. Being a clean and efficient source of electrical power for both mobile and stationary applications [1], fuel cells based on hydrogen are in high demand. Meanwhile, especially for mobile applications, methanol has been identified as a suitable (transportable) fuel that can be easily processed on board to hydrogen-rich gas for the solid polymer fuel cell (SPFC), the main candidate for transport applications [3]. Although fuel cells are considered as the efficient source for power generation, the efficient supply of pure hydrogen or hydrogen rich feed from methanol and poisoning are issues that still hinder their full-scale commercial use. The production of hydrogen from the gasification of coal, biomass and solid waste is not efficient based on cost to production ratio. The same is true for the production of hydrogen by water electrolysis.

Research efforts have focused recently to develop photochemical methods for the production of hydrogen. Heterogeneous photocatalysis is one of the promising approaches for production of hydrogen [18–28]. This technique is based upon the photo-excitation of a semiconductor catalyst, with the absorption of photons of energy greater than the band gap, leading to the formation of oxidation (photogenerated holes,  $h_{vb}^+$ ) and reduction (photogenerated electrons,  $e_{cb}^-$ ). The potential of the valance band ( $V_{vb}$ ) and conduction band ( $V_{cb}$ ) edges play a vital role in predicting the type of reactions that can occur at the surface of the semiconductor photocatalyst. The magnitude of these potentials depends upon the nature of the solvent and pH of the system. Another important factor that makes photocatalysis productive is the ability of the solvent to suppress the unwanted electron–hole recombination either by capturing valance band holes or conduction band electrons. Water is the most commonly used solvent in photocatalysis and most readily available feedstock for the photocatalytic hydrogen production but the main problem associated with the production of hydrogen through water splitting are the formation of explosive mixtures of hydrogen and oxygen and relatively low yield of hydrogen. Organic compounds, primarily oxygenated hydrocarbons such as methanol, are an alternative source. The saturated hydrocarbons and stable aromatic compounds, due to their stable electronic configuration and non-polar nature, are unable to suppress the electron–hole pair recombination. Methanol is liquid at room temperature with high carbon to hydrogen ratio compared to water and is considered an organic counterpart of water. Due to the presence of polarity and its ability to donate the lone pairs of electrons, it can be used as an alternative for water. The above-mentioned properties make it quite suitable for the photocatalytic production of hydrogen. Discovery of novel processes for producing hydrogen may greatly advance the cause of achieving a clean-burning economy based on hydrogen. It is believed that the use of hydrogen as fuel offers the potential to reduce our current dependence on fossil fuels in the future.

In the present work, we developed a novel process for the production of hydrogen gas from methanol. The process is based on photocatalytic splitting of methanol in the presence of a semiconductor photocatalyst catalyst,  $WO_3$ , using UV laser as a light source. A laser beam of 355 nm and a specially designed reaction cell was employed for this purpose. The major reaction product, i.e. molecular hydrogen ( $H_2$ ) and other gases, such as  $CH_4$  and  $CO$ , were observed at a high reaction rate at room temperature. It is worth mentioning that a complete transformation of liquid methanol was observed in gaseous products without the formation of any major product in the liquid phase. The traces of some products such as  $CH_3COOH$ ,  $(CH_3O)_2CO$  were also observed.

## 2. Experimental details

The setup employed in this study has been described in detail in our earlier publications [25–28]. However, a brief description is mentioned here. To study the Photocatalytic splitting of methanol into hydrogen and other gaseous products, a Pyrex cell (35 mm diameter and 120 mm length), equipped with optical grade quartz windows for transmission of UV visible laser beam was designed and fabricated. The cell was equipped with ports and rubber septums for sampling. The important parameters which affect the hydrogen yield are the amount of the photocatalyst and laser energy. The dependence of hydrogen yield on these parameters was carefully studied. The optimization of the amount of catalyst was studied in the range of 50–2000 mg while laser energy was studied in the 20–300 mJ/pulse range. To study the photocatalytic conversion of methanol, the optimized amount of photocatalyst was suspended in 50 ml of methanol. The suspension was then irradiated with the optimized laser energy. All the experiments were performed in an argon environment. The evolved gases were analyzed by removing 100  $\mu$ l of gas samples from the dead volume of the photocatalytic reactor by using a gas tight syringe at regular time intervals. The samples were analyzed by using gas chromatograph (Shimadzu, Model GC-17) equipped with a 30 m molecular sieve 5A plot column and a TCD detector. A 355 nm laser beam, was generated from the third harmonic of a Spectra Physics Nd:YAG laser (Model GCR 250). The pulse width of the laser was  $\sim 8$  ns having a 10 Hz repetition rate. The laser beam was directed into the center of the reaction chamber using a set of mirrors and collimators. For all the measurements, the laser beam diameter was kept constant at 10 mm. This diameter of the laser beam was fixed to ensure the exposure of the same volume of the catalyst and to study the parametric dependence under the same photon flux. All the experiments were performed for a laser irradiation period of 90 min except for the laser energy dependence and catalyst particle density optimization experiments, which were performed for a period of 30 min. The effect of water addition on hydrogen production was studied by irradiating the mixtures of methanol under the same condition as pure methanol. The

methanol–water mixtures were prepared by adding different proportions of water in methanol. All the experiments were performed at room temperature and atmospheric pressure.

### 3. Results and discussion

The photocatalytic oxidation of methanol was studied by irradiating the suspension of methanol and  $\text{WO}_3$  with 355 nm laser radiation. It was noticed that the amount of hydrogen produced from methanol strongly depends upon laser energy, catalyst concentration in the fixed volume of methanol, laser beam diameter and stirring rate. A small change in these parameters affected the product yield significantly. As it was difficult to optimize all the parameters simultaneously, the two crucial parameters; i.e. laser energy and particle density, were optimized and the other two parameters, i.e. laser beam diameter and stirring rate were kept constant. The effect of focused laser beam was minimized by expanding the beam to a diameter of 10 mm.

#### 3.1. Optimization of photocatalyst particle density

The amount of catalyst was carefully optimized for maximum yield of hydrogen produced during the photocatalytic process. The hydrogen yield, for various concentrations of  $\text{WO}_3$  suspended in 50 ml of methanol and fixed laser energy of 150 mJ was measured for 30 min and is plotted in Fig. 1. A linear increase in amount of hydrogen produced can be noticed in the 100–500 mg range. Further increase in the amount of catalyst in the 600–1000 mg range, fails to enhance the yield of hydrogen proportional to the amount of catalyst. This trend indicates that the activity of the catalyst increases with the increase in particle density initially to a certain range, but as the stirring rate is kept constant, the number of particles exposed per unit area per unit time remains the same; further increasing the concentration of the catalyst does not affect the yield of hydrogen significantly beyond 500 mg. Based on

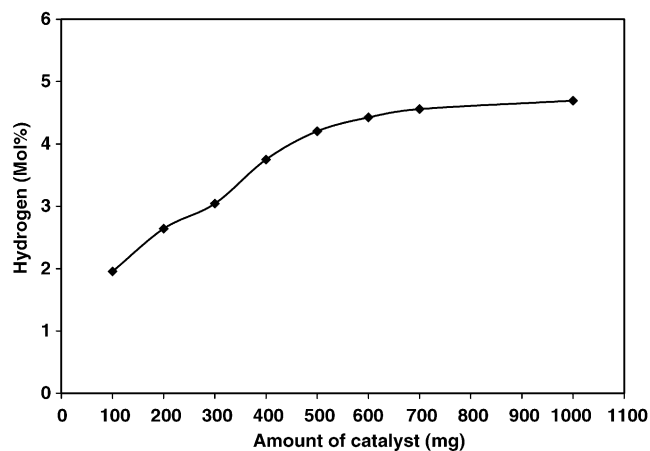


Fig. 1. Hydrogen yield as a function of catalyst particle density.

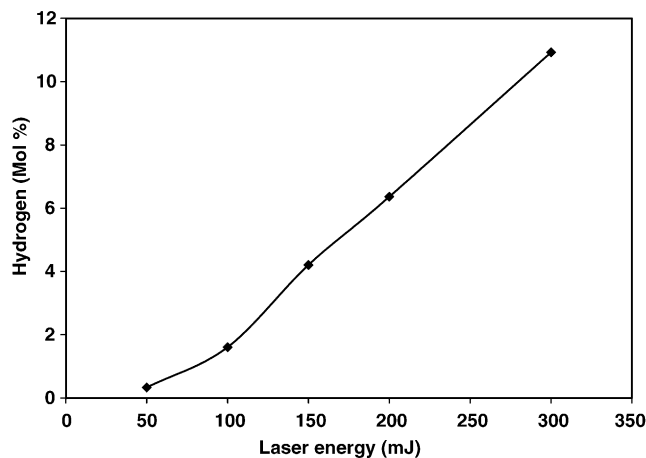


Fig. 2. Hydrogen yield as a function of laser energy.

this observation an amount of 500 mg was applied for rest of the experiments.

#### 3.2. Optimization of laser energy

Fig. 2 depicts the hydrogen yield plotted versus the laser energy for  $\text{WO}_3$  catalysts at 355 nm laser irradiation. During these experiments, the optimized amount of the catalyst from the previous step, i.e. 500 mg of the catalyst was suspended in 50 ml of methanol and the yield of hydrogen was measured for different laser energies ranging from 50 to 300 mJ/pulse. It can be noticed that the hydrogen yield shows strong dependence on the incident photon flux (laser energy). The hydrogen production is low in 50–100 mJ regions due to the low number of photons but a linear increase in the hydrogen yield has been observed in the 150–300 mJ/pulse laser energy range.

#### 3.3. Photocatalytic oxidation of methanol

Although there was an increase in hydrogen production with the increase in the number of incident photons, the laser energy of 150 mJ/pulse was applied for rest of the experiments. The photocatalytic oxidation of methanol was studied by suspending the optimized amount of 500 mg of  $\text{WO}_3$  in 50 ml of methanol. The suspension was irradiated with 355 nm laser photons of 150 mJ/pulse energy. The yield of evolved gases as function of laser illumination time is presented in Fig. 3. Beside hydrogen, the other gases produced were carbon monoxide and methane. The hydrogen yield ( $\cong 20$  mol%) is quite substantial over a 90 min of laser exposure. No liquid product, in significant measurable amount, was observed. This indicates that the photocatalytic process leads to complete oxidation of methanol.  $\text{WO}_3$  is an n-type semiconductor with a band gap of 2.8 eV. It has the valence and conduction band edge of +3.1 V and +0.4 V in the aqueous medium, respectively [29]. Although the exact potential of its band edges are not known in aprotic solvents like

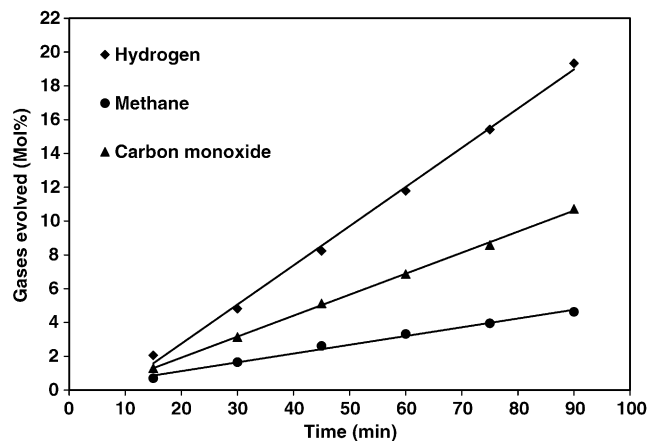
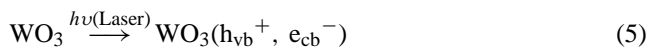
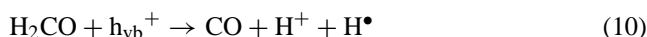


Fig. 3. The evolved gases as a function of time with 500 mg of  $\text{WO}_3$  and 150 mJ laser energy.

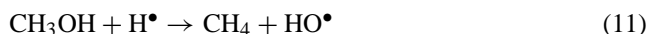
methanol, it is well documented in the literature [30,31] that the band edges are shifted to more negative potentials compared to protic solvents like water. The high yield of hydrogen (Fig. 3) also confirms the shifting of the conduction band edge to a value negative than 0.0 V (the potential for  $\text{H}^+/\text{H}_2$  couple) versus normal hydrogen electrode (NHE). The  $\text{WO}_3$  particles absorb 355 nm photons that causes the generation of valance band holes ( $h_{\text{vb}}^+$ ) and conduction band electrons ( $e_{\text{cb}}^-$ ). These photon-generated holes serve as oxidation sites for the adsorbed methanol molecules, i.e.



The formaldehyde produced during the process decomposes immediately by donating electron to the valance band holes to give carbon monoxide and additional hydrogen as follows:



Free radical mechanism is responsible for the formation of methane; i.e.



The above mechanism clearly indicates that a significant fraction of hydrogen is produced via free radical mechanism that proceeds through the photocatalytic dissociation of methanol.

It was observed that the color of the catalyst changes from light yellow to dark blue during photocatalytic reforming of methanol. The yellow tungsten oxide ( $\text{WO}_3$ ) has slightly distorted monoclinic structure; consisting of  $\text{WO}_6$  octahedra, arranged in various corner-sharing or edge-sharing

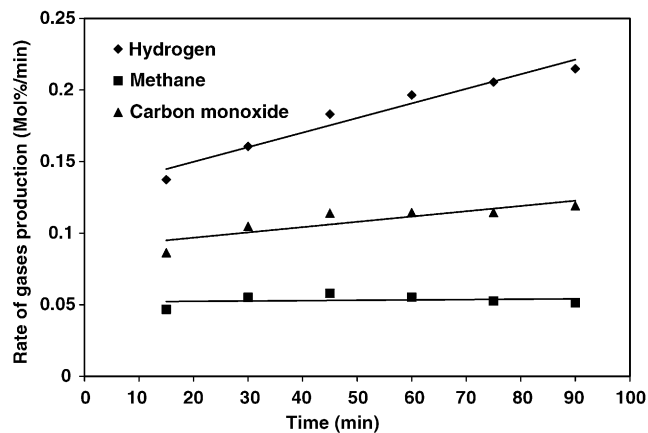
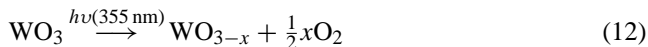


Fig. 4. The rate of production of evolved gases as a function of time with 500 mg of  $\text{WO}_3$  and 150 mJ laser energy.

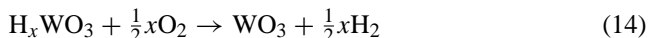
configurations [32,33]. In this configuration, each tungsten atom exists as  $\text{W}^{6+}$ . Absorption of light causes the transfer of an electron from the valence band of an oxygen atom to the conduction band of a tungsten atom. This weakens the tungsten-oxygen bond, allowing lattice oxygen to be driven out creating a defect site. The additional electron then moves from one tungsten atom to another [34].



The  $\text{H}^+$  ions produced as a result of the photocatalytic oxidation of water are then inserted or intercalated at the defect sites created by the absorption of UV light.



With this formation of these defect sites and reversible intercalation or insertion, the structural distortion decreases and blue color is observed [35]. To verify the assumption the dark blue catalyst was kept in oxygen free environment for several days, no change in the catalyst was observed. The catalyst regenerated its original color when heated in the presence of oxygen, i.e.



The rate of production of the gases produced as a result of photocatalytic reforming of methanol is depicted in Fig. 4. Here, an increase in the rate of production of hydrogen was observed with time. This increase in the rate of formation of hydrogen is an evidence of the increased activity of the catalyst with laser illumination time.

The production of hydrogen by the direct photolysis of methanol by laser photons either by single or multi photon absorption was estimated by performing blank (without  $\text{WO}_3$ ) experiment under the same conditions as in presence of  $\text{WO}_3$ . Only small amounts of hydrogen were observed, less than 1% of the amount of hydrogen produced in the presence of catalyst. A comparison of the hydrogen produced during photolysis and photocatalysis experiments, under same experimental conditions is presented in Fig. 5.

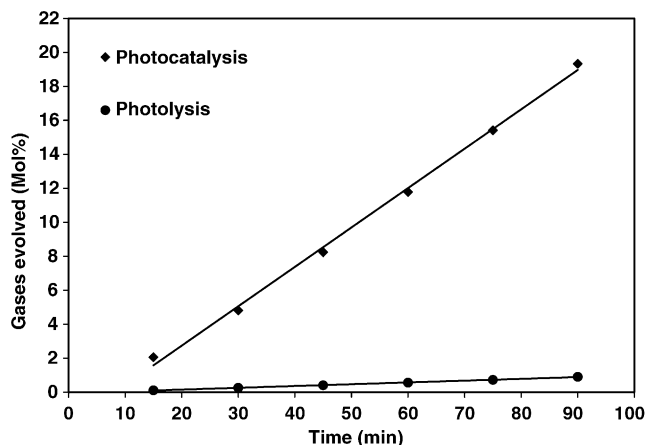


Fig. 5. Comparison of the hydrogen produced during photolysis and photocatalysis under same experimental conditions.

### 3.4. Effect of $WO_3$ aging on methanol reforming

The effect of aging on the activity of  $WO_3$  was studied by exposing the reduced catalyst under experimental conditions similar to a fresh one. For this purpose, the fresh catalyst was exposed to laser illumination for a period of 90 min and the evolved hydrogen was measured at regular intervals. After 90 min, the exposed suspension with reduced catalyst was preserved in the dark environment for 15 days. After 15 days, the same suspension was exposed to 355 nm laser photons and we measured the yield of evolved gases. The same procedure was repeated again after 1 month. A comparison of evolved hydrogen on fresh, after 15 days of first exposure and after 1 month of the second exposure is presented in Fig. 6. No decrease in the activity of the catalyst was observed with aging of the catalyst; rather, an increase was observed compared to the fresh catalyst. This effect may be because for a pure catalyst, a fraction of photons is consumed in the reduction of the catalyst and once the catalyst is fully reduced; all the incident photons applied are consumed in the production of hydrogen.

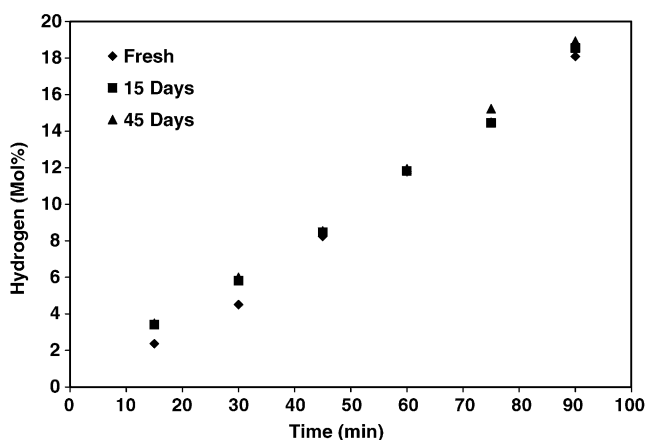


Fig. 6. Effect of the aging of the catalyst on the production of hydrogen.

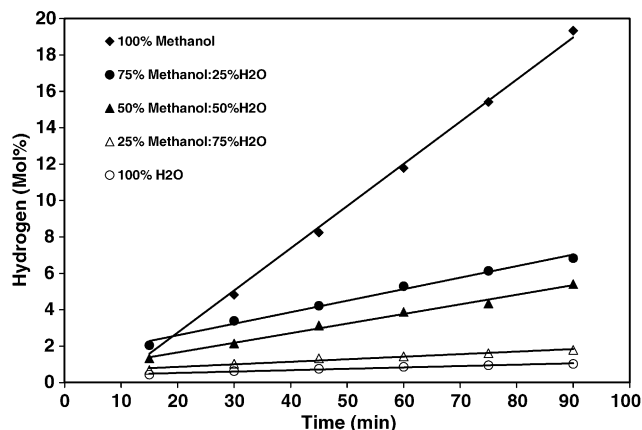
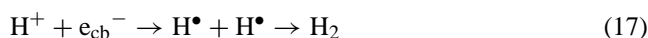
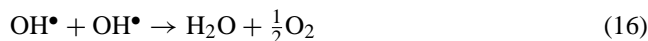


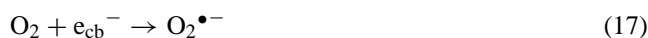
Fig. 7. Effect of the water addition on the production of hydrogen.

### 3.5. Effect of water addition on methanol reforming

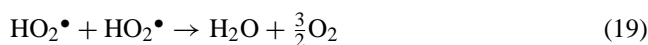
The effect of water on photocatalytic reforming of methanol was studied by illuminating the  $WO_3$  suspensions containing different proportions of methanol and water ranging from 75% to 25% methanol with a step of 25%. The amount of gases evolved, especially hydrogen, was compared with that for pure methanol and pure water. A comparison of hydrogen produced for various proportions of water in methanol with that of pure methanol and pure water is presented in Fig. 7. A substantial decrease in hydrogen production was observed with increasing concentration of water. As mentioned earlier, water and methanol have comparable properties in terms of reactivity and electron donating behavior. The presence of water in the methanol initiates the competition between methanol and water for valence band holes. Water splits into hydroxyl radicals ( $OH^\bullet$ ) and  $H^+$  ions through water oxidation. The hydroxyl radicals generate oxygen while  $H^+$  ions form hydrogen by capturing conduction band electrons; i.e.



Moreover, with the formation of oxygen in the system (Eq. (16)), a competing environment is established between oxygen and photogenerated  $H^+$  ions for conduction band electrons with the formation of super oxide ions. These super oxide ions serve as a sink for photogenerated  $H^+$  ions causing a decrease in hydrogen production as mentioned below:



The  $HO_2^\bullet$  radicals lead to the additional formation of oxygen.



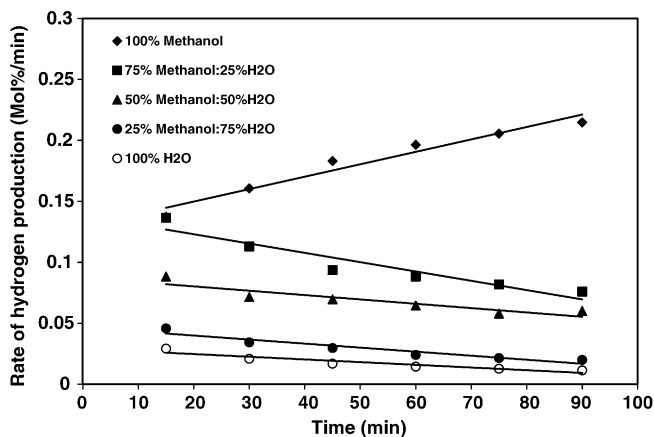


Fig. 8. Effect of the water addition on the rate of hydrogen production.

In addition, the increasing concentration of water also affects the position of the valence and conduction band edges. With increasing concentration of water, the shifting of the conduction band edges to positive value leads to the capture of conduction band electrons more and more difficult causing a considerable decrease in hydrogen production.

A comparison of the rate of hydrogen production for various concentrations of water in methanol with that for pure methanol and pure water is presented in Fig. 8. It can be noticed that the increasing concentration of water significantly decreases the rate of production of hydrogen and hinders the methanol reforming process. A similar behavior was observed for other gases ( $\text{CH}_4$ ,  $\text{CO}$ ).

#### 4. Conclusions

A hydrogen yield of 20 mol% over a period of 90 min of laser exposure to methanol was achieved; this is quite substantial at room temperature as compared to conventional methods using lamps. Apart from the reduction of the catalyst, i.e. loss of lattice oxygen and formation of  $\text{H}_x\text{WO}_{3-x}$  type species, the catalyst was found stable under laser illumination over a longer time. The study of the aging of the catalyst proved that there was no deactivation of catalyst rather an increase in the activity of the catalyst was observed. A substantial decrease in hydrogen production was observed with increasing concentration of water. Similarly, the addition of water was detrimental in the yield of other evolved gases.

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#### References

- [1] W. Dönitz, *Int. J. Hydrogen Energy* 23 (7) (1998) 611.
- [2] H.G. Düsterwald, B. Höhle, H. Kraut, J. Meusinger, R. Peters, U. Stimming, *Chem. Eng. Technol.* 20 (9) (1997) 617.
- [3] K. Kordesch, J. Gsellmann, M. Cifrain, Revival of alkaline fuel cell hybrid systems for electric vehicles, in: *Proceedings of the 1998 Fuel Cell Seminar Abstracts*, November 16–19, 1998, Palm Springs, CA, p. 387.
- [4] J.R. Rostrup-Nielsen, *Catalytic Steam Reforming*, Springer-Verlag, New York, NY, 1984.
- [5] *Catalyst Handbook*, Wolfe Publishing Ltd, Frome, England, 1989.
- [6] C.E. Thomas, I.F. Kuhn, B.D. James, F.D. Lomax, G.N. Baum, *Int. J. Hydrogen Energy* 23 (6) (1998) 507.
- [7] J.S. Oklany, K. Hou, R. Hughes, *Appl. Catal. A: Gen.* 170 (1998) 13.
- [8] J. Ogden, *Int. J. Hydrogen Energy* 24 (1999) 709.
- [9] A.J. Appleby, *Energy: Int. J.* 78 (21) (1996) 521.
- [10] A. Petersen, C.S. Nielsen, S.L. Jorgensen, *Catal. Today* 46 (1998) 193.
- [11] Y. Lin, M. Rei, *Int. J. Hydrogen Energy* 25 (2000) 211.
- [12] S.Y. Lin, Y. Suzuki, H. Hatano, M. Harada, *Energy Fuels* 15 (2001) 339.
- [13] S. Sato, S.Y. Lin, Y. Suzuki, H. Hatano, *Fuel* 82 (2003) 561.
- [14] P. Reuse, A. Renken, K. Haas-Santo, O. Görke, K. Schubert, *Chem. Eng. J.* 101 (2004) 133.
- [15] A. Rouge, B. Spoetzl, S. Schenk, K. Gebauer, A. Renken, *Chem. Eng. Sci.* 56 (4) (2001) 1419.
- [16] L.F. Brown, *Int. J. Hydrogen Energy* 26 (2001) 381.
- [17] K. Lee, W.S. Nam, G.Y. Han, *Int. J. Hydrogen Energy* 29 (2004) 1343.
- [18] M.H. Kim, E.K. Lee, J.H. Jun, S.J. Kong, G.Y. Han, B.K. Lee, T.-J. Lee, K.J. Yoon, *Int. J. Hydrogen Energy* 29 (2004) 187.
- [19] J.C. Amphlett, K.A.M. Creber, J.M. Davis, R.F. Mann, B.A. Peppley, D.M. Stokes, *Int. J. Hydrogen Energy* 19 (1994) 131.
- [20] M.I. Litter, *Appl. Catal. B: Environ.* 23 (1999) 89.
- [21] M.R. Hoffmann, S.T. Martin, W. Choi, D. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [22] M.A. Fox, M.T. Dulay, *Chem. Rev.* 93 (1993) 341.
- [23] K. Rajashwer, *J. Appl. Electrochem.* 25 (1995) 1067.
- [24] O. Legrini, E. Oliveros, A.M. Braun, *Chem. Rev.* 93 (1993) 671.
- [25] M.A. Gondal, A. Hameed, A. Al-Suwaiyan, *Appl. Catal. A: Gen.* 243 (2003) 165.
- [26] M.A. Gondal, A. Hameed, Z.H. Yamani, A. Al-Suwaiyan, *Chem. Phys. Lett.* 385 (2004) 111.
- [27] A. Hameed, M.A. Gondal, *J. Mol. Catal. A* 219 (2004) 109.
- [28] M.A. Gondal, A. Hameed, Z.H. Yamani, A. Al-Suwaiyan, *Appl. Catal. A: Gen.* 268 (2004) 159.
- [29] G.R. Bamwenda, H. Arakawa, *Appl. Catal. A: Gen.* 210 (2001) 181.
- [30] G. Redmond, A. O'Keefe, C. Burgess, C. MacHale, D.J. Fitzmaurice, *Phys. Chem.* 97 (1993) 11081–11086.
- [31] H.O. Finklea, *Semiconductor Electrodes*, Elsevier, Amsterdam, 1988.
- [32] A. Hjelm, C.G. Granqvist, J.M. Wills, *Phys. Rev. B* 54 (1996) 2436.
- [33] C.G. Granqvist, *Sol. Energy Mater. Sol. Cells* 60 (2000) 201.
- [34] L. Se-Hee, M. Hyeonsik, C. Cheong, T. Edwin, M. Angelo, K.B. David, D.K. Satyen, *Electrochim. Acta* 44 (1999) 3111.
- [35] A. Kuzmin, J. Purans, E. Cazzanelli, C. Vinegoni, G. Mariotto, *J. Appl. Phys.* 84 (1998) 5515.