

Production of hydrogen-rich syngas using p-type NiO catalyst: a laser-based photocatalytic approach

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Abstract

An innovative approach based on laser-induced photocatalytic approach, a H-rich mixture was produced by using p-type NiO, for the reforming of methanol at ambient temperature has been developed. A hydrogen-rich mixture of hydrogen (>70%) and carbon monoxide (<30%) along with a small concentration of methane (<2%) was observed. No liquid products in measurable quantities were observed for methanol. The effect of chain elongation on the composition of syngas production was studied by using higher alcohols such as ethanol, propanol and isopropanol as feedstock. For higher alcohols, a significant decrease in CO production and increase in H₂/CO ratio was observed with the increase in chain length and complexity. The effect of water addition on hydrogen production was also studied by irradiating the mixtures of methanol and water under the same conditions as pure methanol.

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1. Introduction

From the beginning of previous century, scientific community has recognized hydrogen as a potential source of fuel. Current uses of hydrogen are in industrial processes, rocket fuel, and spacecraft propulsion. With further research and development, this fuel could also serve as an alternative source of energy for heating and lighting homes, generating electricity and fueling motor vehicles. There is an increasing interest in the development of fuel processing technologies and catalysts to produce H₂ from a suitable high energy density liquid fuel for the future fuel cells. Solid polymer fuel cells (SPFCs) appear to be the most promising fuel cell technology for mobile power applications or for small stationary power units [1–4]. The ideal fuel for SPFC is pure hydrogen, but technical limitations allows the use of hydrogen-rich gas streams obtained from fuels such as methanol. Methanol is cheap, easy to produce from natural gas or petroleum, and has a

ratio of four hydrogen atoms to one carbon atom, which is higher than any other potential liquid fuel. The selection of methanol as a chemical carrier for hydrogen is mainly due to its availability, high energy density, and easy storage and transportation [5,6]. Methanol can be converted to hydrogen by several means, including methanol steam reforming [7,8], methanol partial oxidation [9–13], and oxidative methanol reforming [11,13]. At present, most of the hydrogen produced on an industrial scale is by the process of steam reforming or as a by-product of petroleum refining and chemicals production. The steam reforming process for the production of hydrogen or syngas is highly endothermic and requires extreme experimental conditions such as high temperatures [7,8].

Hydrogen can also be generated from methanol by partial oxidation of methanol reaction [9–13]. This reaction can yield a product gas containing up to 75% hydrogen. However, partial oxidation of methanol reaction is a highly exothermic process [13]. The formation of hot spots is one of the main drawbacks from using the partial oxidation process as the formation of these hot zones in the catalyst can result in sintering, thus lowering the catalyst activity [14,15].

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Nowadays, efforts are underway to develop photochemical methods for the production of hydrogen. Heterogeneous photocatalysis is one of the most promising approaches in this regard [16–23]. This technique is based upon the photoexcitation of a semiconductor catalyst, with the absorption of the photons of energy greater than the band gap, leading to better oxidation (formation of photogenerated holes, h_{vb}^+) and reduction (formation of 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 be occurred 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 the valance band holes or conduction band electron. Water is the most commonly used solvent in photocatalysis and most readily available chemical feedstock for the photocatalytic hydrogen production but the main problems associated with the production of hydrogen through water splitting are the formation of explosive mixture of hydrogen and oxygen and low yield of hydrogen. The other alternative source is organic compounds; primarily oxygenated hydrocarbons such as methanol. 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. As mentioned above, methanol is liquid at room temperature with high carbon to hydrogen ratio compared to water and is considered as organic counterpart of water. Due to the presence of polarity and its ability to donate the lone electron pair, methanol can be used as alternative for water. The above-mentioned properties make it quite suitable for the photocatalytic production of hydrogen. Discovery of a novel process for producing hydrogen like laser-based photocatalytic reforming of methanol would greatly advance the cause of achieving a clean-burning economy based on hydrogen and reduce the current dependence on fossil fuels.

We developed an innovative process for efficient production of hydrogen-rich syngas from methanol by using a 355 nm pulsed laser as a light source. The process is based on photocatalytic splitting of methanol in the presence of a semiconductor photocatalyst, NiO. The major reaction product, i.e. molecular hydrogen (H_2) and carbon monoxide (CO) were observed in high H_2/CO ratio at a high rate and room temperature. It is worth mentioning here that a complete transformation of liquid methanol was observed in gaseous products without the formation of any major product in the liquid phase. Efforts have been made to enrich the product mixture with hydrogen which includes the experiments with the mixture of methanol with water in the presence of NiO. The effect of the chain elongation and complexity on H_2/CO was studied by replacing methanol with ethanol, propanol and isopropanol and the results were compared with that of pure methanol.

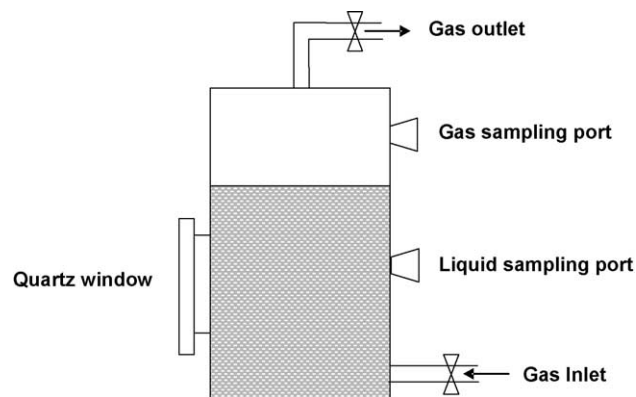


Fig. 1. Schematic diagram of the cell used for laser-induced photocatalytic reforming of methanol into syngas.

2. Experimental details

A Pyrex cell (total volume = 130 ml) equipped with optical grade quartz window (diameter = 2.0 cm) for transmission of UV laser beam was fabricated to study the photocatalytic reforming of methanol into syngas and other gaseous products [22–26]. A schematic diagram of the cell is depicted in Fig. 1. Based on experimental observation, the parameters that influence the yield of product gases, i.e. catalyst particle density and laser energy were optimized for high yield of hydrogen. The optimization of the amount of catalyst studied was in the range of 50–2000 mg while laser energy was optimized in the range of 20–300 mJ. To study photocatalytic conversion of methanol, the optimized amount of NiO 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 μ l of gas sample 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 30 m molecular sieve 5A plot column and a TCD detector. A 355 nm laser beam, generated from the third harmonic of a Spectra Physics Nd:YAG laser (Model GCR 250) was employed as a light source. For all the experiments, the expanded beam of 10 mm diameter was used. 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 chain elongation and complexity was studied by replacing methanol with higher alcohols (ethanol, propanol and isopropanol) and results were compared with principle solvent (methanol). 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 reforming of methanol was studied by illuminating the colloidal suspension of methanol and an optimized amount of NiO at an optimized energy of 355 nm laser radiation. The optimization of these two parameters was essential as the slight change in these parameters may effect the yield of product gases. The amount of NiO was optimized by exposing the colloidal suspensions containing different concentrations of NiO ranging from 100 to 1000 mg with a fixed energy laser beam for a period of 30 min and the hydrogen yield was considered as an indicator to identify the amount of catalyst for maximum yield. A plot of hydrogen yield as a function of particle density is presented in Fig. 2, where a sharp increase in the yield of hydrogen in 100–500 mg range was observed. Although the formation of hydrogen increases with the further increase in the particle density in the 500–1000 mg range, the increase was slow as compared to 100–500 mg range. With the increase in the particle density, the number of the particles exposed per unit area increases till an optimum concentration is reached. As the stirring rate and the total volume of colloidal methanol suspension is kept constant, further increase in particle density beyond optimum density fails to contribute significantly to hydrogen yield increase. The exposure to a constant photon flux and fixed beam diameter of 10 mm was another restriction on the noticeable increase in the yield of methanol beyond certain limits. Based on these observation an amount of 500 mg was applied in further experiments.

The dependence of hydrogen yield on the laser energy was carried out and is presented in Fig. 3. A linear dependence in hydrogen production was observed with the increase in laser energy (photon flux) for a fixed amount of NiO. A rate of 0.0638 mol%/mJ for hydrogen production was observed. With the increase in photon flux the number of exposed catalyst particles increases causing a significant increase in the yield of hydrogen was observed. This linear increase was not observed when the optimization experiments were per-

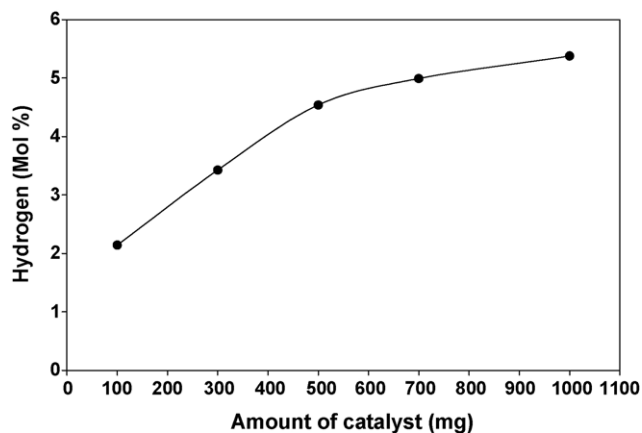


Fig. 2. Optimization of amount of catalyst between 100 and 1000 mg range for maximum yield of hydrogen.

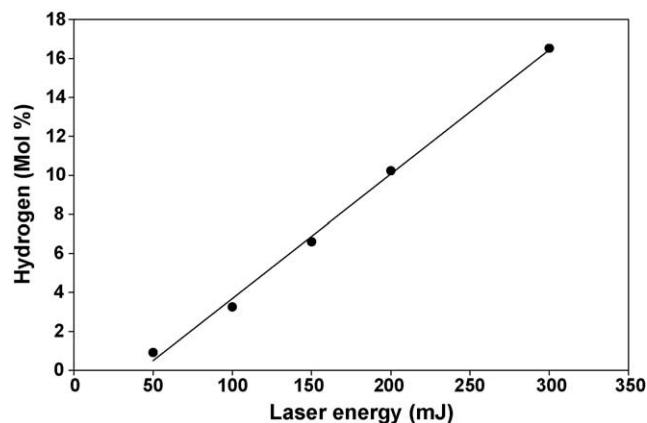


Fig. 3. Optimization of laser energy between 50 and 300 mJ range for maximum yield of hydrogen.

formed in aqueous medium during water splitting experiments [24,25]. The reason being the formation of oxygen due to photocatalytic water splitting process and the competition between H^+ ions and oxygen causing a substantial decrease in hydrogen yield. As there was no possibility of oxygen production in the splitting of methanol, thus a linear increase in hydrogen yield was observed in the present work. Another possible reason might be the direct photolysis of methanol involving single- or multi-photon absorption that may lead to the breaking of carbon–hydrogen bond, causing an increase in the yield of hydrogen, with the increase in laser energy. The contribution of direct photolysis was investigated by performing the same reactions without NiO. It was observed that the contribution in hydrogen yield due to photolysis was less than 0.1% of the total hydrogen produced as a result of photocatalytic process. Keeping in view the linear dependence of hydrogen yield on laser energy a laser energy of 150 mJ was applied for rest of the experiments.

The photo-catalytic production of syngas from methanol was studied by illuminating the colloidal suspension of 500 mg of NiO in 50 ml solution of methanol with 355 nm laser photons at 150 mJ energy. Hydrogen and carbon monoxide were observed as major gaseous products while a small concentration of methane in the gas phase and a minor concentration of products in the liquid phase indicated that the photocatalytic reforming process leads to complete transformation of methanol into gaseous products. The evolution of all the gases (H_2 , CO, CH_4) as a function of time, produced due to methanol reforming, is presented in Fig. 4. NiO is least studied due to its photocatalytic properties but well studied as an heterogeneous catalyst especially as hydrogenation catalyst [27]. NiO has wide range of applications due to its good chemical stability as well as for its excellent optical and electrical properties [28]. It is p-type semiconductor with a band gap of 3.5 eV and the potentials of the valance and conduction band edges at +3.0 and -0.5 V, respectively [29]. The band edges are highly suitable for the oxidation of water, formation of hydrogen and reduction of water in the presence of oxygen [24]. Although the exact potentials of its band edges

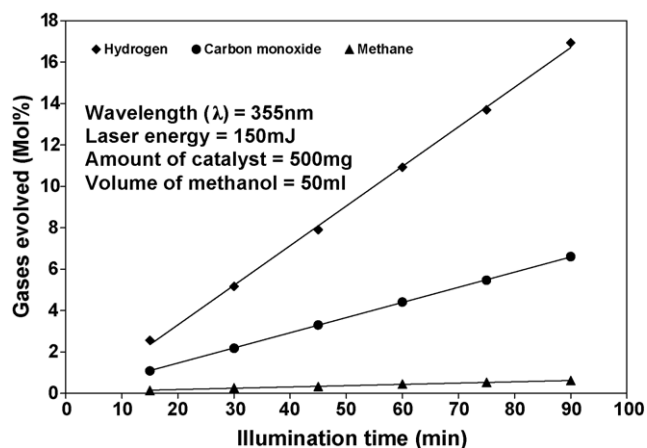
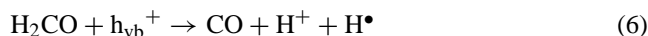
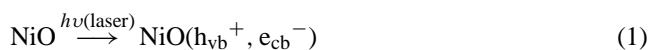
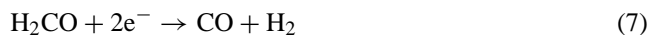


Fig. 4. Comparison of evolved gases over NiO under laser illumination.

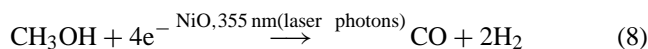
are not known in non-aqueous solvents like methanol, it is well documented [30,31] that the band edges are shifted to potentials that are more negative in aprotic compared to protic solvents. The high yield of hydrogen (Fig. 4) also confirms the shifting of the conduction band edge to a value negative than 0.0 V (the potential for H^+/H_2 couple) versus normal hydrogen electrode (NHE). The absorption of 355nm laser photons by NiO particles generates the valance band holes (h_{vb}^+) and conduction band electrons (e_{cb}^-) in the valance and conduction band respectively. These photon-generated holes serve as oxidation centers for the adsorbed methanol molecules while the photoexcited conduction band electrons reduces the H^+ ions, produced because of methanol oxidation, to hydrogen atoms simultaneously. The reaction mechanism can be represented by the set of following equations:



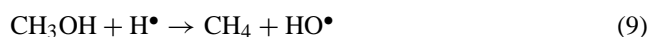
or



The overall reaction is a four-electron process:



The formation of methane is only possible through free radical mechanism, i.e.:

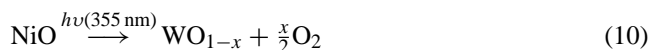


The careful analysis of the above mechanism indicates that a significant fraction of hydrogen is produced via free radical

mechanism that proceeds through the photocatalytic dissociation of methanol.

During the photocatalytic methanol reforming experiments, it was observed that the color of the catalyst changes from green to black. It was also observed that this color was only limited to the catalyst particles while the solution was colorless. Nickel oxide with the distorted rock salt structure has been known to show anti-ferromagnetic insulating behavior when it has stoichiometric structure. The nickel oxide shows, however, considerable semi-conductivity with the formation of defect sites or oxygen vacancies when exposed to laser photons [24]. The conduction is explained as a result of electron hopping between the Ni^{2+} and Ni^{3+} ions. The oxygen vacancies give the oxide additional catalytic activity [29] due to reduction of Ni^{2+} to Ni^+ as explained in the following paragraph.

Absorption of a photon of energy equal to or greater than the band gap energy ($E > E_g$) causes the transfer of an electron from the valance band of oxygen (2p) to the conduction band of Ni (3d) atom and in turn the reduction of Ni^{2+} to Ni^+ . This electron transfer process weakens the $Ni^{+2}-O$ bond allowing lattice oxygen to be driven out creating a “defect” or “tape” site and leads to the formation of a hole in the valance band. The hole in the valance band oxidizes the adsorbed methanol producing H^+ ions. These H^+ ions are inserted in the photo-generated defect sites to give H_xNiO_{1-x} type species before being converted to hydrogen, which impart black color to the catalyst. The other possibility is the direct insertion of molecular hydrogen through homolytic bond fission [24], i.e.:



Due to the reduction of NiO with the intercalation of hydrogen, the structural distortion decreases and a black color is observed [24]. The regeneration of the catalyst was observed in the presence of oxygen at elevated temperatures supporting the formation of reduced NiO.

The rate of production of gases produced because of the photocatalytic reforming of methanol is presented in Fig. 5, where an increase in the rate of production of hydrogen was observed with the reduction of the catalyst with time and supports the consumption of hydrogen or H^+ ions in the reduction of NiO, which decreases, with the passage of time. The increase in H_2/CO ratio with time as presented in Fig. 6, predicts the increase in production of hydrogen as the rate of production of CO remains nearly constant (Fig. 5) throughout the experiment.

In this work, various measures were adopted to reduce the production of carbon monoxide and enhance the H_2/CO ratio. One of these measures was the use of methanol water mixture instead of pure methanol. The idea was to use CO and enhance the formation of hydrogen by inducing water gas shift reaction in the reaction mixture at room temperature. The progress

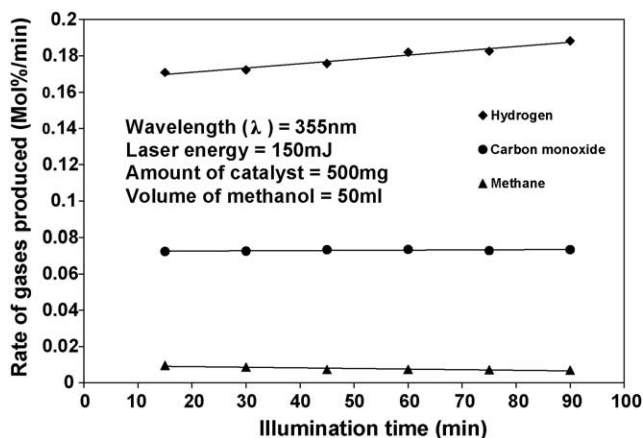


Fig. 5. Comparison of the rate of production of gases over NiO under laser illumination.

of the reaction was observed by monitoring the evolution of carbon dioxide gas but CO_2 was observed in trace amounts, which led to the conclusion that the water-gas shift reaction is less probable at room temperature and requires elevated temperatures. On the other hand, a decrease in CO production and an increase in H_2/CO ratio were observed. The effect of water on the production of syngas was studied by illuminating the NiO suspensions containing different proportions of methanol and water ranging from 75% to 25% methanol with a step of 25%. The amount and the ratio of gases evolved (H_2 and CO) were compared to those for pure methanol. No methane was observed even with the lowest concentration of water, i.e. 25%. A comparison of H_2 and CO produced for various proportions of water in methanol with that of pure methanol is presented in Figs. 7 and 8. A decrease in H_2 and CO production was observed with increasing concentration of water. The decrease in H_2 production was less as compared to CO. Water and methanol has 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. Wa-

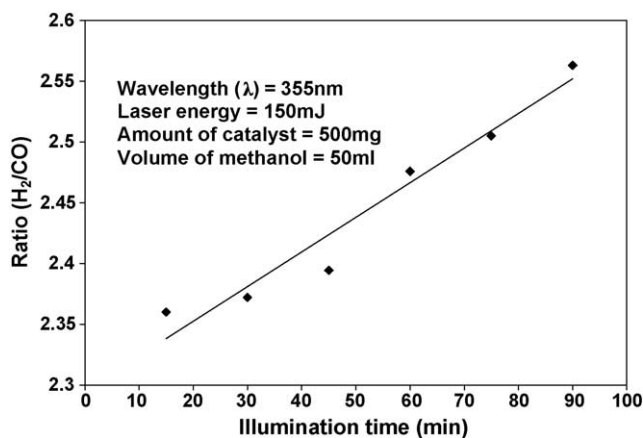


Fig. 6. Variation in H_2/CO ratio as a function of time for pure methanol.

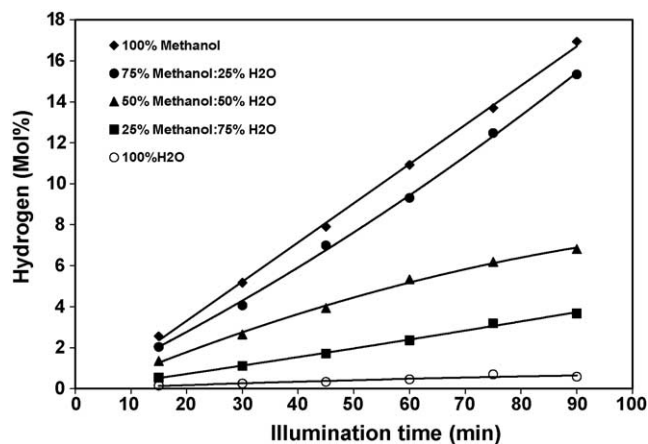


Fig. 7. Effect of water addition on the production of hydrogen during photocatalytic methanol reforming.

ter splits into hydroxyl radicals (OH^\bullet) and H^+ ions through oxidation by the valence band holes. The hydroxyl radicals generate oxygen while H^+ ions form hydrogen by capturing conduction band electrons. With the formation of oxygen due to water splitting in the system, a competing environment is established between oxygen and photogenerated H^+ ions for conduction band electrons, which lead to the formation of superoxide ions. These superoxide ions serve as sink for photogenerated H^+ ions causing a decrease in hydrogen production. The whole process can be explained by the set of following equations:

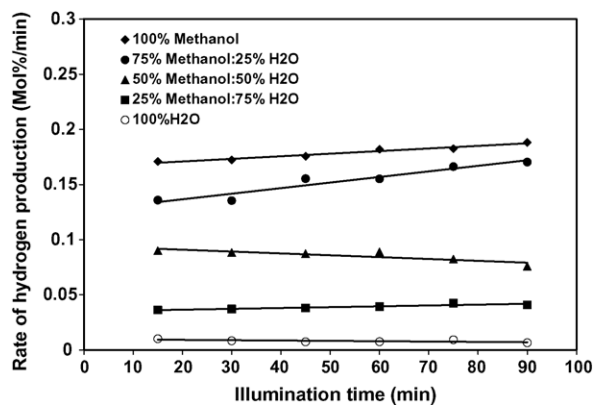
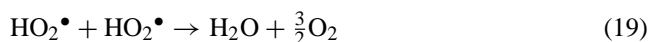
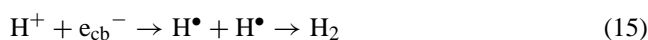
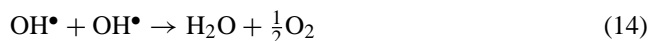


Fig. 8. Effect of water addition on the rate of hydrogen during photocatalytic methanol reforming.

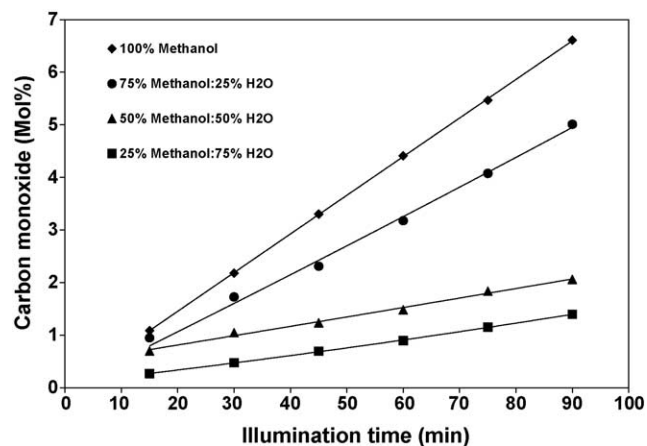


Fig. 9. Effect of water addition on the production of carbon monoxide during photocatalytic methanol reforming.

Another perceptible effect of the increasing concentration of water is the shifting of the conduction band edges to positive value compared to pure methanol, which enhances the extent of the competing process such as reduction of water that leads to the formation of hydroxyl ions and decrease in the production of hydrogen. The water molecules present in the system also competes with the formaldehyde that serves as precursor for CO and additional hydrogen formation thus causing a decrease in the production of both gases.

A comparison of the rate of H₂ and CO production for increase in concentration of water in methanol with that for pure methanol is presented in Figs. 8 and 9 where it can be observed that the increase concentration of water beyond 25% drastically hinders the methanol reforming process. It was observed that with the increase in water concentration the H₂/CO ratio increases. A high H₂/CO ratio (>3.5) with high yield of syngas compared to pure methanol (>2.5) was observed for 25%:75% (water:methanol) mixture. Although an increase in H₂/CO ratio was observed with increasing concentration of water, a significantly low yield of syngas compared to pure methanol was observed. A comparison of H₂/CO ratio for various concentrations of water is presented in Fig. 10.

The H₂/CO ratio attempted to be improved by replacing methanol with higher alcohols such as ethanol, propanol and isopropanol. A comparison of the evolved hydrogen, carbon monoxide and H₂/CO ratio for ethanol, propanol and isopropanol with that of methanol is presented in Figs. 11–13, respectively. For all the alcohols, the hydrogen yield was comparable with that of pure methanol while a significant decrease in carbon monoxide yield was observed. This effect is mainly due to the decrease in the formation of formaldehyde for higher alcohols as it involves carbon-to-carbon bond breaking. The extent of carbon-to-carbon bond breaking decreases with the increase in chain elongation and complexity as these factors contributes in enhancing the steric hindrance in the molecule. The use of higher alcohols was found advan-

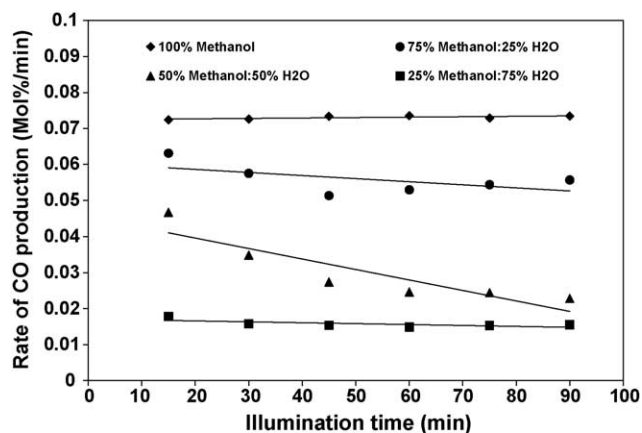


Fig. 10. Effect of water addition on the rate of hydrogen production during photocatalytic methanol reforming.

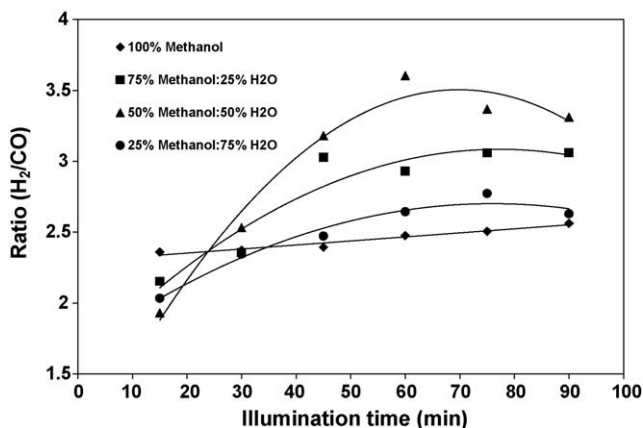


Fig. 11. Effect of water addition to H₂/CO ratio during photocatalytic methanol reforming.

tageous compared to the use of water to reduce the concentration of CO in the syngas mixture, as the yield of hydrogen was comparable to that of methanol with a substantial decrease in the evolution of CO. A high H₂/CO ratio of >4.0

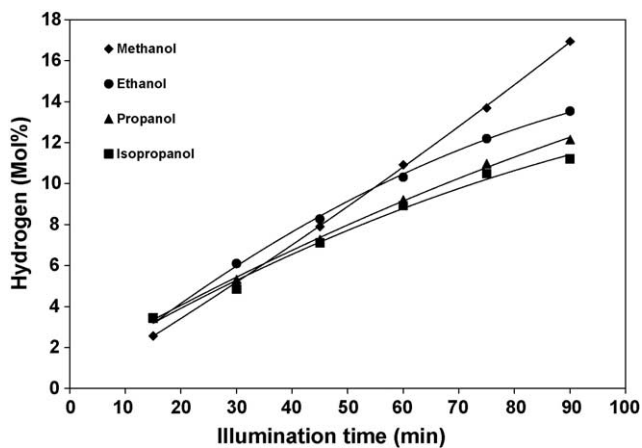


Fig. 12. Comparison of hydrogen production for methanol, ethanol, propanol and isopropanol.

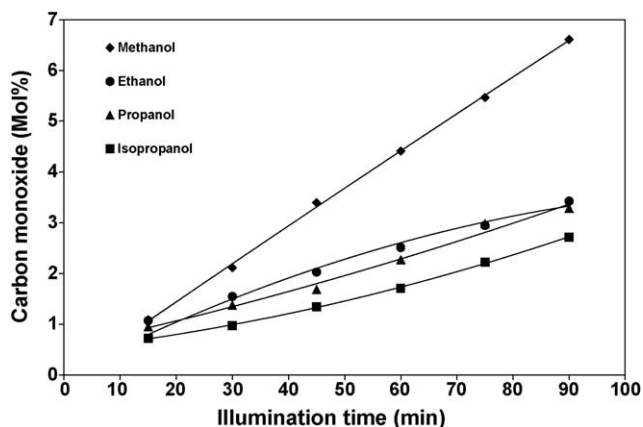


Fig. 13. Comparison of carbon monoxide production for ethanol, propanol and isopropanol with that of methanol.

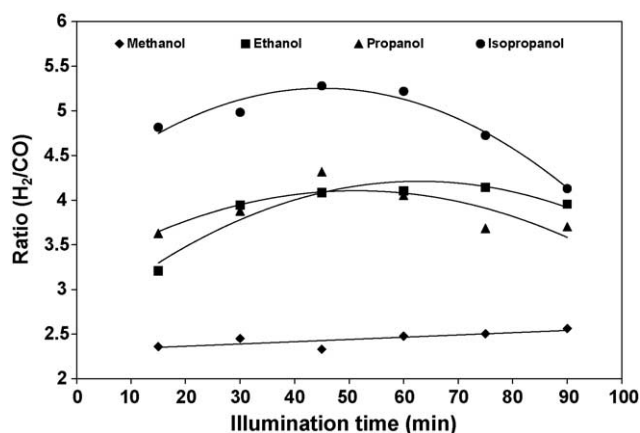


Fig. 14. Comparison of H₂/CO ratio for methanol, ethanol, propanol and isopropanol.

was observed for all the alcohols with a maximum of >5.5 for isopropanol (Fig. 14).

4. Conclusions

Photocatalytic splitting of methanol in the presence of a semiconductor photocatalyst, NiO using unique source of radiation like 355 nm laser proved to be an efficient process for generation of hydrogen. The major reaction products, i.e. molecular hydrogen (H₂) and carbon monoxide (CO) were observed in high H₂/CO ratio at very high rate of formation. The effect of chain elongation using higher alcohols such as ethanol, propanol and isopropanol as feedstock showed no traces of methane. For these higher alcohols, significant decrease in CO production and increase in H₂/CO ratio (>4.5) was observed with the increase in chain length and complexity. An increase in H₂/CO ratio (>3.5) was observed for the addition of 25% water in pure methanol. Although there was an increase in H₂/CO ratio (>3.0) compared to pure methanol (H₂/CO > 2.5), a substantial decrease in the production of

syngas was observed with the increasing concentration of water inside the methanol.

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