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Comparative Study on the Photocatalytic Hydrogen Production from Methanol over Cu-, Pd-, Co- and Au-Loaded TiO₂

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Abstract — Photocatalytic hydrogen production from a methanol-water solution was investigated in a semi-continuous reactor over different metal-loaded TiO₂ catalysts under UltraViolet (UV) light irradiation. The catalysts were mainly prepared by the incipient wetness impregnation method by varying the metal weight ratio in the range of 1-10 wt%. The effects of metal loading and H₂ pre-treatment on the photocatalytic activity were investigated. In addition, the activity of the catalysts was also compared with a reference Au-TiO₂ catalyst from the World Gold Council (WGC). The photocatalysts were characterized by using X-Ray Diffraction (XRD) and N₂ physisorption before and after the activity measurements. The photocatalytic activity decreased in the order of Pd > Au > Cu > Co in the comparative study of Cu-TiO₂, Co-TiO₂, Au-TiO₂ and Pd-TiO₂. Optimum hydrogen evolution was achieved with 5 wt% Pd-TiO₂ and 5 wt% Cu-TiO₂.

Résumé — Étude comparative de production d'hydrogène par photocatalyse à partir de méthanol et à l'aide de différentes phases actives (Cu, Pd, Co et Au) supportées sur TiO₂ — La production d'hydrogène assistée par photocatalyse à partir d'une solution diluée de méthanol a été réalisée dans un réacteur semi-continu avec l'aide de différents catalyseurs supportés par TiO₂ et sous irradiation UV. Les catalyseurs ont été préparés par imprégnation par capillarité en faisant varier le pourcentage massique du métal choisi entre 1 et 10 %. L'influence de ce pourcentage, le prétraitement sous H₂ et le matériau semi-conducteur utilisé pour la photocatalyse ont été étudiés. D'autres expériences ont été menées concernant l'activité catalytique des matériaux sélectionnés et les résultats ont été comparés avec ceux obtenus avec un catalyseur de référence provenant du *World Gold Council* (WGC), or supporté sur TiO₂. Les photocatalyseurs ont également été caractérisés par Diffraction des Rayons X (DRX) et physisorption de l'azote, avant et après réaction. Il a été observé que l'activité photocatalytique diminuait pour les phases actives dans l'ordre décroissant suivant: Pd > Au > Cu > Co ; résultats obtenus lors de l'étude comparative entre les catalyseurs Cu-TiO₂, Co-TiO₂, Au-TiO₂ et Pd-TiO₂. La production optimale d'hydrogène a été obtenue avec les catalyseurs 5 % massique Pd-TiO₂ et 5 % massique Cu-TiO₂.

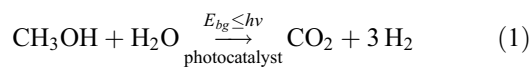
INTRODUCTION

Hydrogen is often regarded as a potential future energy carrier, which can be easily obtained from methanol *via* several processes. Compared with thermochemical processes, photocatalytic reforming is an effective approach to produce hydrogen under ambient conditions and using sunlight [1].

Some of the previous studies are summarized in Table 1, [2–10]. In most of the cases listed in Table 1, TiO₂ is the most widely used semiconductor for various photocatalytic applications due to its relatively low cost, abundance, stability and low toxicity.

Noble metal-loaded TiO₂ has extensively been proved to be a good photocatalyst for hydrogen production, mainly because of its ability to enhance photoproduced electron–hole pair separation and photoinduced reduction processes [4, 11, 12]. However, non-precious metal-loaded TiO₂ may be cost-effective compared with noble metal-loaded TiO₂ since it also shows significant photocatalytic activity in hydrogen generation [13, 14].

In this study, we have investigated photoreforming of methanol (Eq. 1) with the use of different metal-loaded TiO₂ photocatalysts in a semi-continuous reactor set-up under UV light irradiation:



The effects of several parameters on the hydrogen production were studied, including metal loading, H₂ pre-treatment and semiconductor material.

1 EXPERIMENTAL

1.1 Catalyst Preparation

All catalysts were prepared by using the incipient wetness impregnation method and TiO₂ (P25-Degussa) was used as the photoactive semiconductor. The appropriate mass of metal precursor was dissolved in deionized water to give the desired metal concentration. The volume added to the catalyst was just sufficient to fill the pores of the support. The impregnated support was then dried in an oven at 110°C overnight, and was calcined in a muffle furnace (Nabertherm- L15/12/P320). The calcined catalysts were lightly ground and sieved to < 53 μm before use. The metal content of the final catalyst was determined by the concentration of the metal precursor used in the impregnation, and was denoted by the weight percentage of metal in the catalyst: $\text{Wt}\% = (\text{wt}_X/\text{wt}_{X+\text{TiO}_2}) \times 100$. The Au-TiO₂ catalyst reported in this study is the reference catalyst from the World Gold Council (WGC) prepared by a deposition precipitation

method [15]. All the metal precursors and calcination conditions are summarized in Table 2, [16, 17].

1.2 Photocatalytic Activity Measurements

As shown in Figure 1, the photocatalytic activity measurements were performed in a custom made cylindrical quartz reactor (volume ~1.2 L) and kept inside the photoreaction chamber (Luzchem CCP- 4V). The chamber was equipped with 14 UVC lamps (Luzchem LZC-UVC: 15 W, 254 nm) and a magnetic stirrer. During irradiation, the temperature inside the photoreaction chamber was continuously monitored and always kept within 3°C above room temperature. Typically, 0.25 g powder of photocatalyst was dispersed in the reactor containing 500 mL of 50 vol.% methanol aqueous solution. Prior to the irradiation, the photocatalyst suspension in methanol solution was deaerated thoroughly for 30 min by a 100 mL/min flow of Ar. The reactor effluent was analyzed on-line with a Thermal Conductivity Detector (TCD) micro gas chromatograph (Agilent Technologies 3000) with a molecular sieve column (MolSieve 5 A). Ar was used as a carrier gas and the GC response was first calibrated by introducing a known flow of hydrogen into the system. All the gas lines were heated to prevent condensation of methanol and water.

In some experiments, the catalysts were reduced *in situ* prior to activity tests in a stream of 10 vol.% H₂/Ar mixture flowing at 100 mL/min at ambient temperature for 1 h to investigate the effect of H₂ pre-treatment.

1.3 Catalyst Characterization

X-Ray powder Diffraction (XRD) patterns were obtained using a Bruker D8 Advance X-Ray Diffractometer with Cu–Kα radiation (Kα = 1.54 Å) in the scanning angle (2θ) range of 20–80°. The specific surface areas of the catalysts were measured by N₂ physisorption using the Brunauer–Emmett–Teller (BET) method (Micromeritics Tristar II 3020). To remove traces of water and impurities from the catalyst surface, all samples were degassed (Micromeritics VacPrep 061) overnight at 200°C before the measurement.

2 RESULTS AND DISCUSSION

2.1 Photocatalytic Activity

The comparison of photocatalytic activity over different metal-loaded catalysts is shown in Figure 2. The photocatalytic activity decreased in the order of Pd > Au > Cu. However, after 10 h of reaction, the hydrogen evolution changed to Au > Pd > Cu. This is in agreement with the results of Sreethawong and Yoshikawa [18] on similar

TABLE 1
Previous studies on photocatalyst development for hydrogen production

Ref No.	Reactants	Catalyst and preparation method	Light source	Reaction conditions	Experiment	Results obtained
[2]	Methanol (liquid and gas phases)	TiO ₂ and 1% Au/TiO ₂ Flame spray pyrolysis	Iron halogenide Hg arc lamp (330-450 nm)	Plexiglass reactor 55±5°C	The performance of the suspension and vapor phase reactors was investigated	Intermediate product: formaldehyde Final products: H ₂ and CO ₂ . Optimal results: A 30% higher reaction rate was attained with the vapor phase reactor
[3]	Ethanol and glycerol solutions	CuO _x -TiO ₂ Water-in-oil microemulsion synthesis Wet impregnation (Cu loading was 2.5% by weight)	UV	20°C Pyrex batch reactor (250 mL) Cat. wt: 500 mg	The effect of the catalyst preparation method and the stability of the CuO _x -TiO ₂ catalysts were studied with respect to carbonaceous deposits and copper leaching	The catalyst prepared by the embedded method showed the best performance
[4]	Methanol	Au/ TiO ₂ Deposition-precipitation method	300 W Xe lamp	Pyrex reactor Cat. wt: 0.3 g	The effects of: 1. Au particle size, 2. the initial methanol concentration, 3. the initial pH value, on H ₂ production rate and CO selectivity	<ul style="list-style-type: none"> - The H₂ production rate increased with decreasing Au particle size from 10 to smaller than 3 nm - The CO concentration decreased with reducing Au particle size - The rate varied as a function of the initial methanol concentration as a Langmuir-type curve - The molar ratio of CO/H₂ showed a weak increasing trend with increasing methanol concentration - Both acidic and basic solutions resulted in a considerable decrease in the rate of H₂ production and CO concentration
[5]	Methanol	Metal-titania (Pd, Au, Ir, Pt, Ru, Rh, Ni) Incipient wetness	400 W Xe arc lamp	Ambient temperature; Pyrex flask (100 mL) Cat. wt: 0.2 g	The model for the reaction was presented	<ul style="list-style-type: none"> - Pd was the best when comparing similar loading - In terms of molar loading of metal, Pt was a little better than Pd
[6]	Methane (methane hydrates)	Tungsten oxide doped with Cu, Pt, La/Cu	Hg vapor quartz lamp	1 MPa; 100°C; Quartz reactor (1 L)	The methanol production with various promoted tungsten oxide catalysts was investigated	Final products: methanol and H ₂ By-products: ethane, oxygen, formic acid and CO ₂ The catalysts doped with La showed the highest methane conversion and methanol yield

(continued)

TABLE 1 (continued)

Ref No.	Reactants	Catalyst and preparation method	Light source	Reaction conditions	Experiment	Results obtained
[7]	Methanol/water solution	CuO-TiO ₂ Impregnation method	400 W Hg lamp	Pyrex reactor (1.45 L) Cat. wt: 1 g	The effects of: 1. Cu content 2. Initial methanol concentration on H ₂ generation activity The stability and recovery of catalysts over extended time was investigated	– The optimum Cu content was 9.1 mol% – The H ₂ generation rate could be increased by increasing methanol concentration – The H ₂ generation rate dropped under long irradiation time mainly due to the accumulation of byproducts, reduction of CuO and Cu leaching
[8]	Methane and water	Pt/TiO ₂ Impregnation method and photo-deposition method	300 W Xe lamp (both UV and visible light)	50°C; 1 atm; Fixed bed Quartz flow reactor; Cat. wt: 0.5 g Cat. size: 400-600 μm	The effects of 1. Photocatalyst structure 2. Catalyst preparation method 3. Reaction conditions (CH ₄ and H ₂ O concentration, light intensity) on the H ₂ production rate were studied The reaction mechanism was also investigated	By-products: C ₂ H ₆ and CO Final products: H ₂ and CO ₂ Optimal results: – the catalyst prepared by the photodeposition method showed much higher activity than the impregnation method; – the optimum concentration of CH ₄ to sustain the high activity with moderate intermediates was around 50%; – the H ₂ production rate was almost constant for moderate H ₂ O concentration (0.28-15%). With increasing light intensity, the H ₂ production rate increased first, and then the increase became small
[9]	Methanol and water	Au/TiO ₂ Flame spray pyrolysis	Iron halogenide mercury arc lamp (330-450 nm)	45-mL cylindrical quartz vessel Reaction medium: Pure water or 6 vol.% methanol aqueous solution	The addition of methanol and the deposition of gold particles on titanium dioxide were investigated	The highest rate of hydrogen production was attained with gold-modified titanium dioxide Addition of methanol to the reactant suspension led to an increase in the hydrogen production rate
[10]	Methanol, ethanol, glycol, glycerin/water	Lanthanide-doped titania (Gd, Eu, Yb, Ho) Incipient wetness method; cat. wt: 0.1 g	300 W Ultra-Vitalux (Osram) lamps	Reactor: Pyrex round-bottom flask (250 cc) Reaction medium: water and alcohol (50:1)	A series of platinized lanthanide-doped titania were tested for photocatalytic water splitting to find out the effect of lanthanide oxide type. Methanol, ethanol, glycol or glycerin were used to investigate the effect of sacrificial agents	– The best performance was obtained for the catalyst containing 0.5 mol% of Gd, Eu, Yb or Ho oxides as the dopant; – No oxygen was observed in the reaction products; – The best sacrificial agents were methanol and ethanol acting as the oxygen scavenger, and the worst was glucose or fructose.

catalysts. No significant hydrogen evolution is detected over the Co-TiO₂ catalysts under UV irradiation.

H₂ pre-treatment lead to a detrimental effect on the hydrogen evolution, as shown in Figure 3. This is in agreement

with the results reported by Wu *et al.* [19] and Oros-Ruiz *et al.* [12] for TiO₂-supported metal photocatalysts, although the H₂ pre-treatment was performed at much higher temperatures in the previous reports.

TABLE 2
Metal precursors and calcination conditions for prepared catalysts

Catalyst	Metal precursor	Calcination conditions
Cu-TiO ₂	Cu(NO ₃) ₂ ·3H ₂ O	200°C for 4 h
Pd-TiO ₂	PdCl ₂	500°C for 2 h [16]
Co-TiO ₂	Co(NO ₃) ₂ ·6H ₂ O	400°C for 4 h [17]

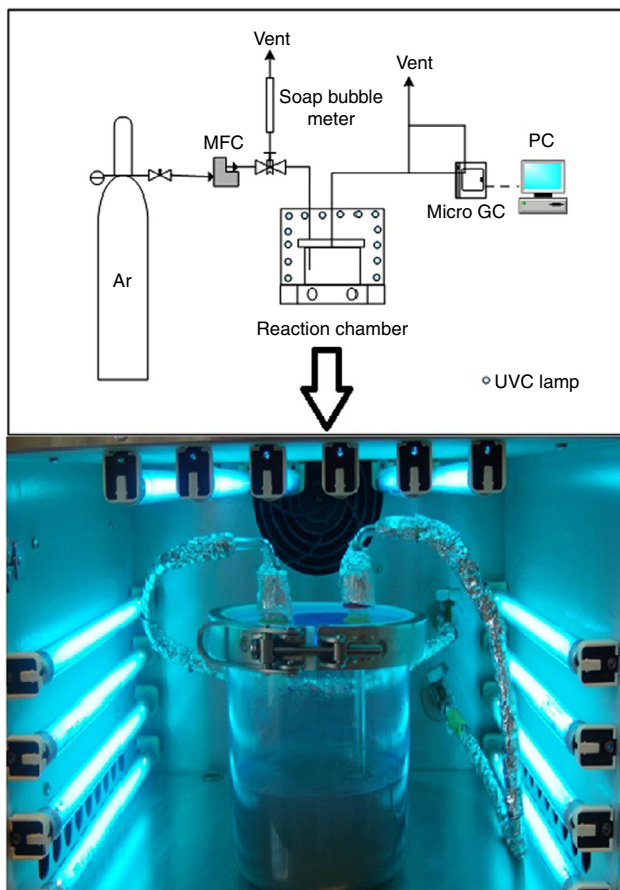


Figure 1
The photoreactor system utilized for the activity measurements.

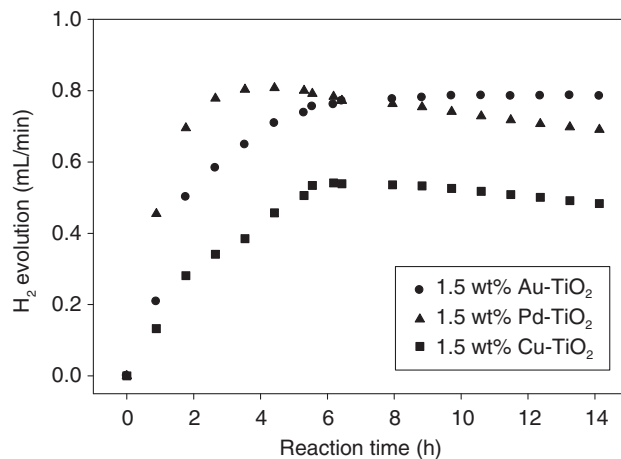


Figure 2
Comparison of photocatalytic activity over different metal-loaded catalysts. Reactor composition: 500 mL of 50 vol.% methanol aqueous solution. Catalyst weight: 0.25 g.

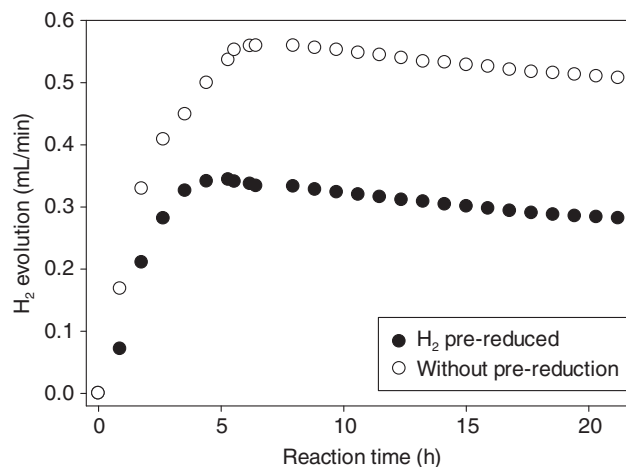


Figure 3
Effect of pre-reduction treatment in hydrogen over the 10 wt% Cu-TiO₂ catalysts. Feed composition: 500 mL of 50 vol.% methanol solution. Catalyst weight: 0.25 g.

The evolution of photocatalytic hydrogen over a 10 wt% Cu-TiO₂ was studied in the conditions of the initial methanol concentration being 50 vol.% at room temperature for 24 hours, as shown in Figure 4. The hydrogen evolution increases significantly at the beginning of the reaction and after approximately 5 hours, the hydrogen evolution reaches a maximum level and after that a small decrease in hydrogen evolution was observed. The hydrogen evolution can be recovered by refilling the reactor with fresh methanol solution to the initial concentration.

The results indicate that the Cu-TiO₂ photocatalyst is a relatively stable catalyst for hydrogen production from methanol and that the decrease in hydrogen evolution is mainly due to the consumption of methanol from the solution.

2.2 Effect of Metal Loading

The effect of metal loading on the hydrogen evolution is shown in Figure 5. No hydrogen evolution is detected with

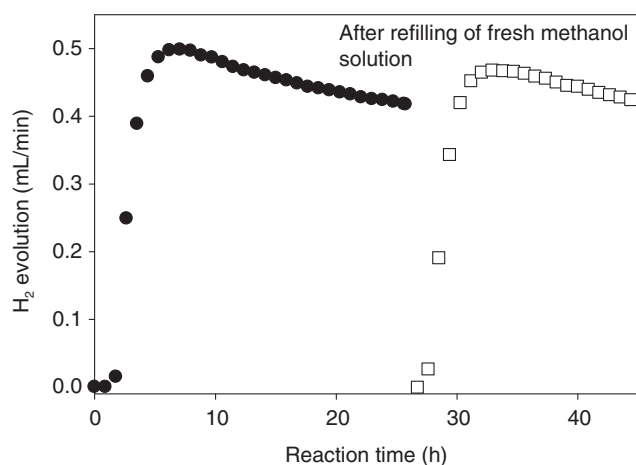


Figure 4

H₂ evolution *versus* time on stream in photoreforming of methanol. Feed composition: 500 mL of 50 vol.% methanol solution. Catalyst weight: 0.25 g.

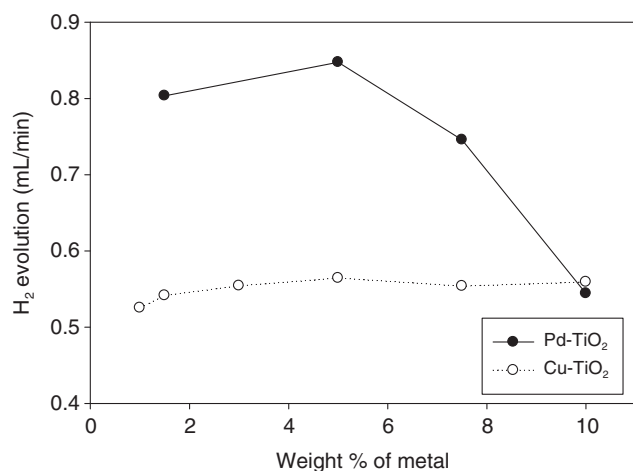


Figure 5

Effect of metal loading on hydrogen evolution. Reactor composition: 500 mL of 50 vol.% methanol aqueous solution. Catalyst weight: 0.25 g.

pure TiO₂ (P25-Degussa). The photocatalytic activity increased with Pd loading up to 5 wt% and then decreased with a further increase in palladium loading. In the case of copper loading, the change in the hydrogen evolution with copper loading is very small compared with Pd-TiO₂ catalysts. However, photocatalytic activity increased with copper loading up to 5 wt% and then showed a nearly constant hydrogen evolution with a further increase in copper loading. The photocatalytic activity decreased (Pd) or remained constant (Cu) above approximately 5 wt% metal loading.

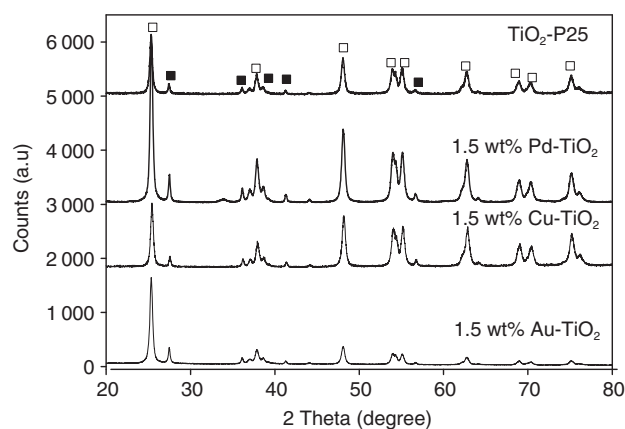


Figure 6

XRD patterns of different metal-loaded TiO₂ catalysts. Anatase (□) and Rutile (■).

The optimal loadings for Cu and Pd are somewhat higher than the reported values from Sreethawong and Yoshikawa [18], which are in the range 1-2 wt%. The reason for this could be the preparation method and metal dispersion. They also observed a relatively large change in the BET surface area when changing the metal loading. The BET surface area of the impregnated catalysts presented in this work did not change significantly when the metals were introduced (Sect. 2.4). The presence of a certain amount of metal particles on the surface of the semiconductor acts as a sink of electrons to avoid rapid recombination of the electron-hole pairs. Further increase in metal loading will prevent the transmission of light to the TiO₂ semiconductor surface. The Co-TiO₂ catalysts showed no detectable hydrogen evolution, and are hence not included in the comparison.

2.3 X-Ray Diffraction (XRD) Analysis

In the XRD patterns of the fresh catalysts, no detectable diffraction peaks of CuO, PdO or metallic Au crystallites could be detected for metal loadings of 1.5 wt%, as shown in Figure 6. This is most likely due to the relatively low content or because of the high dispersion of the particles on the TiO₂ surface.

No significant changes in the characteristic peaks of TiO₂ (P25) were observed for the fresh catalysts, indicating that there was no phase transformation in the TiO₂ support during the preparation. This is in agreement with the results of Raj and Viswanathan [20], where they concluded that the effect of rutilation of TiO₂ (P25) is not significant at temperatures below 500°C.

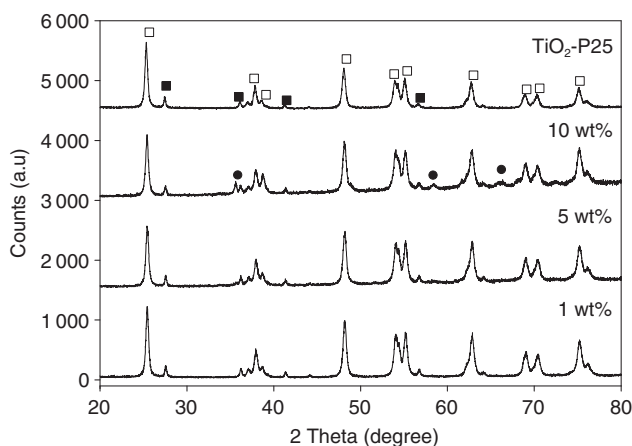


Figure 7

XRD patterns of fresh Cu-TiO₂ catalysts. Anatase (□), Rutile (■) and CuO (●).

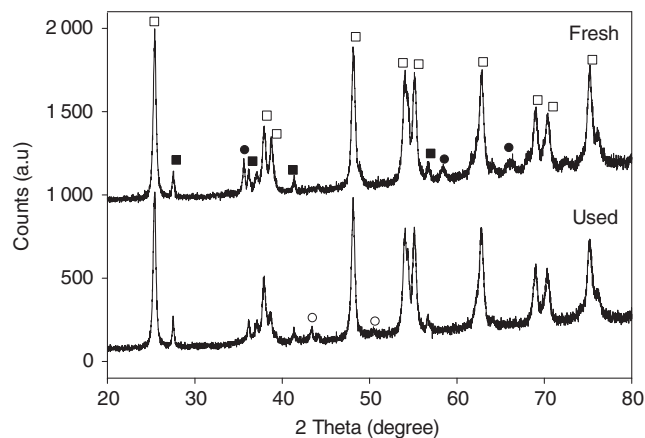


Figure 8

XRD patterns of fresh and used 10 wt% Cu-TiO₂ catalysts. Anatase (□), Rutile (■), Cu (○) and CuO (●).

Figure 7 shows XRD patterns of fresh Cu-TiO₂ catalysts. When the copper loading is more than 5 wt%, the XRD peaks corresponding to crystalline CuO were observed at 2θ of 35, 58 and 66° and the intensity increased with increasing copper loading, in agreement with the literature [7, 18]. CuO crystallite size analysis from XRD line broadening is difficult because of overlapping peaks between CuO and TiO₂. However, for the 10 wt% CuTiO₂ sample, the average crystallite size of CuO was estimated to be 32 nm from the Full Width at Half Maximum (FWHM) of the XRD main peak at $2\theta = 35^\circ$ using the Scherrer equation.

The copper in all the fresh catalysts is present as CuO. However, a change in the state of the copper after reaction is observed in the diffractograms in Figure 8. The peaks corresponding to metallic copper are clearly visible after reaction. This indicates that Cu is reduced in the active state.

As shown in Figure 9, the XRD peaks corresponding to crystalline PdO were observed at $2\theta = 34$ and 60, and the intensity increased with increasing palladium loading. The average crystallite sizes of PdO were calculated from the FWHM of the XRD main peak at $2\theta = 33^\circ$ using the Scherrer equation. The particle size appears to be independent of the metal loading and is estimated to be 10 nm for all the samples.

2.4 BET Surface Areas of the Catalysts

The BET surface areas of fresh and used catalysts are presented in Table 3. The photocatalysts did not show any significant change in the surface area after being exposed to the reaction conditions. Bin Xu *et al.* [21] also observed a small

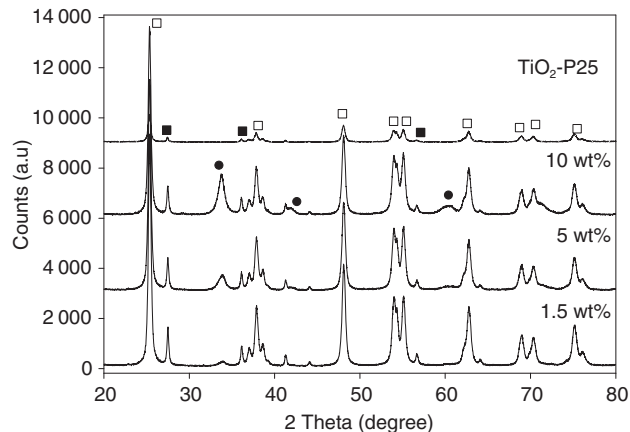


Figure 9

XRD patterns of fresh Pd-TiO₂ catalysts. Anatase (□), Rutile (■) and PdO (●).

change in the BET surface area with different amounts of CuO loading and reported that the loadings of CuO do not have a significant effect on the surface morphology of the support. As discussed in the previous section, photocatalytic activity increased with metal loading up to 5 wt% and then showed a decrease in hydrogen evolution or nearly constant hydrogen evolution with a further increase in metal loading. However, the BET surface area of the catalyst with high metal loading is only slightly lower than for the lower metal loading catalysts, indicating that the BET surface area may not be an important parameter in the photocatalytic activity. The BET surface areas of the 1.5 wt% catalysts are presented in Table 3. The values for the catalysts with other metal

TABLE 3
The BET surface areas of fresh and used catalysts (1.5 wt%)

Catalyst	BET surface area (m ² /g)	
	Fresh catalysts	Used catalysts*
Au-TiO ₂	52	-
Pd-TiO ₂	47	45
Cu-TiO ₂	49	47

* After exposure to reaction conditions for 15 h.

loadings are not significantly different (all close to 50 m²/g), and are hence not included in the table.

CONCLUSIONS

The photocatalytic activity decreased in the order of Pd > Au > Cu according to the results in the comparative study of Cu-TiO₂, Au-TiO₂ and Pd-TiO₂. Hydrogen evolution is not detected with the Co-TiO₂ catalyst. Optimum hydrogen evolution was achieved with 5 wt% Pd-TiO₂ and 5 wt% Cu-TiO₂ in the experimental conditions applied in this study. The BET surface area is not an important parameter for the photocatalytic at the applied conditions. No significant changes in the characteristic XRD peaks of TiO₂-P25 were observed for the fresh catalysts, indicating that there was no phase transformation in the TiO₂ support during the preparation. Finally, it can be concluded that methanol photoreforming may provide a potential low-cost method for the production of hydrogen from renewable sources and that TiO₂ loaded with non-precious metals such as copper is also a promising catalyst for producing hydrogen from methanol because of its photoactivity, stability and cost when compared with noble metal-loaded photocatalysts.

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