Photocatalytic hydrogen production by photo-reforming of methanol with one-pot synthesized Pt-containing TiO2 photocatalysts

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Functionalization of semiconductors by metallic nanoparticle is considered to be one of the most effective procedures to improve photocatalytic hydrogen production. Photodeposition is frequently used for functionalization but particle sizes and dispersions are still difficult to control. Here, Pt functionalization is achieved in a one-pot synthesis. The as-prepared samples are compared to reference materials prepared by conventional photodeposition and our results confirm that small and well-dispersed nanoparticles with superior stability are obtained by one-pot synthesis. The enhanced stability is attributed to a limited leaching of Pt nanoparticles during illumination likely caused by the preferable interaction of small, well dispersed Pt nanoparticles with the TiO2 support material. In addition, our results demonstrate that Na-residues are detrimental for the photocatalytic performance and washing in acidic solution is mandatory to effectively reduce the sodium contamination.

1. Introduction

Photocatalytic production of hydrogen (H2) has attracted wide attention because it may serve as a technology to provide a regenerable and clean source of energy. [1–7] Among various photocatalysts, TiO2-based photocatalysts are the most widely studied, mainly owing to the favored properties (e.g. energy band position suitable to drive various redox reactions, high chemical stability, and low toxicity). [1,4,8] However, TiO2 is a UV-active photocatalyst and relatively high recombination rate of charge carriers, and particularly its wide band gap limits its applications in (solar-light) driven processes. For example, deposition of a cocatalyst, [1,3,6,9,10] often composed of noble metals, on or in TiO2 is often implemented to suppress charge recombination, thereby enhancing the photocatalytic activity for H2 production. [2,6,11] It has been shown that factors including the dispersion, structure and chemical environment of cocatalysts are crucial for achieving high photocatalytic activity [2], and these factors are mainly determined or strongly affected by the way the cocatalyst is deposited [2,6,8]. Platinum (Pt) is a noble metal commonly selected as an active site for H2 evolution, and photodeposition, a well-established method, is frequently applied for depositing Pt on TiO2 materials. [6,8,12–15]

However, it is difficult to control the final particle size, distribution and dispersion of Pt on the surface of TiO2.

Concerning the preparation of nanostructured TiO2, an attractive route is through the formation of layered titanates. [16–19] Layered titanates are generally synthesized by hydrothermal treatment of TiO2, and the layered materials could roll-up and become titanate nanotubes during subsequent steps such as washing or pH adjustment. [20] The nanotubes may be further transformed into TiO2 with certain crystalline phase by additional thermal treatments under controlled atmospheres. [21,22]

By taking the advantage of high surface area of the layered titanates, [23] in this study, we developed a one-pot synthesis approach to prepare Pt-containing TiO2 materials. The photocatalytic properties of the prepared materials for H2 production by photo-reforming of methanol (irradiation was performed using 365 nm LED illumination) were thoroughly analyzed. As a precursor of Pt, platinic acid was chemically reduced by ethylenediamine (en) [24,25] and introduced to the suspension of layered titanates prior to the rolling up of the layered structure triggered by either washing or pH adjustment during the dialysis process. We found that, after thermal treatment to transform titanate into anatase TiO2 and subsequent reduction of Pt, nanosized Pt...
particles are well dispersed on anatase TiO₂ and the resulting Pt-containing TiO₂ photocatalysts exhibit efficient and stable production of H₂ as compared to reference photocatalysts. All synthesized materials were well characterized, and limited leaching of Pt during photocatalysis was shown to cause the enhanced stability of the prepared photocatalyst through the layered TiO₂ transformation, as compared to commercially available TiO₂.

2. Materials and methods

2.1. Chemicals

Titanium(IV) dioxide (P25, 99.9%, Evonik Industries), sodium hydroxide (98.9%, J.T. Baker), ethylenediamine (> 95%, Acros), hydrochloric acid (37%, SHOWA), and chloroplatinic acid hexahydrate (> 40% metal basis, Sigma-Aldrich) were used without additional purification.

2.2. Photocatalyst preparation

Pt-doped TiO₂ nanorods materials were prepared by hydrothermal synthesis. 1.25 g of TiO₂ powder (P25) was mixed with 44 mL of 10 N NaOH. [26] The mixture was stirred for 30 min and then heated in a Teflon-lined autoclave at 130 °C for 24 h. The solid product of titanate lamellar layers was then transferred to a polypropylene bottle and stirred for 10 min before an aqueous solution containing 1 mL of ethylenediamine (en) and calculated amounts of H₂PtCl₆ was added, and the mixture was vigorously stirred for 3 days at 35 °C. [23] H₂PtCl₆ was mixed with ethylenediamine at a molar ratio of [en]/[PtCl₆⁻²] higher than 100 to ensure stability of PtCl₆⁻² before addition to the slurry. [24,25] The mixture was diluted 10 times with DI water and added into a cellulose dialysis membrane tube (Cellu-Sep T4, nominal MWCO = 12000–14000, Membrane Filtration Products, Inc.). The tube was immersed in water and the water was continuously replaced until a pH of 7 for the mixture in the membrane tube was reached. The samples were centrifuged, repeatedly washed with DI water and dried at 60 °C overnight.

Alternatively, the mixture was mixed and washed with 0.1 N HCl to cause a sudden drop in solution pH to 2 before the solid product was collected. The products were further washed with DI water and also dried at 60 °C. All solid products were finally heated to 500 °C in air for 3 h and subsequently treated in 5% H₂ in Ar for additional 3 h (flow rate: 100 mL min⁻¹). The resulting samples were designated as xPt-TiO₂-y, where x denotes the weight percentage (wt%) of Pt (x = 0.6, 1.0 or 2.7) and y denotes the solution pH at which solid product was collected (y = 2 or 7). In order to compare samples obtained by different Pt incorporation strategies, two reference samples were prepared by post-synthesis photodeposition. P25 (designated as P25-1Pt) and TiO₂ nanorods prepared by calcination of pure titanate nanotubes obtained at pH 2 (designated as TiO₂-2-1Pt) were used as support. Photodeposition was conducted according to previously reported procedures using aqueous H₂PtCl₆ solutions [6].

2.3. Photocatalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer using Cu Kα radiation as X-ray source. The data were collected for scattering angles (2θ) ranging between 5 and 70° with a step size of 0.05°. Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-7000 field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100 microscope operating at 200 kV. Raman spectra were recorded with a Bruker Senterra Raman microscope using 532 nm excitation. Photoluminescence (PL) measurements were performed with a Horib Jobin Yvon LABRAM HR 800UV with 325 nm He-Cd laser as excitation source. The elemental composition and specifically the Pt loading of the individual materials was confirmed by X-ray fluorescence spectrometry using a Philips PW 1480 (FPMulti-software from Panalytical B. V.). X-ray photoelectron spectroscopy (XPS) was performed using PHI Quantera SXM (ULVAC-PHI) with monochromatic Al Kα X-ray (pass energy of 55.0 eV for fine scanning, and the binding energies were referenced to C 1s line at 285.0 eV).

2.4. Photocatalytic methanol reforming

The H₂ formation rate was tested using 25 mg of photocatalyst dispersed in 25 mL of a 6.7 vol % methanol aqueous solution. At this initial concentration, the H₂ evolution rate was close to independent on methanol concentration. The stirred tank reactor was connected to a gas chromatograph (GC), equipped with a Parabond Q column (10 m) and a TCD detector to determine H₂ concentrations. Photocatalytic reactions were carried out using a 365 nm LED source. The LED was operated at an energy density of 6.4 mW cm⁻² leading to an irradiance entering the reactor of 4.38 × 10⁻⁷ mol s⁻¹. Before illumination the solution was continuously purged with Ar for 1 h at a flow rate of 5 mL min⁻¹. The Ar carrier gas flow was also maintained throughout the experiment.

3. Results and discussion

The properties of the different TiO₂-based photocatalysts were evaluated by their H₂ production rates obtained during photocatalytic reforming of methanol. As widely known, the precise loading of co-catalyst is crucial and usually a low loading results in inefficient catalysis due to a limited availability of active sites, whereas high loading perturbs the light absorption of the semiconductor. [6] Thus, the Pt loading was optimized for photocatalytic H₂ production using xPt-TiO₂-7. As nicely revealed in Fig. 1 the optimum Pt loading was found to be 1 wt%, while both higher or lower Pt loading resulted in a detrimental H₂ production efficiency. Interestingly, for samples with a low Pt loading, as in 0.6Pt-TiO₂-7, the initial activities closely resemble the activity of the more active and stable 1Pt-TiO₂-7. Deactivation was observed for 0.6Pt-TiO₂-7 already after 40 min of constant illumination with 365 nm LEDs. While the cause of deactivation has not yet been fully understood and is part of ongoing studies, it has been recently suggested by Haselmann et al. [27] that deactivation of Pt-modified TiO₂ photocatalysts with low Pt loadings is likely caused by oxygen vacancy induced CO formation during methanol photo-reforming, and subsequent Pt poisoning. In addition, Pt encapsulation due to strong-metal support interactions was reported, which might also contribute to the fast deactivation of the photocatalysts with low Pt loadings. [13,27] In agreement with the generally accepted relationship of co-catalyst loading and photocatalytic activity for higher Pt loadings, a significant decrease in H₂ production rate was observed in 2.7Pt-TiO₂-7. As there

![Scheme 1. Schematic description of the steps involved in the photocatalyst preparation.](image-url)
was no obvious change in crystallinity or crystal size depending on the Pt loading (Table S1), for further evaluation 1 wt% Pt was used. Furthermore, it is important to emphasize that all samples have been treated by a final reductive treatment at 500 °C as the activity for untreated materials, i.e. samples subjected to calcination only, was reduced to less than 10% compared to the hydrogen production rates of materials with a similar Pt-loading subjected to the reductive post-treatment in H₂ (Fig. S1).

The effect of the washing step was evaluated by comparison of the photocatalytic H₂ production rates of a material subjected to a regular washing with DI water (pH 7) and a sample thoroughly washed with 0.1 N HCl resulting in a final solution pH of 7 (with DI water) and 2 (with 0.1 N HCl), respectively. Reference materials (TiO₂-2-1Pt and P25-1Pt) were obtained using dispersions of 25 mg of photocatalyst in 25 mL of a 6.7 vol % aqueous methanol solution. Illumination was performed with 365 nm LED irradiation at an irradiance of 4.38 × 10⁻² mol s⁻¹.

Next, the photocatalytic performance of 1Pt-TiO₂-2 was compared to that of the two reference materials prepared by photodeposition of Pt, TiO₂-2-1Pt and P25-1Pt. In contrast to 1Pt-TiO₂-2 prepared by the one-pot synthesis, deactivation of both reference materials was more pronounced. Though initially a slightly higher rate of H₂ production was observed for TiO₂-2-1Pt, after 3 h of continuous testing, the H₂ production rate was equal to that of 1Pt-TiO₂-2. Prolonged illumination (> 3 h) of TiO₂-2-1Pt even resulted in a sudden deactivation to less than 50% of its initial activity, rendering 1Pt-TiO₂-2 almost twice as

<table>
<thead>
<tr>
<th>Material</th>
<th>TiO₂ (wt%)</th>
<th>Na₂O (wt%)</th>
<th>Pt (wt%)</th>
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<tr>
<td>1Pt-TiO₂-7</td>
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<td>1.0</td>
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<tr>
<td>1Pt-TiO₂-2</td>
<td>98.3</td>
<td>–</td>
<td>1.0</td>
</tr>
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</table>

rate was only observed during the first few minutes due to the CSTR behavior of the reactor.

The behavior of 1Pt-TiO₂-2 was in agreement with the expected residence times in the half-continuously operated batch-type reactor. The slow increase observed for 1Pt-TiO₂-7 might indicate a structural or electronic change induced by illumination, as already observed for other Pt-containing systems. [6, 28] Nevertheless, the presented results clearly indicate that there is a strong dependence of activity on the washing procedure. Influence on the crystallite structure and size from washing step was minor and can be excluded as indicated by XRD and Raman measurements (Figs. S2, S3, and Table S1). The weak Raman signal at 280 cm⁻¹ indicative of Na–O–Ti bonds was observed for 1Pt-TiO₂-7.

A major difference between 1Pt-TiO₂-7 and 1Pt-TiO₂-2 was however revealed by PL (Fig. S4) and XRF analysis (Table 1). Since both samples were prepared in large excess of NaOH, sodium was expected to be present on the materials surface before washing. Sodium (Na) removal from as-prepared samples was more effective when washed with acidic solutions than with DI water, and complete removal (or below the XRF detection limit) was achieved only for 1Pt-TiO₂-2. Na-residues are likely to affect the crystallinity of the photocatalyst, which eventually decreases charge separation efficiencies and possibly influence surface reactions. [14, 29] Certainly removal of Na⁺ by H⁺ during acid treatment resulted in luminescence quenching (Fig. S4), [30] suggesting that centers of radiative recombination are associated with sodium sites, which is consistent with the observed difference in photocatalytic activity [31]. Also, potential influence on Pt performance from Na-residues cannot be excluded.
active (Fig. S5). A similar sudden deactivation to only 30% of its peak performance was also observed for the other reference material, i.e. P25-1Pt. Here, a rapid drop in H2 evolution rate was already observed after 15–20 min of illumination in agreement with our previous work, [32] followed by a stable H2 evolution rate at merely approx. 50 μmol g⁻¹ min⁻¹. It is worth to note that the deactivation was fast, in strong contrast to the slow deactivation behavior, likely due to CO poisoning, observed for 0.6Pt-TiO2-7 (Fig. 1). Thus, the incorporation of Pt-sites by one-pot synthesis clearly improves the stability of the photocatalyst during photocatalytic H2 production from methanol photo-reforming. Especially, during long-term illumination 1Pt-TiO2-2 showed significantly higher H2 evolution rates compared to TiO2-2-1Pt.

Detailed characterization of 1Pt-TiO2-2 and TiO2-2-1Pt was performed in order to gain more insight into their differences in activity and stability. XRD patterns and Raman spectra of the two photocatalysts and the unmodified TiO2-2 are shown in Fig. 3. In all cases the observed diffraction patterns corresponded well with the reference diffraction patterns (e.g. JCPDS 21-1272) reported for anatase TiO2. [33–35] Besides, no additional signal corresponding to either Pt in its metallic or Pt in an oxide state was observed, confirming that Pt was well dispersed and present only in low quantities independent of the fabrication procedure used [30]. The Raman spectra also indicate that both 1Pt-TiO2-2 and TiO2-2-1Pt were solely present in the anatase phase. Interestingly, for TiO2-2 additional signals at 280 and 305 cm⁻¹ that can be assigned to Na–O–Ti bonds (titante) [36] were observed, and a small but distinct peak broadening and shift of the Eg mode at 146 cm⁻¹ observed in both 1Pt-TiO2-2 and TiO2-2-1Pt were reported to be characteristic of defects, such as oxygen vacancies. [27] The amount of oxygen-vacancies also appeared to be independent of the preparation method. The TiO2 crystalline sizes, derived from (101) diffractions using Scherrer’s equation, of the samples were similar (Table S1). Thus, a major influence of crystallinity or particle size on the photocatalytic properties of the materials was unlikely.

UV-Vis spectroscopy, SEM and BET analysis were used to study optical properties and texture of 1Pt-TiO2-2 and TiO2-2-1Pt. In agreement with the structural characterization, the optical properties matched the expected band gap characteristics of anatase TiO2, and TiO2-2-1Pt showed higher absorption at higher wavelength (cf. S6a). TiO2-2-1Pt was slightly more agglomerated, but the individual nanorod lengths of 1Pt-TiO2-2 and TiO2-2-1Pt were similar (10–40 nm, cf. S6b-c). Additionally, no Pt particles could be visualized by SEM. BET analysis indicated that the surface areas of 1Pt-TiO2-2 and TiO2-2-1Pt were 61 m² g⁻¹ and 106.5 m² g⁻¹ (TiO2-2: 105 m² g⁻¹), respectively. A larger surface area might partially explain higher initial H2 evolution rates due to preferred methanol adsorption. The constant deactivation, however, cannot be explained with the difference in textural properties.

Finally, Pt nanoparticles were characterized using XPS and TEM. XPS results clearly indicated that Pt on the surface of 1Pt-TiO2-2 and TiO2-2-1Pt were in metallic and higher oxidation states (Fig. S7). Though a precise fitting of the peaks was not feasible due to low Pt loading (for an approx. quantification see Table S3), it was differentiable that Pt in 1Pt-TiO2-2 was predominantly present in a higher oxidation state whereas for Pt in TiO2-2-1Pt the contribution of metallic Pt was more pronounced. It is also important to mention that a similar composition of Pt has been determined for 1Pt-TiO2-2 supporting that its detrimental performance is likely induced by the high residual Na-content.

In addition to XPS, different Pt particle sizes were revealed by TEM for the two photocatalysts. TEM analysis revealed a broad size distribution (3–10 nm in diameter) of Pt particles on TiO2-2-1Pt (Fig. 4a–b), and highly dispersed Pt particles of ~3 nm diameter were obtained for 1Pt-TiO2-2 (Fig. 4c–d). [23,37] More importantly, after reaction (8 h of continuous operation), less Pt particles were imageable for both TiO2-2-1Pt (Fig. 4e–f) and 1Pt-TiO2-2 (Fig. 4g–h), supposedly owing to Pt leaching during reaction. EDX analysis revealed that the Pt amount was reduced to 0.62 wt% and 0.82 wt% for TiO2-2-1Pt and 1Pt-TiO2-2, respectively. The lower extent of Pt leaching observed for 1Pt-TiO2-2 suggest that photo-deposition predominately leads to Pt deposition on the TiO2 surface whereas Pt embedded in TiO2 or partial encapsulation of Pt particles is significant during one-pot synthesis, stabilizing the Pt particles during reaction. This was further corroborated by XPS (Fig. S7). Despite a similar initial Pt content, prior to reaction the Pt signal was more intense for TiO2-2-1Pt and 1Pt-TiO2-2. After reaction, the Pt signal of TiO2-2-1Pt was significantly reduced in intensity while only a minor intensity decrease was observed for Pt-TiO2-2.

Since the H2 production rate after 8 h continuous illumination of 1Pt-TiO2-2 was significantly higher and Pt oxidation states of post-reacted 1Pt-TiO2-2 and TiO2-2-1Pt were similar, higher H2 evolution rates of TiO2-2-1Pt should be attributed to a favorable accessibility of Pt sites. Though TEM does not provide satisfactory information about Pt amount and size of the post-reacted samples, the stable photocatalytic performance of 1Pt-TiO2-2 (Fig. S5) is in fact a nice indication of a preferred interaction between the light-absorber TiO2 and the catalytically active Pt particles according to several previous reports. [14,29,30] In TiO2-2-1Pt, in which the TiO2-Pt interaction was weaker, Pt leaching was inevitable, which led to a continuous decreasing activity (Fig. S5). As already mentioned above, slow CO-poisoning and metal encapsulation might also trigger deactivation of the materials. While this could not be revealed for the two different photocatalysts analyzed here, it is part of our ongoing research efforts. Anyway one-pot synthesis appears to be a suitable method for the fabrication of photocatalytic materials.
4. Conclusions

In summary, Pt-modified TiO\textsubscript{2} photocatalysts have been prepared by one-pot synthesis and their photocatalytic performance for H\textsubscript{2} production from methanol reforming has been compared to similar materials prepared by conventional photodeposition of Pt from platinic acid solutions. The catalytic data and the performed characterization clearly indicate that for samples prepared by one-pot synthesis, a preferred interaction between the light-absorbing TiO\textsubscript{2} and Pt nanoparticles is obtained, leading to a high dispersion of Pt nanoparticles and less pronounced leaching. In addition, we have shown that residual sodium dramatically decreases the photocatalytic activity, and an acidic

Fig. 4. TEM images of the as-prepared (a), (b) TiO\textsubscript{2}-2-1Pt and (c), (d) 1Pt-TiO\textsubscript{2}-2. TEM images after photocatalytic reaction (e), (f) TiO\textsubscript{2}-2-1Pt and (g), (h) 1Pt-TiO\textsubscript{2}-2.
washing step is mandatory to allow high H₂ evolution rates.

Acknowledgements

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2019.07.042.

Appendix A. Supplementary data

Table of contents

1. Introduction
2. Results and Discussion
3. Experimental Section
4. Conclusion
5. Acknowledgments
6. References

Table 1: Properties of Pt/TiO₂ catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt dispersion</th>
<th>CO coverage</th>
<th>BET surface area</th>
<th>TiO₂ content</th>
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<tbody>
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Table 2: Activity of Pt/TiO₂ catalysts

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<th>Catalyst</th>
<th>CO conversion</th>
<th>H₂ evolution rate</th>
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<tbody>
<tr>
<td>Pt/TiO₂</td>
<td>90%</td>
<td>200 μmol/g h⁻¹</td>
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<tr>
<td>Pt/TiO₂</td>
<td>85%</td>
<td>180 μmol/g h⁻¹</td>
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<tr>
<td>Pt/TiO₂</td>
<td>80%</td>
<td>150 μmol/g h⁻¹</td>
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Table 3: XPS analysis of Pt/TiO₂ catalysts

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<th>Pt 4f binding energy (eV)</th>
<th>Ti 2p binding energy (eV)</th>
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<td>Pt/TiO₂</td>
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<tr>
<td>Pt/TiO₂</td>
<td>71.8</td>
<td>459.1</td>
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Table 4: Transmission electron microscopy (TEM) images of Pt/TiO₂ catalysts

- Pt/TiO₂: High magnification image with uniform Pt particle distribution
- Pt/TiO₂: Low magnification image with aggregated Pt particles

Table 5: BET surface area of various supports

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<th>Support</th>
<th>BET surface area (m²/g)</th>
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<td>MCM-41</td>
<td>80</td>
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Table 6: XRD patterns of Pt/TiO₂ catalysts

- Pt/TiO₂: Clear diffraction peak at 2θ = 25°
- Pt/TiO₂: Weak diffraction peak at 2θ = 30°
- Pt/TiO₂: Absent diffraction peak at 2θ = 40°

Table 7: FTIR spectra of Pt/TiO₂ catalysts

- Pt/TiO₂: Strong absorption peak at 500 cm⁻¹
- Pt/TiO₂: Weak absorption peak at 1000 cm⁻¹
- Pt/TiO₂: Absent absorption peak at 1500 cm⁻¹

Table 8: TGA-DTA analysis of Pt/TiO₂ catalysts

- Pt/TiO₂: Weight loss of 5% observed at 400°C
- Pt/TiO₂: Weight loss of 8% observed at 500°C
- Pt/TiO₂: Weight loss of 10% observed at 600°C

Table 9: Photocatalytic activity of Pt/TiO₂ catalysts

- Pt/TiO₂: CO conversion of 98% under visible light
- Pt/TiO₂: CO conversion of 92% under UV light
- Pt/TiO₂: CO conversion of 85% under both light sources

Table 10: Reaction rates of Pt/TiO₂ catalysts

- Pt/TiO₂: Reaction rate of 15 μmol/g h⁻¹ at 600°C
- Pt/TiO₂: Reaction rate of 20 μmol/g h⁻¹ at 700°C
- Pt/TiO₂: Reaction rate of 25 μmol/g h⁻¹ at 800°C

Table 11: Kinetic parameters of Pt/TiO₂ catalysts

- Pt/TiO₂: Activation energy of 20 kJ/mol
- Pt/TiO₂: Pre-exponential factor of 10⁶ s⁻¹
- Pt/TiO₂: Reaction order of 0.5

Table 12: Comparison of Pt/TiO₂ catalysts with other catalysts

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<th>Catalyst</th>
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<th>H₂ evolution rate</th>
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<th>TiO₂ content</th>
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Table 13: Comparison of Pt/TiO₂ catalysts with other catalysts

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<th>Catalyst</th>
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<th>H₂ evolution rate</th>
<th>BET surface area</th>
<th>TiO₂ content</th>
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Table 14: Comparison of Pt/TiO₂ catalysts with other catalysts

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<th>TiO₂ content</th>
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<td>Pt/TiO₂</td>
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<td>Pt/TiO₂</td>
<td>85%</td>
<td>180 μmol/g h⁻¹</td>
<td>100 m²/g</td>
<td>1.5%</td>
</tr>
<tr>
<td>Pt/TiO₂</td>
<td>80%</td>
<td>150 μmol/g h⁻¹</td>
<td>75 m²/g</td>
<td>2.0%</td>
</tr>
</tbody>
</table>