

Research Note

Suppressing CO formation by anion adsorption and Pt deposition on TiO₂ in H₂ production from photocatalytic reforming of methanol

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Abstract

H₂ with ultra-low CO concentration less than 10 ppm was produced via photocatalytic reforming of methanol on Pt/TiO₂ catalyst adsorbed with sulfate or phosphate ion. The platinum loaded on TiO₂ not only enhances the rate of H₂ production but also considerably suppresses CO formation. The sulfate and phosphate ions adsorbed on TiO₂ were found to further suppress the CO formation, without evidently decreasing the rate of H₂ production.

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1. Introduction

The concerns about the depletion of fossil fuel reserves and the pollution caused by continuously increasing energy demands make H₂ an attractive alternative energy source [1]. Methanol is one of the most promising sources for hydrogen production because it has a high hydrogen/carbon ratio and can also be obtained either from fossil resources or from biomass [2].

H₂ production from photocatalytic reaction attracts much attention in the past few years [3–5]. Titania-based catalysts, such as Pt/TiO₂ [6,7], are efficient catalysts for photocatalytic reforming of methanol to produce hydrogen. However, the primary H₂ production from photocatalytic reforming of methanol was always accompanied by the formation of the by-product carbon monoxide [8,9], as shown in Scheme 1.

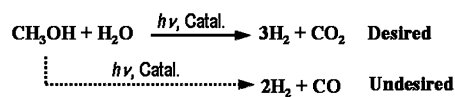
CO present in H₂ is harmful to many catalysts, particularly harmful to the Pt-based anode catalyst in proton exchange membrane (PEM) fuel cells because CO even with a very low concentration could lead to the poisoning of the Pt-based an-

ode catalyst [10]. So, it is highly desired to suppress the CO formation in photocatalytic reforming of methanol.

This communication reports that the CO concentration in H₂ can be dramatically reduced to several ppm via photocatalytic reforming of methanol on TiO₂-based catalyst by depositing Pt on TiO₂ in combination with the addition of trace amount of inorganic anions, such as SO₄²⁻ and H₂PO₄⁻, in the reaction system, without evidently decreasing the rate of H₂ production.

2. Experimental

All chemicals used in these experiments were of analytical reagent grade and used without further treatment. The Pt/TiO₂ catalysts were prepared by incipient wetness method. The commercial Degussa P25 power (composed of 20 wt% rutile and 80 wt% anatase, BET surface area 53 m²/g) was impregnated with an aqueous solution of H₂PtCl₆·6H₂O, followed by drying in an oven at 383 K overnight. The obtained powder was ground and then reduced at 473 K in flowing hydrogen for 2 h.



Scheme 1. Photocatalytic reforming of methanol for hydrogen production.

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The photocatalytic reaction was performed with a Pyrex reaction cell connected to a closed gas circulation and evacuation system. The photocatalyst was dispersed in a reaction cell containing 200 ml methanol aqueous solution. The light source was a 300 W Xe lamp. A shutter window and a water filter were placed between the Xe lamp and the reaction cell in order to remove IR light illumination. Prior to illumination, the reaction system was deaerated by evacuation. The gaseous products were analyzed by an on-line gas chromatograph (Shanghai GC-920, TDX-01 carbon molecular sieve packed column, Ar carrier gas). The chromatograph was equipped with a thermal conductivity detector, a flame ionization detector and a methanizer. The amount of H₂ was measured by the thermal conductivity detector. The flame ionization detector was used to analyze CO, which was converted into CH₄ after passing the methanizer. Response factors for gas products were obtained by using appropriate standards.

3. Results and discussion

Fig. 1 shows the rate of H₂ production and the molar ratio of CO/H₂ in photocatalytic reforming of methanol on pure TiO₂ (Degussa P25) and Pt/TiO₂ catalysts. For pure TiO₂, the rate of H₂ production is very low and the CO concentration in H₂ is as high as 30,000 ppm. However, after loading appropriate amount Pt on TiO₂, the rate of H₂ production is significantly increased and CO concentration is found to decrease evidently. When Pt loading is higher than 0.05 wt%, the rate of H₂ production reaches a plateau and the CO concentration in H₂ drops to a very low level, i.e. from 30,000 ppm to less than 10 ppm.

For a Pt/TiO₂ catalyst with Pt loading less than 0.05 wt%, CO concentration in H₂ is still very high, e.g. about 2500 ppm CO in H₂ with 0.02 wt% Pt loading. As shown in Fig. 2, it is interesting to find that the CO concentration (expressed as the molar ratio of CO/H₂) can be further decreased by the addition of some inorganic anions in the reaction system. The addition of Na₂SO₄, NaH₂PO₄, NaHCO₃, NaNO₃, and NaCl in the reaction solution can effectively suppress the CO formation, although this suppression extent is dependent on the choice of different anions. Since all the salts contain the same

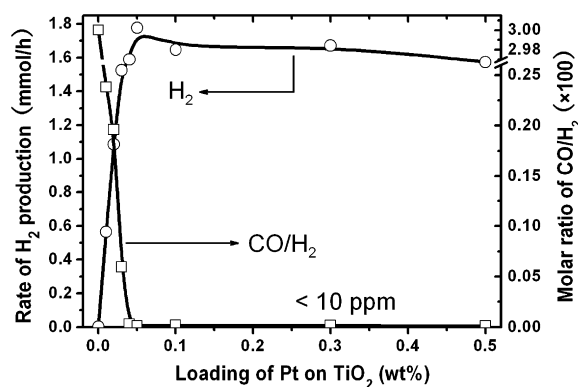


Fig. 1. The rate of H₂ production and molar ratio of CO/H₂ as a function of different amount of Pt loaded on TiO₂ in photocatalytic reforming of methanol. Reaction conditions: 200 ml 5.0 M methanol solution; 0.3 g Pt/TiO₂ catalyst; 300 W Xe lamp.

cation, Na⁺, the variations in the rate of H₂ production and CO selectivity are mainly ascribed to the effect of different anions. The order of suppression effect increases in the following sequence: Cl⁻ < NO₃⁻ < HCO₃⁻ < SO₄²⁻ < H₂PO₄⁻. The CO concentration can be decreased to about 10 ppm if a small amount of Na₂SO₄ or NaH₂PO₄ was added in the reaction system. For example, the CO concentration is dramatically decreased from about 2500 ppm to 10 ppm on the addition of sulfate of 0.1 mM, or the addition of phosphate of 0.025 mM. The CO concentration could be further decreased to even few ppm if the concentration of sulfate or phosphate increased up to 0.3 mM. However, as shown in Fig. 3, no evident decrease in the H₂ production rate is observed after the addition of most of these anions in the reaction solution, except for phosphate ions, which reduces the rate of H₂ production possibly by decreasing the pH value of the reaction solution [11].

Surface intermediate species, such as CH₂O(a), CH₂OO(a) and HCOO(a) are always detected by in situ FT-IR spectroscopy from photocatalytic reforming of methanol on Pt/TiO₂ catalyst [12]. It was proposed that photocatalytic reforming of

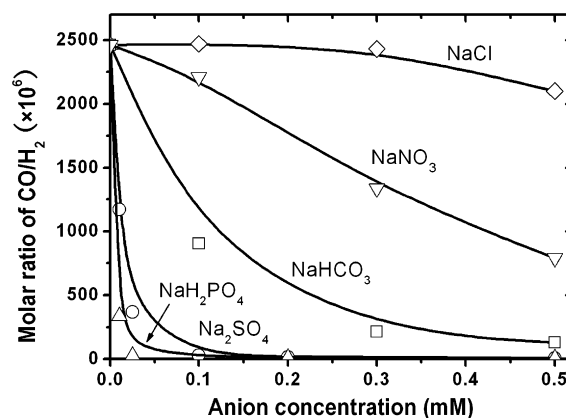


Fig. 2. Effect of inorganic anions (SO₄²⁻, H₂PO₄⁻, HCO₃⁻, NO₃⁻, and Cl⁻) on CO selectivity (expressed as the molar ratio of CO/H₂) in photocatalytic reforming of methanol on Pt/TiO₂ catalyst. Conditions: 200 ml 5.0 M methanol solution; 0.1 g 0.02 wt% Pt/TiO₂; 300 W Xe lamp.

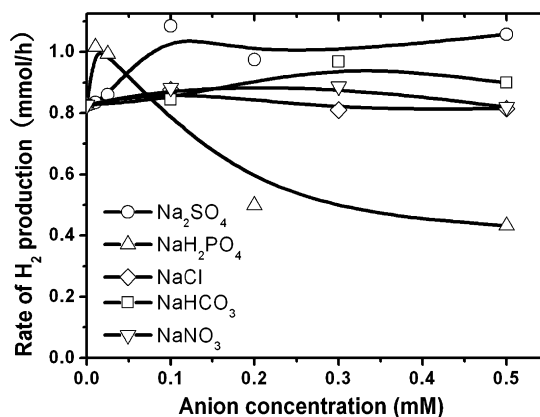


Fig. 3. Effect of inorganic anions (SO₄²⁻, H₂PO₄⁻, HCO₃⁻, NO₃⁻, and Cl⁻) on the rate of H₂ production in photocatalytic reforming of methanol on Pt/TiO₂ catalyst. Conditions: 200 ml 5.0 M methanol solution; 0.1 g 0.02 wt% Pt/TiO₂; 300 W Xe lamp.

methanol proceeded stepwise involving at least two intermediates, formaldehyde and formic acid [7].

We found that both H₂ production and CO formation were considerably suppressed in photocatalytic degradation of formic acid on Pt/TiO₂ catalyst when a small amount of phosphate or sulfate ions were added in the initial HCOOH solution (supporting information Fig. S1). For the pure TiO₂ catalyst, the suppression effect of the phosphate and sulfate ions on CO formation is comparable to that for Pt/TiO₂ catalyst (supporting information Fig. S2). When SO₄²⁻ or H₂PO₄⁻ is pre-adsorbed on Pt/TiO₂ catalyst, CO production is greatly suppressed in photocatalytic reforming of CH₃OH as well as HCOOH (supporting information Fig. S3).

The inorganic anions affect the photocatalytic reaction most likely by means of competitive adsorption on the active sites of TiO₂ catalyst [13,14]. The affinity of these anions for TiO₂ surface is in the order: Cl⁻ < NO₃⁻ < HCO₃⁻ < SO₄²⁻ < H₂PO₄⁻ [13–15], which is the same order as for the suppression effect on CO formation in photocatalytic reforming of methanol. The competitive adsorption of HCOO⁻ with various anions on Pt/TiO₂ was investigated by FT-IR (as shown in supporting information Fig. S4). The spectra of Pt/TiO₂ with pre-adsorbed Cl⁻, NO₃⁻ and HCO₃⁻ are similar to that of Pt/TiO₂, indicating that Cl⁻, NO₃⁻ and HCO₃⁻ anions are weakly adsorbed on TiO₂ or even not adsorbed. However, the spectra of Pt/TiO₂ with pre-adsorbed SO₄²⁻ and H₂PO₄⁻ show some IR absorption in the region 900–1300 cm⁻¹. These FT-IR bands clearly indicate that SO₄²⁻ and H₂PO₄⁻ were strongly adsorbed on TiO₂, most likely on the surface defect sites of TiO₂ (mainly oxygen vacancy sites on TiO₂).

Based on the above results, it is proposed that the adsorption of formic acid on the defect sites of TiO₂ may be competitive with phosphate or sulfate anions. The by-product CO is produced at the defect sites on the surface of TiO₂ via the dehydration reaction of the intermediate formic acid species. The CO production is suppressed by sulfate or phosphate ions because these anions may occupy the defect sites of TiO₂ and make the probability of formic acid adsorbed on TiO₂ decrease.

The recombination of photogenerated electrons and holes at the surface defect sites of TiO₂ (mostly oxygen vacancy sites) was observed by a characteristic luminescence band at about 505 nm [16]. It was found that the visible luminescence band of TiO₂ was easily quenched by the Pt deposited on the surface of TiO₂, and the luminescence intensity became weaker with increasing the Pt loading (supporting information Fig. S5). Based on the fact that the deposited Pt could decrease the intensity of visible luminescence band and simultaneously suppresses the CO formation, it is deduced that the surface defect sites, which are usually the recombination sites for the photogenerated electrons and holes, are the active sites responsible for the CO formation. Therefore, the deposition of Pt on the surface defect sites can effectively suppress the CO formation.

The mechanism of CO formation in photocatalytic reforming of methanol on Pt/TiO₂ catalyst can be proposed as follows. The photogenerated holes migrate to the surface of TiO₂ and oxidize adsorbed CH₃OH to form the intermediate species

[CH₃O], [CH₂O], [HCOO] and finally CO₂ or some CO. The derived formic acid species adsorbed at surface defect sites (mainly oxygen vacancy sites) could easily decompose into CO and water. The deposited Pt or adsorbed anions suppress CO formation by preferentially occupying the surface defect sites on TiO₂, consequently blocking the route to CO formation.

This study sheds light on the mechanism of hydrogen production with ultra-low CO concentration from photocatalytic reforming of not only methanol but also biomass, because the final intermediates such as CHO⁻ and HCOO⁻ derived from biomass reforming are very similar to those of methanol.

In summary, H₂ with ultra-low CO concentration was produced via photocatalytic reforming of methanol on Pt/TiO₂ catalyst with adsorbed SO₄²⁻ or H₂PO₄⁻. The formation of CO can be greatly suppressed by depositing Pt or adsorption of small amount of inorganic anions, such as SO₄²⁻ and H₂PO₄⁻ on TiO₂. The deposited Pt suppresses the CO formation via preferentially occupying the surface defect sites, while the inorganic ions compete to adsorb at surface defect sites where CO is formed mainly via the dehydration of formic acid species.

Acknowledgment

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Supporting information

Supporting information for this article may be found on ScienceDirect, in the online version.

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