

Photocatalytic reaction of $\text{H}_2\text{O} + \text{CO}_2$ over pure and doped Rh/TiO_2

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In the photocatalytic reduction of carbon dioxide to formic acid, formaldehyde and methanol in aqueous suspensions of TiO_2 and Rh/TiO_2 , the effects of doping the TiO_2 with W^{6+} were investigated.

Keywords: Photoinduced formation of CO_2^- ; photoreduction of CO_2 ; photolysis of $\text{H}_2\text{O} + \text{CO}_2$; photosynthesis of formaldehyde, formic acid and methanol; TiO_2 photocatalyst; Rh/TiO_2 photocatalyst; effect of doping of the TiO_2

1. Introduction

Within a programme to study the activation of CO_2 and its transformation into more valuable compounds, we have observed that Rh deposited on TiO_2 is the most effective catalyst in the hydrogenation of CO_2 into organic compounds [1]. The Rh/TiO_2 catalyst also proved to be active in closely related reactions, such as the hydrogenation of CO, the dissociation of CO and the production of CH_4 from a $\text{H}_2\text{O} + \text{CO}$ mixture [2]. To interpret the high efficiency of the TiO_2 support, we assumed the occurrence of an electronic interaction at the Rh–reduced TiO_2 interface, which strongly influences the adsorptive and catalytic properties of the Rh. This assumption seems to be supported by the finding that variation of the electron concentration of the TiO_2 by doping with altrivalent cations affected the catalytic activity of the Rh in the above reactions [3].

These findings motivated us to examine the effects of the electric properties of TiO_2 as a catalyst and a support in the photocatalytic reaction between H_2O and CO_2 , one of the most important and challenging reactions in artificial photosynthesis [4–11].

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2. Experimental

2.1. MATERIALS

The titania was a reagent grade product of British Drog House (BDH). Doping of this TiO₂ sample with W⁶⁺ ions was carried out in the following way: TiO₂ was introduced into the solution of (NH₄)₁₀W₁₂O₄₀(OH)₂·4H₂O, the suspension was dried at 393 K during continuous stirring. After extensive homogenisation the solids were calcined in air at 773 K for 5 h. Surface area (measured by N₂ adsorption at 77 K) of the calcined TiO₂ sample was 18 m²/g, which was practically unaltered by doping. Some measurements were performed with another titania (reagent grade, <125 µm diameter) obtained from Matheson Coleman and Bell Co, Cincinnati (MCB). The surface area of the air sintered sample at 773 K was 10 m²/g.

In the preparation of oxidized Rh/TiO₂, TiO₂ samples (BDH) were impregnated with an aqueous solution of RhCl₃·3H₂O. The suspension was dried at 393 K and heated at 773 K in air for 5 h. Reduced Rh/TiO₂ was prepared by the reduction of the oxidized sample at 473 K for 60 min and cooled down to room temperature in flowing He. The dispersity of Rh (measured by hydrogen adsorption at 300 K) was 36%.

2.2. METHODS

Catalyst powder (0.3 g) was suspended in triply distilled water in a pyrex glass cell. Highly purified CO₂ gas was bubbled at 120 ml per min through a water-suspended catalyst by means of a peristaltic pump. The suspension was illuminated through the pyrex window by a 500 W high pressure Xe lamp. The reaction temperature was set by a surrounding water jacket in which the temperature of circulating water was regulated by an ultra thermostat. Chemical actinometry showed that the radiation power entering the reactor vessel from the lamp used was 680 µW per cm². The exit gas from the reaction flask was led into traps cooled to 273 K, each containing about 10 ml of distilled water. The content of the reaction flask and the traps were filtered, and the liquid was analysed. Formic acid and formaldehyde were analysed by Grant's method [12], while methanol was determined by a Hewlett Packard gas chromatograph using a 2.5 ml long column of Porapak QS.

3. Results and discussion

First, the effects of two TiO₂ samples from different suppliers (MCB and BDH) on the reaction between H₂O and CO₂ were examined. A well-measurable photo-reaction was observed at 333 K, but there was a significant difference between the

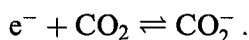
catalytic effects of the two samples. On the more effective TiO₂ (MCB), both HCHO and HCOOH were produced, whereas on the other sample (BDH), only HCHO was detected, and in a smaller amount. Evacuation and mild reduction of the catalysts slightly increased the amount of HCHO, and traces of CH₃OH were then also observed.

Doping of the TiO₂ (BDH) with even a very small amount (0.1 mol%) of WO₃ greatly enhanced the production of HCHO, without the formation of other products.

A significant change in the product distribution occurred when Rh (1%) was deposited on the TiO₂. The amount of HCHO formed was half of that measured on TiO₂ alone, but HCOOH and CH₃OH were also produced. The total amount of products was higher than on TiO₂ alone.

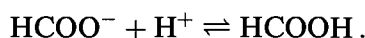
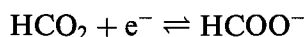
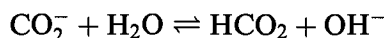
Deposition of Rh on TiO₂ containing 2% WO₃ further increased the amount of HCOOH formed. When the Rh/TiO₂ was preliminarily reduced, the yield of photolysis became higher and the product distribution changed. The major compound formed was now CH₃OH; HCHO and HCOOH were detected only in traces. Characteristic results for different samples are shown in table 1.

In the interpretation of the results obtained it should be taken into account that TiO₂ is an n-type semiconductor, the electric conductivity of which is greatly increased when it is doped with the higher-valent W⁶⁺ [3,13]. The fact that this doping enhanced the rate of photolysis may suggest that the predominant step in the photocatalytic reaction is the generation of photoelectrons and formation of the radical anion CO₂⁻:



This step is promoted by increase of the electron concentration in the TiO₂.

Further steps involve the protonation of CO₂⁻ by H₂O and an additional electron transfer to give HCOOH [7]:



This is followed by further reduction to HCHO.

As the total yield of organic compounds was greatly increased in the presence of Rh, it may be concluded that CO₂ is activated more easily on Rh/TiO₂ than on TiO₂. This leads to a very effective catalyst for the catalysis of CO₂ hydrogenation, even in the dark [1]. Another important factor in this phenomenon, however, is the electronic interaction between Rh and TiO₂ due to the different work functions (the work function of Rh is 5.6 eV, and that of reduced TiO₂ is 4.6 eV); other supported Rh catalysts (Rh/SiO₂, Rh/MgO, Rh/Al₂O₃) are much poorer catalysts than Rh/TiO₂ [1]. It is important to mention that recent spectroscopic evidence revealed that the presence of electron-donating additives on Rh surfaces promotes

Table 1

H₂O + CO₂ photoassisted reactions over TiO₂ and Rh/TiO₂, *T* = 333 K

Catalyst	Pretreatm.	HCOOH ^a (μmol/h)	HCHO ^a (μmol/h)	CH ₃ OH ^a (μmol/h)	Total ^a (μmol/h)
TiO ₂ (MCB)	air, 773 K	0.287	0.45	–	0.757
	air, 773 K	0.283	0.594	–	0.877
TiO ₂ (BDH)	air, 773 K	–	0.257	–	0.257
	air, 773 K	–	0.202	–	0.202
TiO ₂ + 0.1%WO ₃	air, 773 K	–	0.404	–	0.404
	air, 773 K	–	0.353	–	0.353
	air, 773 K	–	0.367	–	0.367
TiO ₂ + 2%WO ₃	air, 773 K	–	0.420	–	0.420
1% Rh/TiO ₂	air, 773 K	0.208	0.111	0.160	0.479
1% Rh + TiO ₂ + 2%WO ₃	air, 773 K	0.449	0.070	0.10	0.619
	air, 773 K	0.488	0.061	0.12	0.669
	reduced at 473 K	traces	traces	0.70	0.70
		traces	traces	1.19	1.19
		traces	traces	0.90	0.90
		traces	traces	1.04	1.04

^a The values presented are steady state values determined in 5 h. The formation of organic compounds occurred even after 20 h of irradiation. The activity of the catalysts decreased only by about 10%. Note that under buffered conditions the amounts of organic compounds were somewhat higher.

formation of the radical anion CO₂^{•−} [14]. Illumination of an adsorbed layer containing neutral CO₂ further increased the surface concentration of CO₂^{•−} both on Rh(111) [15] and on Rh/TiO₂ [16].

In the presence of Rh however, the photoinduced splitting of H₂O and the formation of active hydrogen should also be taken into account. An analogous phenomenon was clearly demonstrated when Pt was deposited on SrTiO₃ [17]. As a result, CH₃OH appeared as a product of photoreduction. The formation of CH₃OH was particularly favoured on the reduced Rh/TiO₂ catalyst, which exhibited the highest photoactivity (table 1). The fact that the amount of HCHO formed is much less on Rh/TiO₂ than on TiO₂ may be due to its fast decomposition on Rh [18] as compared with the decompositions of HCOOH and CH₃OH [19,20].

4. Conclusions

(i) An increase in the electron concentration of TiO₂ enhances the production of organic compounds from the reaction CO₂ + H₂O on both TiO₂ and Rh/TiO₂ as catalysts. (ii) Deposition of Rh on TiO₂ also enhanced the yield of photolysis, and preliminary reduction of the catalyst led to the formation of CH₃OH.

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