Catalysis Letters 27 (1994) 61–65

Photocatalytic reaction of H_2O+CO_2 over pure and doped Rh/TiO_2

Frigyes Solymosi and Imre Tombácz

Institute of Solid State and Radiochemistry, A. József University
and Reaction Kinetics Research Group of the Hungarian Academy of Sciences[1],
PO Box 168, H-6701 Szeged, Hungary

Received 20 January 1994; accepted 30 April 1994

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 $H_2O + CO_2$; 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 $H_2O + CO$ 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 altervalent 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].

---

[1] This laboratory is a part of the Center for Catalysis, Surface and Material Science at the University of Szeged.

2. Experimental

2.1. MATERIALS

The titania was a reagent grade product of British Drog House (BDH). Doping of this TiO_2 sample with W^{6+} ions was carried out in the following way: TiO_2 was introduced into the solution of $(NH_4)_{10}W_{12}O_{40}(OH)_2{\cdot}4H_2O$, 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 N_2 adsorption at 77 K) of the calcined TiO_2 sample was 18 m^2/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 m^2/g.

In the preparation of oxidized Rh/TiO_2, TiO_2 samples (BDH) were impregnated with an aqueous solution of $RhCl_3{\cdot}3H_2O$. The suspension was dried at 393 K and heated at 773 K in air for 5 h. Reduced Rh/TiO_2 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 CO_2 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 cm^2. 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 TiO_2 samples from different suppliers (MCB and BDH) on the reaction between H_2O and CO_2 were examined. A well-measurable photoreaction was observed at 333 K, but there was a significant difference between the catalytic effects of the two samples. On the more effective TiO_2 (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 CH_3OH were then also observed.

Doping of the TiO_2 (BDH) with even a very small amount (0.1 mol%) of WO_3 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 TiO_2. The amount of HCHO formed was half of that measured on TiO_2 alone, but HCOOH and CH_3OH were also produced. The total amount of products was higher than on TiO_2 alone.

Deposition of Rh on TiO_2 containing 2% WO_3 further increased the amount of HCOOH formed. When the Rh/TiO_2 was preliminarily reduced, the yield of photolysis became higher and the product distribution changed. The major compound formed was now CH_3OH; 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 TiO_2 is an n-type semiconductor, the electric conductivity of which is greatly increased when it is doped with the higher-valent W^{6+} [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 CO_2^-:

$$e^- + CO_2 \rightleftharpoons CO_2^- .$$

This step is promoted by increase of the electron concentration in the TiO_2.

Further steps involve the protonation of CO_2^- by H_2O and an additional electron transfer to give HCOOH [7]:

$$CO_2^- + H_2O \rightleftharpoons HCO_2 + OH^-$$

$$HCO_2 + e^- \rightleftharpoons HCOO^-$$

$$HCOO^- + H^+ \rightleftharpoons HCOOH .$$

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 CO_2 is activated more easily on Rh/TiO_2 than on TiO_2. This leads to a very effective catalyst for the catalysis of CO_2 hydrogenation, even in the dark [1]. Another important factor in this phenomenon, however, is the electronic interaction between Rh and TiO_2 due to the different work functions (the work function of Rh is 5.6 eV, and that of reduced TiO_2 is 4.6 eV); other supported Rh catalysts (Rh/SiO_2, Rh/MgO, Rh/Al_2O_3) are much poorer catalysts than Rh/TiO_2 [1]. It is important to mention that recent spectroscopic evidence revealed that the presence of electron-donating additives on Rh surfaces promotes

Table 1
$H_2O + CO_2$ photoassisted reactions over TiO_2 and Rh/TiO_2, $T = 333$ K

Catalyst	Pretreatm.	HCOOH[a] (μmol/h)	HCHO[a] (μmol/h)	CH_3OH[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 CO_2^- [14]. Illumination of an adsorbed layer containing neutral CO_2 further increased the surface concentration of CO_2^- both on Rh(111) [15] and on Rh/TiO_2 [16].

In the presence of Rh however, the photoinduced splitting of H_2O and the formation of active hydrogen should also be taken into account. An analogous phenomenon was clearly demonstrated when Pt was deposited on $SrTiO_3$ [17]. As a result, CH_3OH appeared as a product of photoreduction. The formation of CH_3OH was particularly favoured on the reduced Rh/TiO_2 catalyst, which exhibited the highest photoactivity (table 1). The fact that the amount of HCHO formed is much less on Rh/TiO_2 than on TiO_2 may be due to its fast decomposition on Rh [18] as compared with the decompositions of HCOOH and CH_3OH [19,20].

4. Conclusions

(i) An increase in the electron concentration of TiO_2 enhances the production of organic compounds from the reaction $CO_2 + H_2O$ on both TiO_2 and Rh/TiO_2 as catalysts. (ii) Deposition of Rh on TiO_2 also enhanced the yield of photolysis, and preliminary reduction of the catalyst led to the formation of CH_3OH.

References

[1] F. Solymosi, A. Erdöhelyi and T. Bánsági, J. Catal. 68 (1981) 371.
[2] F. Solymosi, I. Tombácz and M. Kocsis, J. Catal. 75 91982) 78;
F. Solymosi and A. Erdöhelyi, Surf. Sci. 110 (1981) L630;
A. Erdöhelyi and F. Solymosi, J. Catal. 84 (1983) 446;
F. Solymosi, A. Erdöhelyi and I. Tombácz, Appl. Catal. 14 (1985) 65.
[3] F. Solymosi, I. Tombácz and J. Koszta, J. Catal. 95 (1985) 578.
[4] J.S. Conolly, ed., *Photochemical Conversion and Storage of Solar Energy* (Academic Press, New York, 1981).
[5] J.C. Hemminger, R. Carr and G.A. Somorjai, Chem. Phys. Lett. 57 (1978) 100.
[6] T. Inoue, A. Fujishima, S. Konishi and K. Honda, Nature 277 (1979) 637.
[7] M. Halmann, Nature 275 (1978) 115;
M. Halmann, *Energy Resources through Photochemistry and Catalysis* (Academic Press, New York, 1983) p. 507;
B. Aurian-Blayeni, M. Halmann and J. Manassen, Solar Energy 25 (1980) 165;
M. Halmann, V. Katzir, E. Borgarello and J. Kiwi, Solar Energ. Mater. 10 (1984) 85.
[8] S. Yamamura, H. Kojima, J. Iyoda and W. Kawai, J. Electroanal. Chem. 225 (1987) 287.
[9] S. Yanagida, M. Yoshiya, T. Shiragami, C. Pac, H. Mori and H. Fujita, J. Phys. Chem. 94 (1990) 3104.
[10] Z. Goren, J. Willner, A.J. Nelson and A.J. Frank, J. Phys. Chem. 94 (1990) 3784.
[11] M. Anpo and K. Chiba, J. Mol. Catal. 74 (1992) 207.
[12] H.G. Wood and H. Gest, in: *Methods in Enzimology*, Vol. 3, eds. S.P. Colowich and N.O. Kaplan (Academic Press, New York, 1957) p. 288.
[13] K. Hauffe, H. Grunewald and R. Trankler-Greese, Z. Electrochem. 56 (1952) 937.
[14] F. Solymosi and L. Bugyi, J. Chem. Soc. Faraday Trans. I 83 (1987) 2015;
F. Solymosi, J. Mol. Catal. 65 (1991) 337, and references therein.
[15] F. Solymosi and G. Klivényi, Catal. Lett. 22 (1993) 337.
[16] J. Raskó and F. Solymosi, J. Phys. Chem., submitted.
[17] J.-M. Lehn, J.P. Sauvage and R. Ziessel, Nouv. J. Chim. 4 (1980) 623.
[18] J.T. Yates, S.D. Woorley, T.M. Duncan and R.W. Vaughan, J. Chem. Phys. 70 (1979) 1225.
[19] F. Solymosi, J. Kiss and I. Kovács, Surf. Sci. 192 (1987) 47.
[20] F. Solymosi, A. Berkó and T.I. Tarnóczy, Surf. Sci. 141 (1984) 533.