Photosynthesis of CH_4 at a TiO_2 Surface from Gaseous H_2O and CO_2

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UV irradiation of the gas/solid interface of microcrystalline TiO_2 in the presence of water and carbon dioxide in the gas phase at 343 K leads to photoreduction of carbon dioxide to form carbon monoxide, hydrogen and methane.

The imitation of the most important chemical reaction on earth, natural green plant photosynthesis, as a model for a storage reaction for solar energy has attracted much attention in recent years. Chemically storing solar energy under greenhouse-gas neutral conditions could well become a major contribution in solving the world's energy problems ecologically. In contrast to natural systems where atmospheric carbon dioxide is converted into relatively complicated sugar molecules, artificial systems usually yield single-carbon molecules. Some exceptions however, where new carbon–carbon bonds are formed, have also been observed.[1] Up to date the photocatalytic reduction of gaseous carbon dioxide on TiO_2 to methane has been observed with mixed CeO_2–TiO_2 catalysts calcined at 1023 K,[2] with TiO_2 aggregates anchored on Vycor glass[1] and on single-crystal rutile degassed at 725 K.[3] We report here the first photocatalytic reduction of gaseous carbon dioxide to methane in the presence of water over pure, untreated microcrystalline TiO_2 powder at moderate temperatures.

TiO_2 samples (Degussa P25, 30% rutile, 70% anatase) were prepared by immersing quartz wool in a sonicated suspension of TiO_2 in H_2O. These samples contained approximately 50 mg of semiconductor powder on 200 mg quartz wool. CO_2 (Carbagas, 99.998%) was used as received. Deionised water ($\leqslant 0.06$ μS cm^{-1}) was used without further treatment. The experiments were carried out in a closed loop reactor constructed of glass tubing (total volume 1.85 l). The illuminated part of the reactor was made of quartz. Gas circulation was maintained using a bypass regulated diaphragm pump. The full output of a 1000 W Xe short arc lamp filtered by a $CuSO_4$ solution to cut off radiation above 700 nm was used as light source. A gas chromatograph (GC) was connected by a switching valve to the reactor allowing for automated online measurement of the gas composition. Detection limits for CO, CH_4, O_2 and N_2 are 10 ppm (0.8 μmol) and for H_2 35 ppm (3.0 μmol). Acetic acid, formaldehyde and methanol can not be detected with this setup. The temperature of the illuminated semiconductor can not be measured directly with a thermocouple because of the different absorptivity and emissivity of the thermocouple compared with TiO_2. The temperature was therefore determined indirectly from the gas temperature. The accuracy of the method is about ±10 K. In the dark experiments the reaction zone was heated with a heatgun.

To start an experiment, the TiO_2 sample was inserted into the reactor which was then evacuated and flushed with CO_2 until the air contamination was in the order of the impurities of the CO_2 used (<8 ppm N_2, <2 ppm O_2). Gas circulation was started, enough water was added through a septum to saturate the CO_2, and irradiation was started. The gas composition was analysed at least every hour by GC. Whereas CH_4 was detected 30 min after irradiation started, CO was only detectable after 1 hour of irradiation. H_2 could be detected after 3.5 hours of irradiation. The steady state gas temperature reached was 332 K from which a temperature of 343 K of the semiconductor was deduced. The experiment was run for 25 hours. Under these conditions, average production rates of 2.7 μmol h^{-1} CO, 1.4 μmol h^{-1} H_2 and 0.1 μmol h^{-1} CH_4, respectively, have been obtained. Product formation was sustained throughout the whole experiment with an initial decrease of the rates as seen in Fig. 1. During the irradiation, the semiconductor turned grey. In a dark experiment under otherwise identical conditions, no reaction products were found at 343 K after 5 hours. At 553 K, CO_2 can be reduced to CO even in the dark as seen in Fig. 2. The average production rate, however, was only 0.2 μmol h^{-1}, much lower than under irradiation and neither CH_4 nor H_2 could be observed. The CO production rate decreased constantly until it almost reached zero after 25 hours.

Our tentative model to explain the photocatalytic reduction of CO_2 involves the following four reactions [eqns. (1)–(4)] at the surface of TiO_2.

$$2TiO_2 \xrightarrow{h\nu} 2TiO_{2-\delta} + \delta O_2 \qquad (1)$$

$$TiO_{2-\delta} + \delta H_2O \longrightarrow TiO_2 + \delta H_2 \qquad (2)$$

$$TiO_{2-\delta} + \delta CO_2 \longrightarrow TiO_2 + \delta CO \qquad (3)$$

$$4\delta H_2 + \delta CO_2 \longrightarrow \delta CH_4 + 2\delta H_2O \qquad (4)$$

Photoreduction of TiO_2[4] [eqn. (1)] yields partially reduced $TiO_{2-\delta}$ which serves as an electron pool. This reaction is followed by three dark reactions: the reduction of H_2O to H_2 [eqn. (2)],[5] the reduction of CO_2 to CO [eqn. (3)] and the analogue to the Sabatier reaction forming CH_4 [eqn. (4)]. The latter reaction does not necessarily imply direct hydrogenation of CO_2. In reactions (2) and (3) $TiO_{2-\delta}$ is reoxidized. At 343 K the reduction of CO_2 occurs as a purely photochemical reaction. This is confirmed by the absence of product formation without illumination and the linear rise of product concentrations with

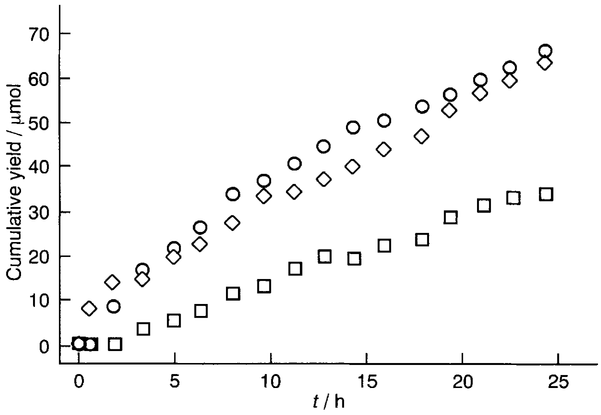

Fig. 1 Product formation at the gas/solid interface of irradiated TiO_2 at 343 K in the presence of H_2O and CO_2. (○) CO, (□) H_2, (◇) CH_4 (×20).

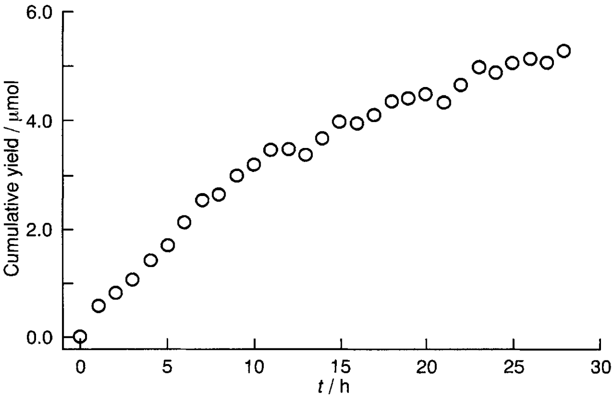

Fig. 2 CO formation on TiO_2 at 553 K in the dark

time. The dark reaction at 553 K can be explained by a reaction of CO_2 with initially present oxygen deficient semiconductor $TiO_{2-\delta}$ [eqn. (3)], as has been proposed for the CO_2 reduction with $SrTiO_3$.[6] As $TiO_{2-\delta}$ becomes oxidized and the photolytic step [eqn. (1)] is missing, the reaction eventually stops as seen in Fig. 2. From the total amount of CO produced in this experiment we calculate δ to be of the order of 10^{-4} in our starting material. This reaction does not proceed at 343 K and therefore seems to need an activation energy of more than about 3 kJ mol^{-1}. At present it is not clear whether $TiO_{2-\delta}$ should be described as Ti^{III} or metallic Ti^0 containing samples. For the semiconductor before irradiation we prefer the first description whereas for the samples that turned grey during the irradiation the second description seems more appropriate as titanium(III) samples are generally blue. Another point still open for discussion is that we only find about 45% of the oxygen in the form of CO on the product side. As we failed to detect any oxygen during illumination we ascribe the missing oxygen to photoadsorption.[7]

We have demonstrated for the first time the formation of CH_4 as a product of the photoreduction of CO_2 at TiO_2 at moderate temperatures. The overall reaction involves photolytic and thermal steps. To investigate the mechanism in detail a miniaturised reactor is under construction that will allow for simultaneous optical characterisation of the samples. It will also allow for *in situ* FTIR measurements to identify surface species.

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