Photocatalytic Conversion of Acetate into Molecular Hydrogen and Hydrocarbons over Surface Modified TiO_2: pH Dependent Formation of Kolbe and Hofer-Moest Products

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The photocatalytic generation of H_2 and hydrocarbons from aqueous acetic acid has been studied employing surface modified TiO_2 P25 particles. Additionally, the effect of pH and the surface modification of semiconductor by various co-catalysts (Pt, Ag, Au, Rh, CoO, CuO, RuO_2 and IrO_2) on the reaction product formation during the photochemical as well as photoelectrochemical oxidation of acetic acid have been investigated. The obtained results confirm an enhanced photocatalytic activity for H_2 and hydrocarbons evolution when the TiO_2 surface is loaded with Pt. The reaction products resulting from the photocatalytic decomposition of aqueous acetic acid were determined quantitatively in the gas phase. The main by-products, as a result of the dual-function photocatalysis, include H_2, CO_2 and CH_4 in the gas phase. Furthermore, traces of C_2H_6, C_3H_8, CO, CH_3CHO, HCHO, CH_3OH, C_2H_5OH and HCOOH were also detected. After 15 h of illumination, the amounts of H_2, CO_2, CH_4 and C_2H_6 evolved at pH 2 were found to be 22, 65, 35 and 2 µmol/h, respectively. The ratio of hydrocarbons to H_2 strongly depends on the pH values *i.e.*, at acidic pH the ratio of CH_4 to H_2 formation was found to be 1.5. On the contrary, at neutral and basic pH values no hydrocarbons were formed and H_2 was found to be the only product with the formation rate of 12 and 5 µmol/h at pH 7 and 11, respectively. It is therefore assumed that the OH^- have a significant effect on the reaction pathways. Due to the fact that methanol and ethanol are formed as reaction products, which are subsequently oxidized to CO_2, water is apparently required for the formation of the major oxidizing agent, that is $^{\bullet}OH$ radical during the overall reaction. Herein, the detailed mechanism for the photocatalytic decomposition of acetic acid at different pH values is presented.