Experimental part

1. Preparation procedure

Rhodium-modified titania (Rh-TiO₂) materials were obtained by impregnation of commercial titania (Showa Denko Ceramics FP6; anatase) with rhodium(III) chloride (RhCl₃; Wako Pure Chemical) followed by calcination. A 6-g portion of titania were suspended in 55 ml of deionized water, and proper amounts of RhCl₃ solution (Rh/Ti molar ratio: 0.001, 0.01 and 0.1%) was added. After mixing components in a dark at room temperature for 1 h, the suspension was heated up (75–80 °C) and mixed until almost complete evaporation of water. Materials were dried at 120 °C overnight, and calcined in air in a rotary furnace at 923 K for 3 h. As a reference material neat titania (0% Rh-TiO₂) was prepared in the similar procedure, without the addition of RhCl₃ solution.

2. Photocatalytic tests and in situ absorption measurements

Photocatalytic activity of obtained materials was studied in the reaction of oxidative decomposition of acetaldehyde (AcH) in air. A 0.05-g portion of the material homogenously distributed in glass cell (dimensions of sample layer: 10 × 10 × 0.2 mm) was inserted in a leak-proof Pyrex reactor (357 mL). The sample was pre-irradiated for 1 h with UV-Vis light using a xenon lamp (150 W; ca. 200 mW cm⁻²) as a light source. The gas phase inside the reactor was purged with air (50% relative humidity), and 0.08 ml (224 ppm) of AcH was injected. The reactor was kept in the dark for to reach equilibrium of adsorption. The amount of AcH and carbon dioxide (CO₂) was measured before and during the irradiation with a micro GC 3000A gas chromatograph (Agilent Technologies). Sample was irradiated with visible light using a xenon lamp equipped with optical filters transmitting wavelengths above 440 nm or 590 nm, or below 550 nm, and IR filter (CF1600). Double-beam photoirradiation experiments were performed using two xenon lamps (150 W) equipped with various short and long pass optical filters and IR filters (the sample was irradiated from the top or the side of a cell). Intensities of the used radiations of the wavelength ranges: 440-550 nm and 590-730 nm, were characterized of similar light intensity (app. 150–175 mW).

In-situ absorption measurements for the samples set in the reaction chamber were conducted with Photonic Multichannel Spectral Analyzer PMA-11 (Type No. C7473-36) consisting of thermoelectric-cooling type BT-CCD image sensors and a xenon lamp MAX 302 (Asahi Spectra) was used as a light source.
Fig. 1. XRD patterns of Rh-TiO$_2$ and a reference sample without rhodium species. Peaks characteristic for rutile-TiO$_2$ are marked with stars.

Fig. 2. Amounts of CO$_2$ and AcH monitored during process of AcH oxidative decomposition in the presence of 0.001% Rh-TiO$_2$ (calcined at 973K) under irradiation with visible light (> 440 nm).

Fig. 3. Rates of CO$_2$ liberation in first two hours of the process of acetaldehyde oxidative decomposition in the presence of materials calcined at 973 K with various Rh concentrations. A horizontal line shows CO$_2$-generation rate in the presence of 0% Rh-TiO$_2$. 
Fig. 4. Differential absorption spectra of 0.01% Rh-TiO$_2$ (with reference to the spectrum of the sample kept in a dark) recorded for the sample kept in a dark in the presence of AcH (left), and irradiated with light from the range 590–730 nm (right) in various times after the irradiation with light from the range 440–550 nm for 1 h.