## Anti-Markovnikov hydration of alkenes over platinum-loaded titanium oxide photocatalyst

Hayato Yuzawa,<sup>a</sup> Shoko Yoneyama,<sup>a</sup> Akihito Yamamoto,<sup>a</sup> Masanori Aoki,<sup>a</sup>

Kazuko Otake,<sup>*a*</sup> Hideaki Itoh<sup>*b*</sup> and Hisao Yoshida<sup>\*,*a*</sup>

<sup>a</sup> Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan.

<sup>b</sup> Division of Environmental Research, EcoTopia Science Institute, Nagoya University, Nagoya 464-8603, Japan.

\* Tel: +81-52-789-4609. Fax: +81-52-789-3178. E-mail: yoshidah@apchem.nagoya-u.ac.jp



Fig. S1 The influence of the specific surface area and titanium oxide crystal phase of the  $Pt(0.1)/TiO_2$ photocatalysts on the products yield (a), and the total yield and selectivity (b) in the photocatalytic hydration of 1-hexene. Red filled circles, red filled triangles, blue blank circles, blue blank triangles, green filled squares and black filled diamonds in panel a correspond to the yields of 1-hexanol, hexanal, 2-hexanol, 2-hexanone, coupling produces and hydrogen, respectively. Purple filled squares, orange filled inverse triangles and orange blank inverse triangles in panel b correspond to the total yield of the alcohols and the carbonyl products, the anti-Markovnikov selectivity and the alcohol selectivity, respectively. Purple half-filled square correspond to the total yield with a  $Pt(0.1)/TiO_2(rutile)$  sample. Rutile titanium oxide (JRC-TIO-6) was donated from Catalysis Society of Japan. The specific surface area of the  $Pt(0.1)/TiO_2$  was controlled by the calcination of the  $TiO_2$  sample before the platinum loading. The above samples were the  $Pt(0.1)/TiO_2$  sample prepared from the uncalcined TiO<sub>2</sub> and those prepared from the TiO<sub>2</sub> calcined at 873 K, 673 K or 473 K for 5 h. The specific surface area of the prepared photocatalysts was calculated by the BET method from the amount of adsorbed nitrogen at 77 K measured with a Quantachrome Monosorb. The reaction condition was: catalyst, 0.2 g; 1-hexene, 1.0 ml (8.0 mmol); water, 1.0 ml (56 mmol); reaction time,60 min; reaction temperature, 305 K; irradiated light wavelength, >370 nm; irradiated light intensities were 3, 10, and 84 mW cm<sup>-2</sup> when measured at 254±10, 365±15 and 405±30 nm, respectively.



Fig. S2 The influence of the specific surface area and titanium oxide crystal phase of the  $Pt(0.1)/TiO_2$ photocatalysts on the products yield (a), and the total yield and selectivity (b) in the photocatalytic hydration of thiophene. Red filled circles, red filled triangles, green filled squares, black filled diamonds and pink blank diamonds in panel a correspond to the yields of 2,3-dihydro-2-hydroxythiophene, 2,3dihydrothiophene-2-one, coupling products, hydrogen and carbon dioxide, respectively. Purple filled squares, orange filled inverse triangles and orange blank inverse triangles in panel b correspond to the total yield of the alcohols and the carbonyl products, the anti-Markovnikov selectivity and the alcohol selectivity, respectively. Purple half-filled square and orange half-filled inverse triangle correspond to the total yield and the alcohol selectivity with a Pt(0.1)/TiO<sub>2</sub>(rutile) sample. Rutile titanium oxide (JRC-TIO-6) was donated from Catalysis Society of Japan. The specific surface area of the  $Pt(0.1)/TiO_2$ samples was controlled by the calcination of the TiO<sub>2</sub> (JRC-TIO-8) before the platinum loading. The above samples were the  $Pt(0.1)/TiO_2$  sample prepared from the uncalcined  $TiO_2$  and the  $Pt(0.1)/TiO_2$ prepared from the TiO<sub>2</sub> calcined at 773 K or 673 K for 5 h. The specific surface area of the prepared photocatalysts was calculated by the BET method from the amount of adsorbed nitrogen at 77 K measured with a Quantachrome Monosorb. The reaction condition was: catalyst, 0.2 g; thiophene, 2.0 ml (24 mmol); water, 8.0 ml (440 mmol); reaction time, 180 min; reaction temperature, 314 K; irradiated light intensities were 23, 80, and 176 mW cm<sup>-2</sup> when measured at 254±10, 365±15 and 405±30 nm, respectively.



Fig. S3 The proposed reaction mechanism of the photocatalytic oxidation of alkene to produce the carbonyl compounds.