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Supplementary Information

Electrochemical hydrogenation of non-aromatic carboxylic acid derivatives as a sustainable synthesis process: from catalyst design to device construction

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Experimental details

Preparation of electrode

Cathode electrode was prepared through a two-step hydrothermal treatment according to the previous literature.²³ Ti mesh (2×2 cm²) was immersed in 1M NaOH and heated at 220 °C for 12 h in a Teflon-lined autoclave. After washing with 0.1 M HCl, the resulting Ti mesh was put in water and heated at 200 °C for 24 h, leading to a formation of white colored electrode of TiO₂-coated Ti mesh.

Electrochemical analysis

Electrochemical hydrogenation of carboxylic acid derivatives was performed through a chronoamperometry using a two-compartment cell with a three electrode system connecting to a potentiostat

(Versastat 4, Princeton Applied Research Inc.). Porous TiO₂ catalysts grown on Ti foil was used as the working electrode.²³ Pt coil was used as a counter electrode. Reaction solution poured in the side with the working electrode includes 0.03 M of a substrate (formic acid, acetic acid, oxamic acid, glyoxylic acid, pyruvic acid, 2-oxopentaonic acid, α -ketoglutaric acid, trimethylpyruvic acid, acrylic acid, or fumaric acid) and 0.2 M of Na₂SO₄ as a support electrolyte in water as a solvent (without adjustment of the pH (around 2–3)). pH-adjusted aqueous solution of 0.2 M Na₂SO₄ was used in the counter side. Ag/AgCl was used as a reference electrode. The reaction was performed by applying –0.7 V (vs. RHE) to the working electrode at 50 °C for 2 h. Note that, in the case with 2-oxopentaonic acid and α -ketoglutaric acid, the reaction was performed at 25 °C to avoid thermal decomposition of the substrate. Resulting products were separated and quantified by high performance liquid chromatography (HPLC) (Prominence, Shimadzu Inc.) equipping a KC-811 column (Shodex Inc.). Cyclic voltammetry is also carried out with one-compartment cell. Adsorption property of the carboxylic acid derivatives on the TiO₂-decorated Ti electrode was tested through an immersion of the electrode into an aqueous solution of the substrate (0.005 M) for 2 h at room temperature. After the immersion, the remaining solution was analysed by the HPLC to quantify the amount of adsorbed substrate.

Computational details

Density functional theory (DFT) B3LYP method was used for estimation of a statistic energy level of molecular orbitals of each substrate. The calculation was performed using Gaussian 03 package (Gaussian Inc.) with 6-31G (d) basis set to fully optimized structures.

The interactions between anatase 101 surface and small molecules were studied with Density-Functional Tight-Binding (DFTB-SCF) method as implemented in DFTB+ software (ver. 1.2).^{24,25} We used tio-0-1 and mio-0-1 parameter sets^{26, 27} and a convergence criteria of 10⁻⁵ au for SCF cycles, and 10⁻³ au for the optimization. Dispersion correction were included using a Lennard-Jones potential between the atoms based on parameters from the Universal Force Field (UFF). Surface absorption models were created on three TiO₂ layer slabs of anatase 101 surfaces, with at least 20 Å vacuum between the slabs. Solvent effects were not considered. The adsorbed molecules and the slab geometry were optimized whereas the cell parameters and bottom TiO₂ layer of the slab were kept constrained. The k-points for the integration of the Brillouin zone at 2x4x1 were chosen using Monkhorst-Pack sampling.²⁸

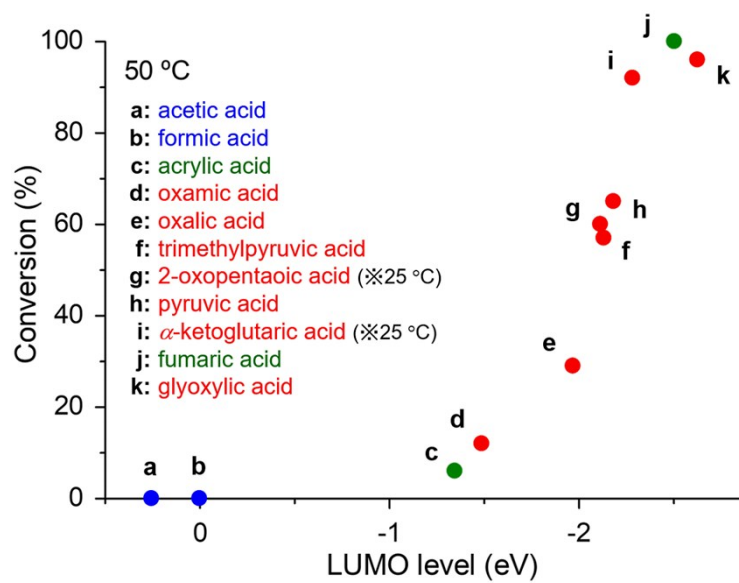


Figure S1. LUMO level and experimental reactivity of a substrate.

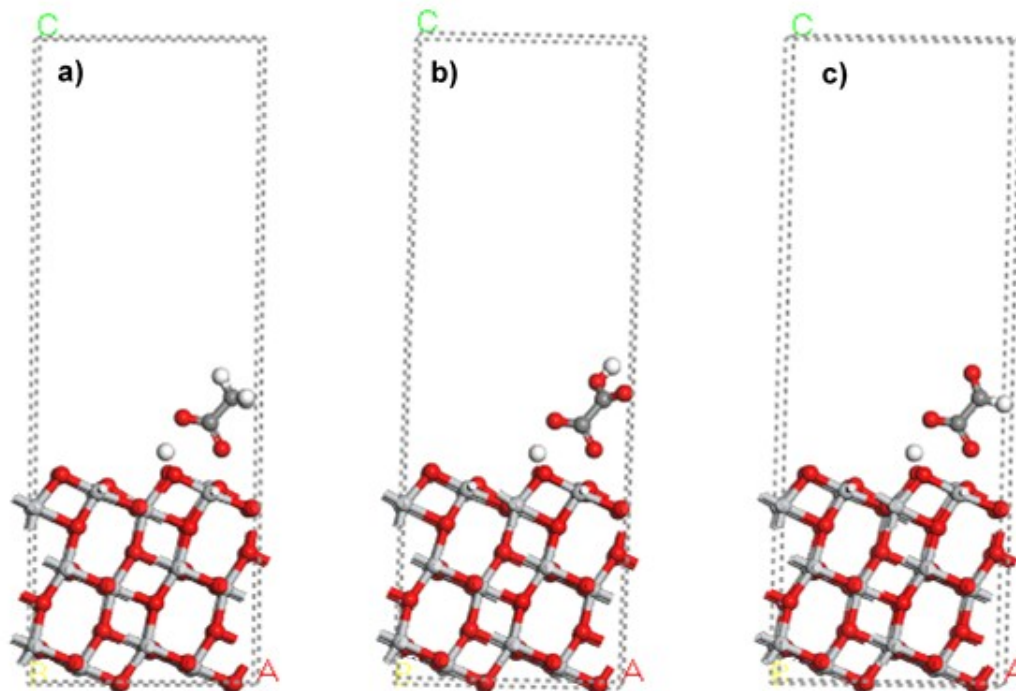


Figure S2. The unit cell of computational models for 101 TiO₂ with the absorbent molecules: a) acetic acid, b) oxalic acid, c) glyoxylic acid.