Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
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Supplementary Material

Introduction of Tensile Strain into Titanium Dioxide for Increased Solid Acid Catalytic Activity

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Experimental

1. Catalyst preparation

Rutile-type titanium dioxide (TiO_2) (Kojundo Chemical Laboratory, 99.9%) was pre-calcined at 900°C for 10 h to form pure rutile phase. The obtained TiO_2 was impregnated with an aqueous solution containing $H_2AuCl_4 \bullet H_2O$ (Kishida Chemical). The amount of the gold precursor was adjusted to the desired mol% Au content relative to TiO_2. After evaporation and drying, the obtained powder was sintered by the spark plasma sintering (SPS) process using an SPS equipment (SPS-211Lx, Fuji Electronic Industrial). A 10 mm diameter graphite die was filled with 0.5 g of the obtained powder, uniaxially pressed at 60 MPa, and sintered at 900°C for 5 min to produce a pellet. The resulting pellet was ground in a mortar to obtain a powder.

2. Characterization

The crystal structure of the sample was investigated by X-ray diffraction (XRD, RINT-2500HLR+, Rigaku) with Cu Kα radiation (λ = 0.15418 nm) at a voltage of 40 kV and a current of 80 mA. Scans were obtained at a speed of 5° min^{-1} with a step width of 0.05° for 2θ values of 10° to 80°. Narrow angle scans were conducted at a speed of 0.5° min^{-1} with a step width of 0.01° for 2θ values of 20° to 30°.

The oxidation state of elements and their compositions over the surface were analyzed by

X-ray photoelectron spectroscopy (XPS, KRATOS Ultra 2, Shimadzu). The binding energies in each measurement were referenced to the core level of the C1s peak (284.8 eV).

3. Acid-catalyzed furfural transformation

The reaction of furfural with alcohol was conducted using catalyst (50 mg) in 2.5 mL alcohol (ethanol or 2-propanol) solution with furfural (41.3 μL, 0.2 mmol) and *n*-decane (19.5 μL, 0.1 mmol) as an internal standard in a pressure-resistant glass reactor (ACE glass). The reaction was performed at 413 K for 1 h, and aliquots were taken by syringe and analyzed by gas chromatography (GC-FID; GC-2014, column DB-1MS, Shimadzu). To confirm the Brønsted acid catalysis, 0.5 μL of 2,6-lutidine was added to the reaction media.

Table S1. Results of reaction of furfural with ethanol over Au-dispersed TiO_2 with SPS treatment at various Au dispersion amounts

Catalyst	Conversion /%	Acetal yield (selectivity)/%
TiO_2 (no SPS)	48	42 (88)
0 mol%Au-TiO_2	42	30 (71)
0.5 mol%Au-TiO_2	51	51 (100)
0.75 mol%Au-TiO_2	71	65 (92)
1.0 mol%Au-TiO_2	60	58 (97)
1.5 mol%Au-TiO_2	65	63 (97)

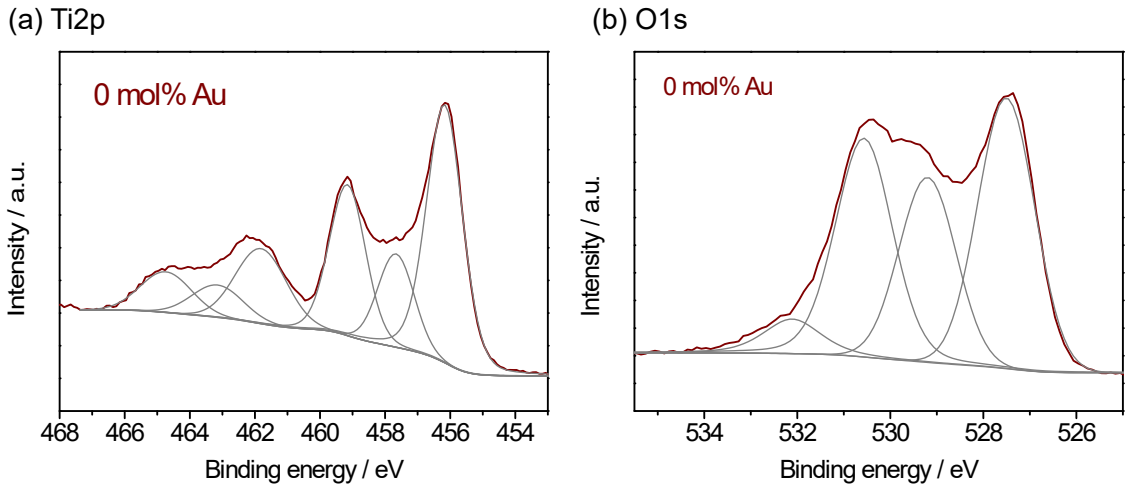

Fig. S1. XPS spectra for Au-free SPS-treated TiO_2 (a) Ti2p. (b) O1s.