Supplementary Materials for

Application of sulfated tin (IV) oxide solid superacid catalyst to partial coupling reaction of α-pinene to produce less viscous high-density fuel

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Experimental Details

Materials

All purchased chemicals were used without further purification. Tin (IV) chloride pentahydrate (SnCl₄·5H₂O, 98%) and sulfuric acid (H₂SO₄, 95%) were purchased from SAMCHUN chemical. Ammonium acetate (CH₃COONH₄, 95%) was purchased from DUKSAN chemical. Turpentine (α-pinene≥95% by GC) and ammonia solution (NH₄OH, 28%) were purchased from JUNSEI chemical.

Catalyst characterization

The X-ray diffraction (XRD) patterns of the catalysts were collected using a D8 ADVANCE equipment (BRUKER, German) with monochromatized Cu Kα₁ (λ = 1.5418 Å) radiation source (40 kV and 40 mA), the samples were scanned in steps of 0.02° in the 2θ range 2°-80° with a rate of 0.5 sec/step.

Field-emission scanning electron microscopy (FE-SEM) was carried out with SUPRA 55VP equipment (Carl Zeiss, Germany). The samples were sputter coated with platinum for 5 nm thickness at 20 mA using Leica EM ACE200 equipment (Leica Microsystems, Germany).

Thermogravimetric analysis (TGA) was conducted with a TGA Q50 instrument (TA Instruments, USA) under nitrogen gas flowing. The samples were held at 120 °C for 10 min to remove physically adsorbed water. After that, the temperature increased to 800 °C at a rate of 10 °C/min, weight loss being recorded.

The temperature-programmed desorption of ammonia (NH₃-TPD) was performed with BELCAT-II catalyst analyzer (Microtrac BEL, Japan). Briefly, the catalysts were pretreated at 150 °C under flowing He (50 mL/min) for 60 min to remove any volatile compounds and moisture. The pretreated samples were cooled to 50 °C and saturated with 5% NH₃ in He flow (50 mL/min) and, subsequently, purged with He (50 mL/min) at 150 °C for 60 min to remove excessive physiosorbed NH₃. After that, the temperature was ramped up to 800 °C at a rate of 10 °C/min, chemisorbed NH₃ being detected with a thermal conductivity detector (TCD).
Operating condition for GC/FID/MS

In general, 1.0 µL of the diluted sample was injected into injector at 250 °C (splitless). For gas chromatography, oven temperature was initially 50 °C for 5 min, then increased to 250 °C at 5 °C/min, and was maintained at 250 °C for 10 min. Carrier gas was helium at a flow rate of 2 mL/min. For flame ionization detector, temperature was set at 300 °C and the flow rate of make-up gas (helium) was 25 mL/min. For mass spectrometry detector, an electron ionization mode was used and the temperatures of transfer line, ion source, and quadruple mass filter were 280, 230, and 150 °C, respectively.
Figure S1. (a-b) Energy dispersive spectroscopy (EDS) spectra and (c-d) elemental quantitative data obtained from intact SnO₂ and SO₄²⁻/SnO₂. The samples were calcined at 550 °C. The sulfur atoms which were introduced by sulfuric acid immersion before calcination was only detected from the SO₄²⁻/SnO₂ sample. (e) Much higher resolution image of SEM-EDS elemental mapping of SO₄²⁻/SnO₂.
Figure S2. TGA curves of intact SnO$_2$ (black line) and SO$_4^{2-}$/SnO$_2$ (red dashed line).
Figure S3. The yields of the monomeric products along the reaction time at (a) 100°C and (b) 110°C. (■) for α-terpinene; (●) for p-cymene; (▲) for limonene; (▼) for γ-terpinene; (◆) for terpinolene; (◄) for isoterpinolene; (►) for p-menth-3,8-diene; (★) for α-pinene.
Figure S4. General chromatogram of dimeric products extracted from GC/FID result. They were classified by their specific m/z 272 peak in mass fragmentation pattern as in previous papers [1].

References