

## *Supplementary Materials for*

# **Application of sulfated tin (IV) oxide solid superacid catalyst to partial coupling reaction of $\alpha$ -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 ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 98%) and sulfuric acid ( $\text{H}_2\text{SO}_4$ , 95%) were purchased from SAMCHUN chemical. Ammonium acetate ( $\text{CH}_3\text{COONH}_4$ , 95%) was purchased from DUKSAN chemical. Turpentine ( $\alpha$ -pinene  $\geq 95\%$  by GC) and ammonia solution ( $\text{NH}_4\text{OH}$ , 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  $\text{Cu K}\alpha_1$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation source (40 kV and 40 mA), the samples were scanned in steps of  $0.02^\circ$  in the  $2\theta$  range  $2^\circ$ - $80^\circ$  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).

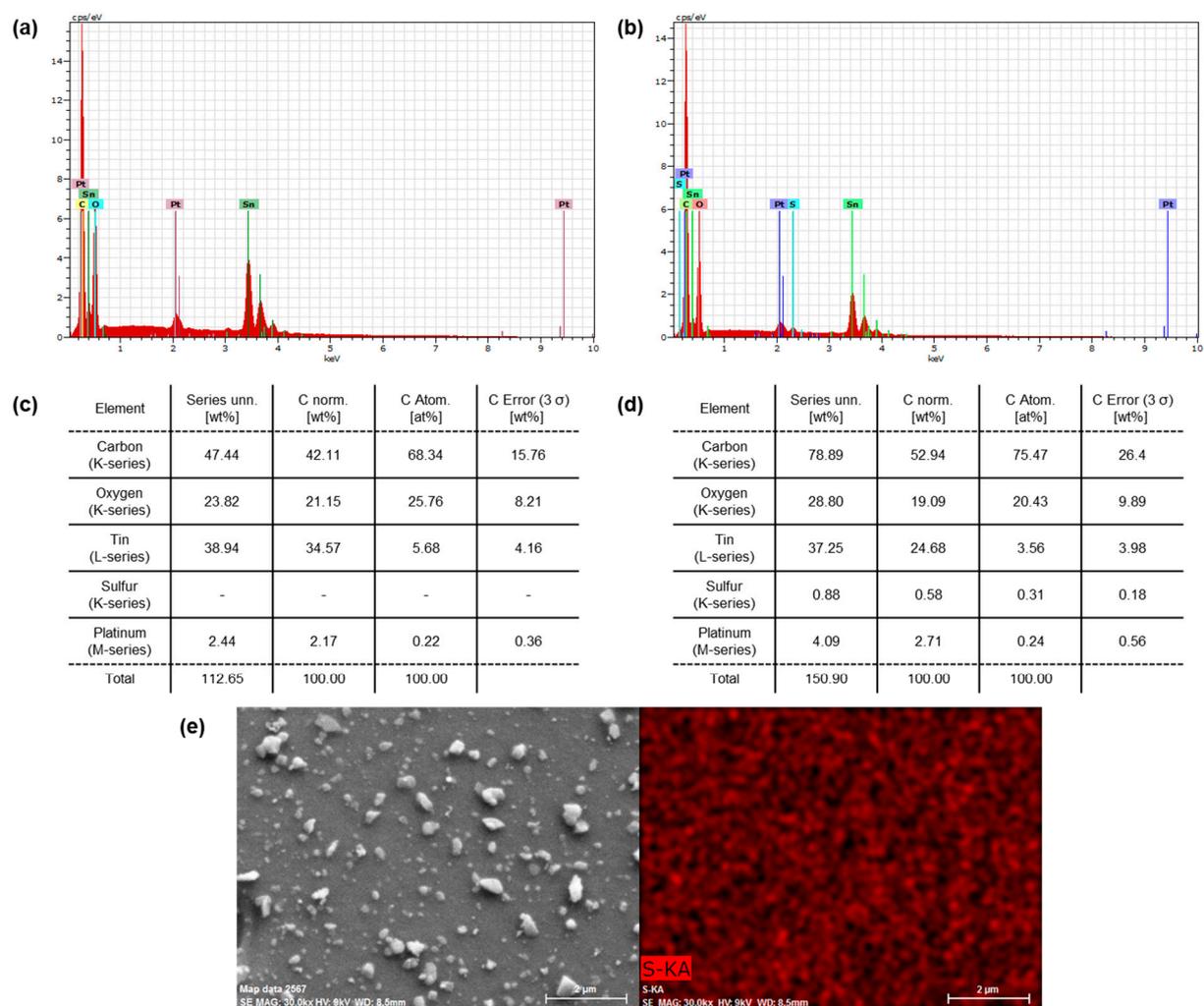
Thermogravimetric analysis (TGA) was conducted with a TGA Q50 instrument (TA Instruments, USA) under nitrogen gas flowing. The samples were held at  $120^\circ\text{C}$  for 10 min to remove physically adsorbed water. After that, the temperature increased to  $800^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$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

The temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) was performed with BELCAT-II catalyst analyzer (Microtrac BEL, Japan). Briefly, the catalysts were pretreated at  $150^\circ\text{C}$  under flowing He (50 mL/min) for 60 min to remove any volatile compounds and moisture. The pretreated samples were cooled to  $50^\circ\text{C}$  and saturated with 5%  $\text{NH}_3$  in He flow (50 mL/min) and, subsequently, purged with He (50 mL/min) at  $150^\circ\text{C}$  for 60 min to remove excessive physisorbed  $\text{NH}_3$ . After that, the temperature was ramped up to  $800^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ , chemisorbed  $\text{NH}_3$  being detected with a thermal conductivity detector (TCD).

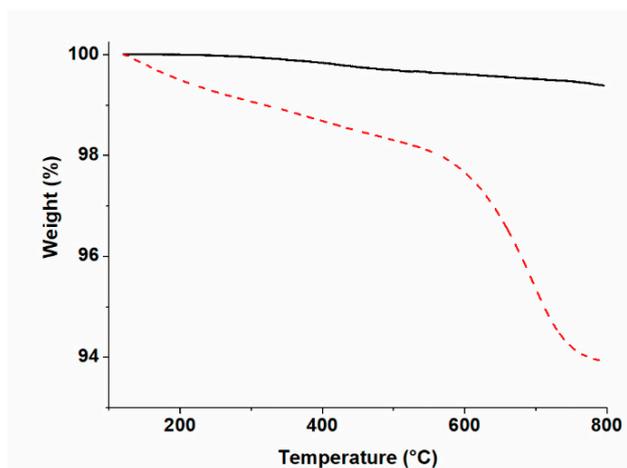
### *Operating condition for GC/FID/MS*

In general, 1.0  $\mu\text{L}$  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.

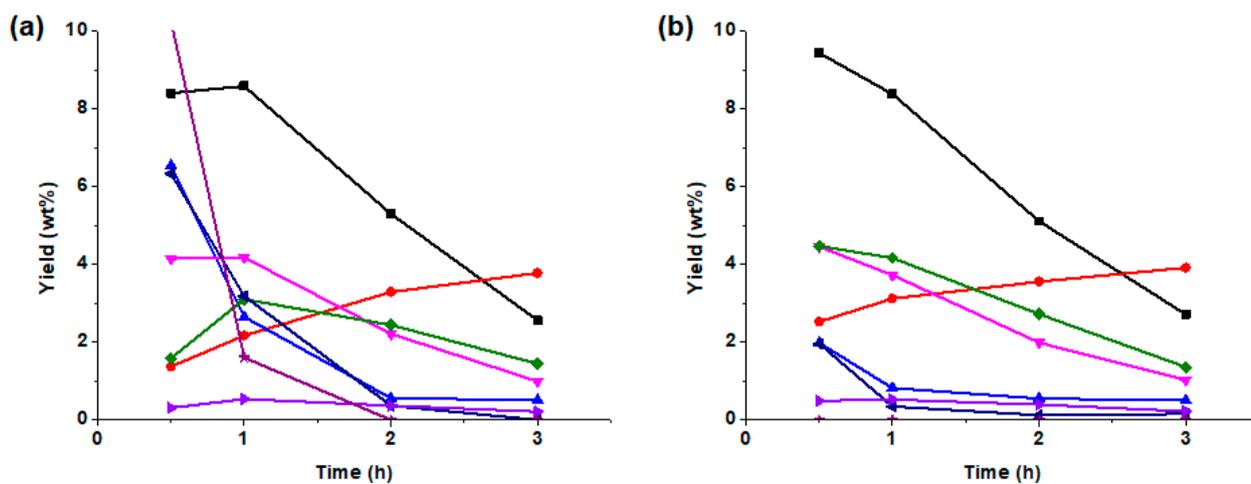
## Supplementary Figures



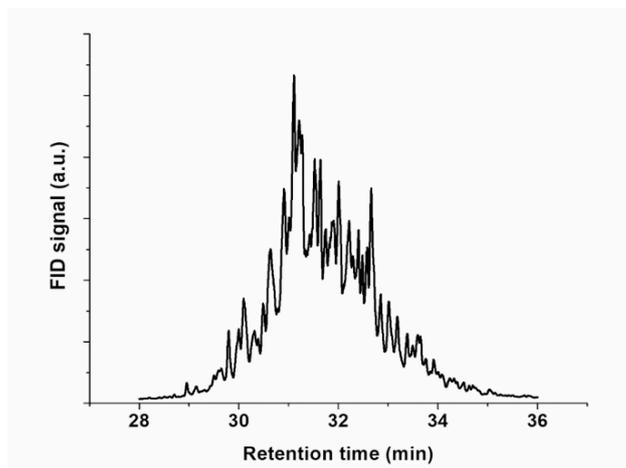
**Figure S1.** (a-b) Energy dispersive spectroscopy (EDS) spectra and (c-d) elemental quantitative data obtained from intact  $\text{SnO}_2$  and  $\text{SO}_4^{2-}/\text{SnO}_2$ . The samples were calcined at 550 °C. The sulfur atoms which were introduced by sulfuric acid immersion before calcination was only detected from the  $\text{SO}_4^{2-}/\text{SnO}_2$  sample. (e) Much higher resolution image of SEM-EDS elemental mapping of  $\text{SO}_4^{2-}/\text{SnO}_2$ .



**Figure S2.** TGA curves of intact SnO<sub>2</sub> (black line) and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> (red dashed line).



**Figure S3.** The yields of the monomeric products along the reaction time at (a) 100°C and (b) 110°C :( $\blacksquare$ ) for  $\alpha$ -terpinene; ( $\bullet$ ) for *p*-cymene; ( $\blacktriangle$ ) for limonene; ( $\blacktriangledown$ ) for  $\gamma$ -terpinene; ( $\blacklozenge$ ) for terpinolene; ( $\blacktriangleleft$ ) for isoterpinolene; ( $\blacktriangleright$ ) for *p*-menth-3,8-diene; ( $\blackstar$ ) for  $\alpha$ -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

- [1] (a) Harvey, B. G.; Wright, M. E.; Quintana, R. L. *Energy & Fuels*, **2009**, *24*(1), 267-273; (b) Zou, J. J.; Chang, N.; Zhang, X.; Wang, L. *ChemCatChem*, **2012**, *4*, 1289-1297; (c) Meylemans, H. A.; Quintana, R. L.; Harvey, B. G. *Fuel*, **2012**, *97*, 560-568; (d) Arias-Ugarte, R.; Wekesa, F. S.; Schunemann, S.; Findlater, M. *Energy & Fuels*, **2015**, *29*, 8162-8167.