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# Conversion of ethanol over calcium stannate catalyst under supercritical conditions

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### *Catalyst synthesis*

The catalyst was synthesized according to Eqs:

$Ca(NO_3)_2 + SnCl_4 + 6NaOH \rightarrow CaSn(OH)_6\downarrow + 2NaNO_3 + 4NaCl$

$CaSn(OH)_6 \rightarrow CaSnO_3 + 3H_2O$ ($T$ = 450 °C)

To obtain $CaSn(OH)_6$, 40 ml of NaOH solution (5.8 g in 50 ml of distilled water) was slowly added dropwise to an equimolar solution of $Ca(NO_3)_2 \cdot 4H_2O$ (5.71 g) and $SnCl_4 \cdot 5H_2O$ (8.48 g) in distilled water (50 ml) with vigorous stirring at room temperature. The resulting precipitate was stirred for 1 hour and kept for 24 hours. Then the precipitate was washed 3 times by resuspension in distilled water (3×100 ml) to remove chloride ions. The resulting $CaSn(OH)_6$ precipitate was dried in air at 120 °C for 8 hours. At the second stage, $CaSn(OH)_6$ was calcined in a muffle furnace in air at a temperature of 450 or 750 °C for 4 hours; the samples are designated $CaSnO_3$ and $CaSnO_3$-750, respectively.

### *Catalytic tests*

Catalytic tests were carried out in a stainless steel flow-type tubular reactor (internal diameter of 4 mm). A catalyst loading 0.20 g (particle size 0.14–0.25 mm) was placed in the center of the reactor, and the remaining volume was filled with quartz sand. Ethanol (rectified) was used as a substrate. The substrate was supplied by a high-pressure liquid pump at a rate of 0.20 ml·min$^{-1}$, which corresponds to 47 ml·h$^{-1}$·$g_{cat}^{-1}$. The reactor was heated when the substrate was supplied. The products were collected in a trap, the samples were taken every 30 min. The pressure was maintained by a back-pressure regulator. The duration of the experiments was 4.5 hours. The products were analyzed on a Chromatec Crystal 5000 gas chromatograph with a Thermo TR-5MS capillary column. Identification of products was carried out by gas chromatography-mass spectrometry using a Thermo Focus GC - DSQ II device with a Thermo TR-5MS capillary column.

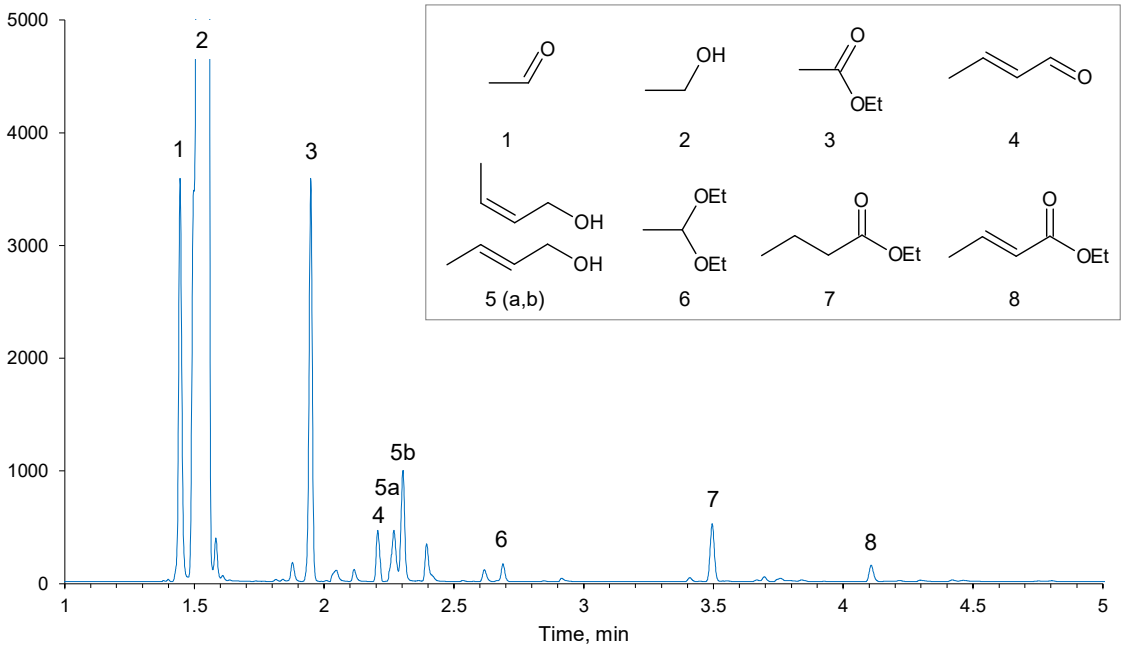


**Figure S1** Chromatogram of products: (*1*) ethanal, (*2*) ethanol, (*3*) ethyl acetate, (*4*) crotonaldehyde, (*5a,b*) *cis/trans*-but-2-en-1-ols, (*6*) 1,1-diethoxyethane, (*7*) ethyl butanoate, (*8*) ethyl crotonoate.
Analysis conditions: column – Thermo TR-5MS (30 m × 0.25 mm ID × 0.25μm); injector and detector temperature 200 °C; column temperature 40→200 °C, 10 deg $min^{-1}$; FID detector; carrier gas – helium; split ratio – 100:1; sample size – 0.2 μl.

***Physico-chemical study of the catalysts***

X-ray diffraction analysis was carried out using a Rigaku D/Max-2500 diffractometer with CuKα radiation in the 2θ range of 10–60°. To process X-ray diffraction data, the STOE WinXPow software package and the PDF-2+ and PDF-4+ database were used.