Redox–Acid Cooperative Bifunctional Catalyst comprising Dilacunary Phosphotungstates and Zeolite Hβ for the synthesis of n-butyl levulinate and succinic acid

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Supplementary Information

Text

2.3.1 Acidity measurements

a) Total acidity by n-butylamine titration. In this method, a 0.025 M solution of n-butylamine in Toluene as well as 0.025 M Trichloroacetic acid (TCA) in Toluene was prepared. The 0.25 g material was allowed for suspension in 25 mL n-butylamine solution for 24 h and the excess base was titrated against Trichloroacetic acid using neutral red as an indicator. Total acidity was calculated by given formula:

Acidity (mmol/gm) = mole/ gm = gm of n-BA/molecular weight of n-BA

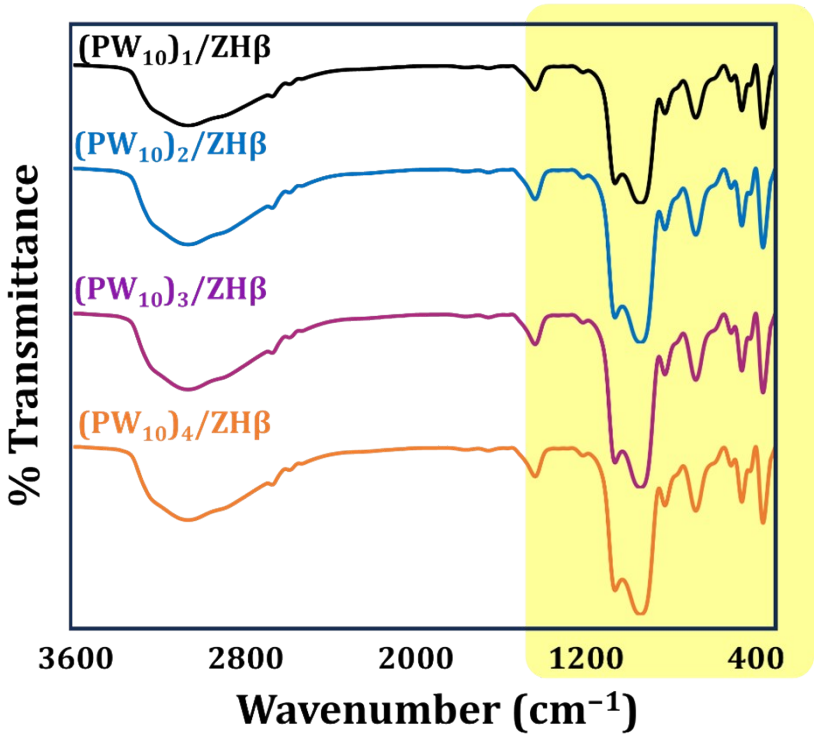
b) The total acidic sites as well as types of acidic sites were determined by potentiometric titration. In which, a suspension of 0.25 g of material was prepared in 25 mL of Acetonitrile and put in for stirring for about 12–15 min and initial electrode potential was measured (which indicates its acidic strength). A 0.05 N n-Butylamine (n-BA) solution in Acetonitrile (0.1 mL) was added to this suspension and allowed to stir for 3 h at 25°C. Then potentiometrically, it was titrated against the same solution of n-Butylamine and the variation in electrode potential was noted with a digital pH meter. The acidic sites were calculated according to the following scale: Ei > 100 mV (very strong sites), 0 < Ei < 100 mV (strong sites), − 100 < Ei < 0 mV (weak sites) and Ei < − 100 mV (very weak sites)

c) The NH_3 temperature-programmed desorption (NH_3-TPD) was conducted using the BELCAT-II equipment manufactured by MicrotracBEL Corp. (Japan). In the presence of a pure helium gas mixture (99.9%, flowing at a rate of 30 mL per minute), a dry catalyst weighing 0.05 g was loaded and subjected to a pre-treatment process at a temperature of 300 °C for a duration of 1 hour. A 10% NH_3 in He gas mixture was used to adsorb ammonia onto the surface of the substance for a duration of 1 hour. Subsequently, the physiosorbed ammonia was eliminated by flushing the material with pure He gas. The temperature programming procedure was a gradual increase in temperature from 100 to 600 °C, with a rate of 10 °C per minute. The emitted NH_3 was then monitored using a thermal conductivity detector (TCD) incorporated in the experimental setup.

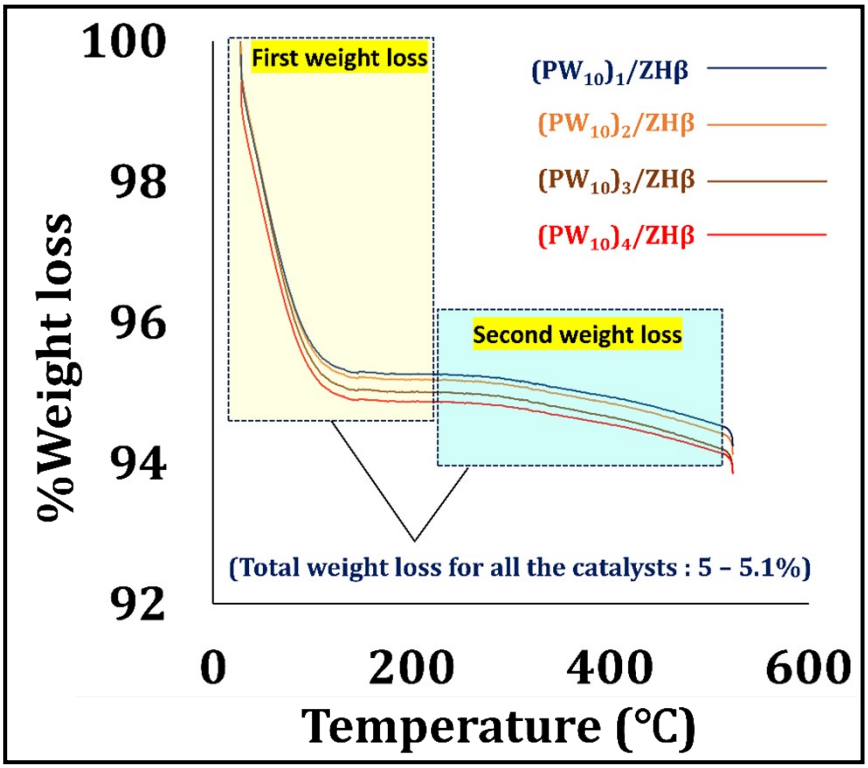
2.3.2 Physicochemical techniques

Cyclic Voltammetric studies were performed on the CHI 660A instrument. The BET (Brunauer–Emmett–Teller) surface area measurements as well as the N_2 adsorption-desorption isotherms (at 77 K) were recorded using Micromeritics ASAP 2010 (USA) volumetric static adsorption instrument. By using the BJH adsorption-desorption method, pore size distributions were calculated. For the elemental analysis, the JSM-7100F EDX-SEM analyser was used. The Mettler Toledo Star SW 7.01 was used under the nitrogen atmosphere for thermogravimetric analysis (TGA) with a flow rate of 2 mL min^{-1} at 25–600 °C (ramp rate of 10 °C min^{-1}). The Fourier Transform Infrared (FT-IR) spectra were recorded in the range 4000–400 cm^{-1} by using a KBr disc on a Shimadzu instrument (IRAffinity-1S). The Powder X-ray diffraction (XRD) patterns for the samples were recorded using a Philips PW-1830 instrument in the 2θ range 5 - 90° (Cu Kα radiation λ = 1.54 Å). The solid-state ^{29}Si MAS NMR spectra were recorded on JOEL ECX 400 MHz High resolution multinuclear FT-NMR spectrometer. Transmission electron microscopy (TEM) was done by coating the samples on the Cu grid and scanned on a JEOL TEM instrument (model-JEM 2100) (JAPAN) with an acceleration voltage of 200 kV using carbon-coated 200 mesh.

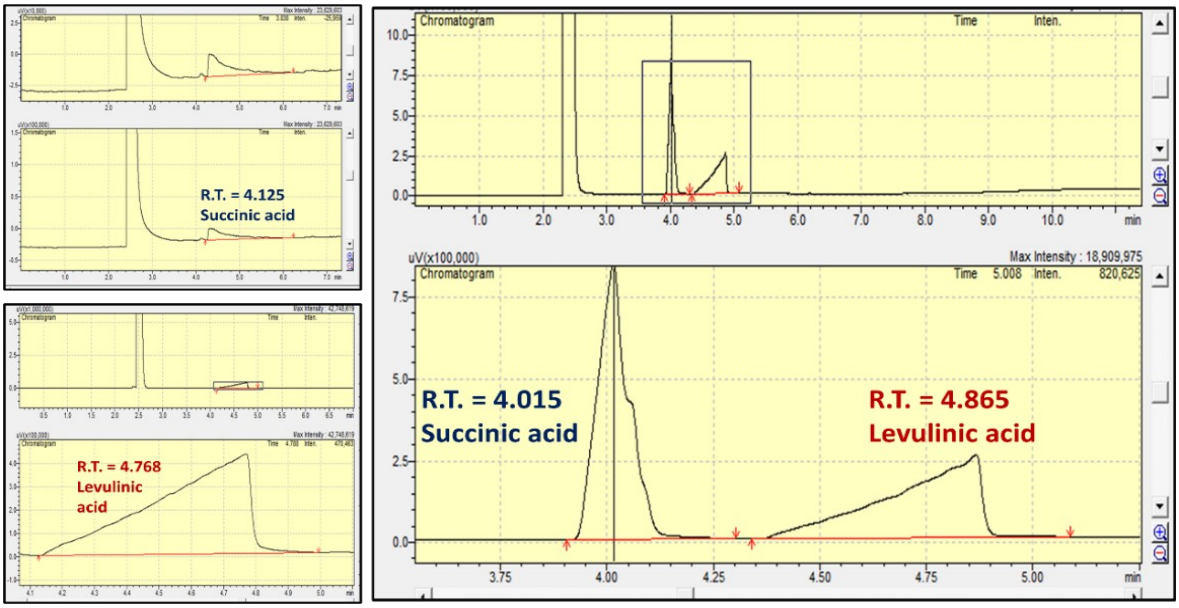
Figures



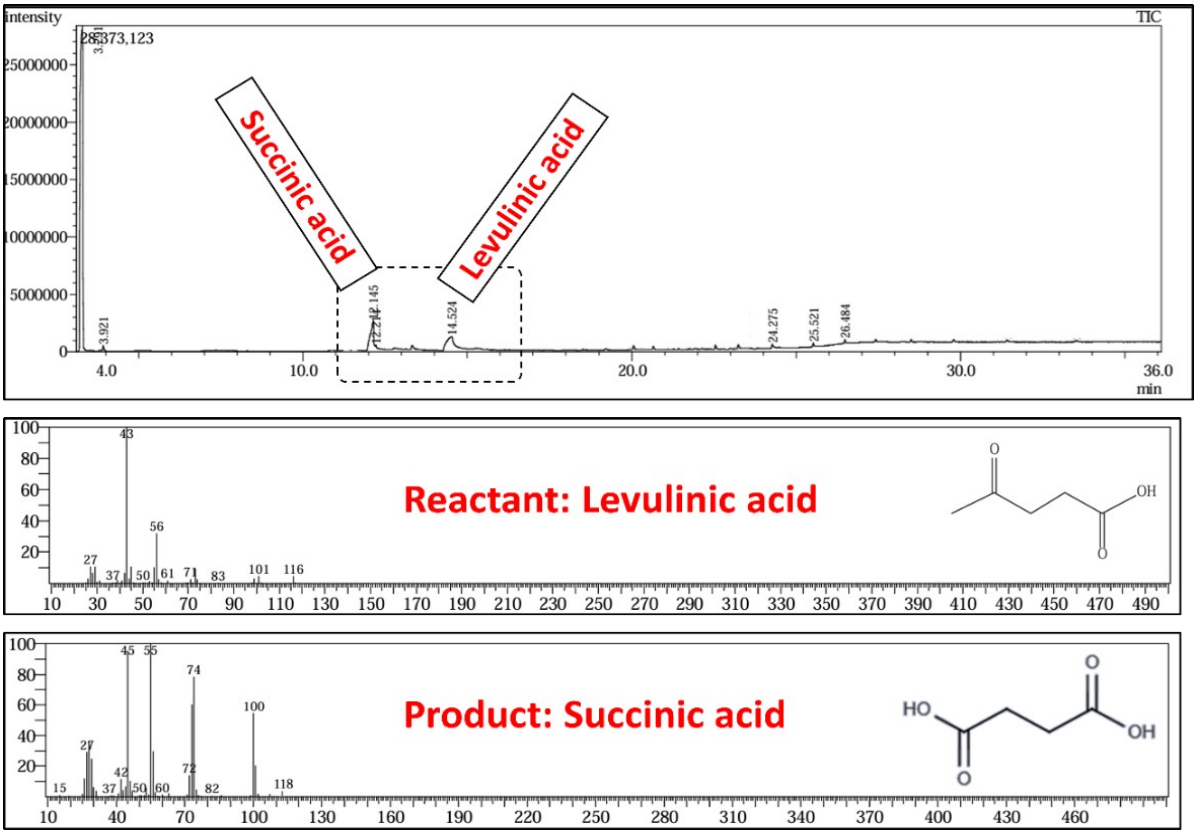
Supplementary Figure 1. FT-IR spectra of catalysts



Supplementary Figure 2. TGA of catalysts



Supplementary Figure 3. GC of standards and the reaction mixture



Supplementary Figure 4. GC-MS profile of reaction mixture