Anchored Dilacunary Phosphotungstates on Zeolite HY: Synthesis and solvent free selective oxidation of Levulinic acid to Succinic acid using environmentally benign oxidant, H_2O_2

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Supplementary Information

2.3 Synthesis of catalyst

Conversion of Zeolite NaY Zeolite HY

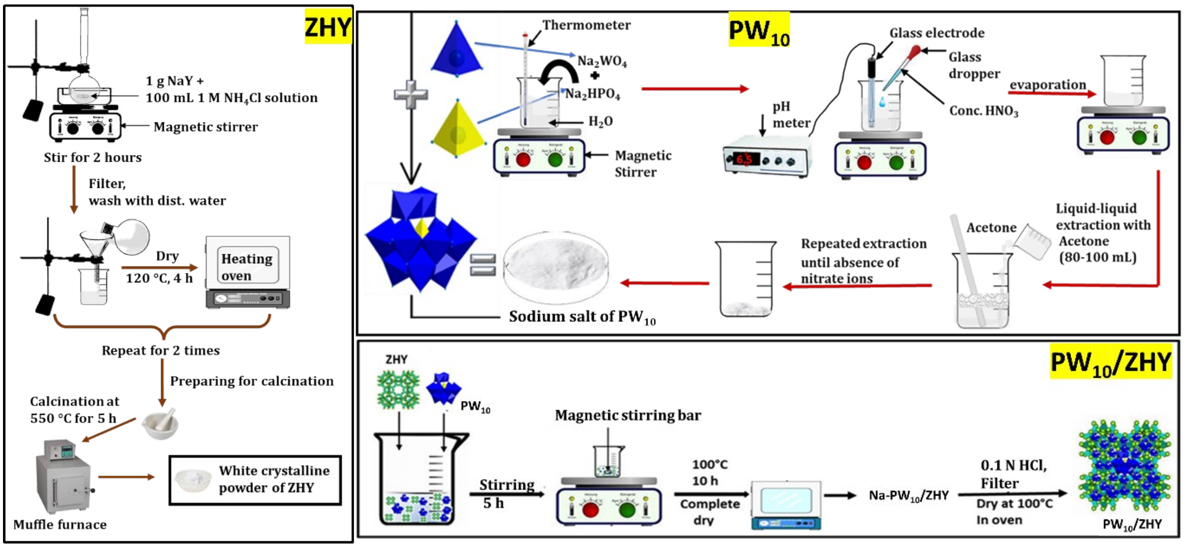
Zeolite NaY was converted to its protonic form (HY) via a conventional ammonium ion-exchange method. Briefly, NaY was exchanged with 1 M NH_4Cl solution at 80 °C for 2 h, followed by filtration, washing, and drying. The exchange procedure was repeated twice to ensure complete replacement of Na^+ ions. This ensures the removal of alkaline counter-ions which would otherwise poison the desired framework acidity. The resulting NH_4Y was calcined in air at 550 °C for 5 h to obtain zeolite HY, designated as ZHY. This treatment is required to thermally decompose the framework ammonium ions into gaseous ammonia, effectively generating the active Brønsted acid sites within the zeolite framework.

Synthesis of sodium salt of PW_{10}

Anhydrous disodium hydrogen phosphate (0.02 mol, 0.2 g) and sodium tungstate dihydrate (0.2 mol, 6.8 g) were dissolved in 150–200 mL of distilled water in stoichiometric ratios. The resulting mixture was heated to 80- 90 °C and its pH was adjusted to 6.5 using conc. nitric acid. Maintaining this narrow, slightly acidic pH range is crucial because the formation and thermodynamic stability of the specific dilacunary structure is highly pH-dependent. Half of the volume was evaporated, and the hetero polyanion was separated using a liquid-liquid extraction method with 80–100 mL of acetone. In order to remove the nitrate ions from the extract, the above extraction was repeated. Eliminating residual nitrate species is essential to prevent unintended secondary oxidative side-reactions during subsequent catalytic testing. The obtained white crystalline solid was air dried and that sodium salt of dilacunary phosphotungstate that was designated as PW_{10}.

Synthesis of the catalyst, Dilacunary phosphotungstate (PW_{10}) Anchored to ZHY

The incipient wet impregnation method was used to synthesize a series of catalysts containing 30% of PW_{10}, and 1 g of zeolite HY. After stirring, dried in an oven, treated with 0.1 N HCl, which serves to maximize protonation and chemically lock/stabilize the anchored clusters via enhanced electrostatic interactions with the zeolite walls, filtered, washed, and dried at 100°C. The washing steps are necessary to clear away any unanchored, weakly physisorbed PW_{10} clusters from the external faces of the zeolite particles, preventing homogeneous leaching. The obtained catalysts were designated as PW_{10}/ZHY (Supplementary Scheme I).

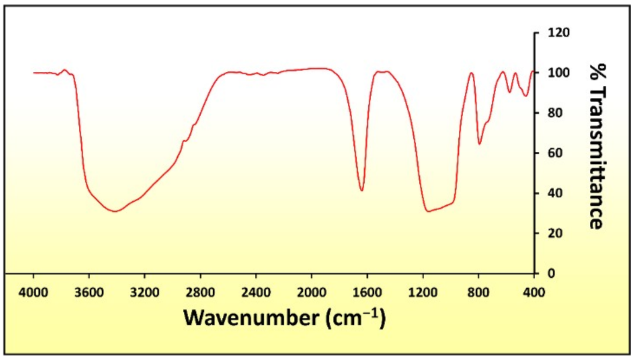


Supplementary Scheme I. Schematic presentation of catalytic methodology

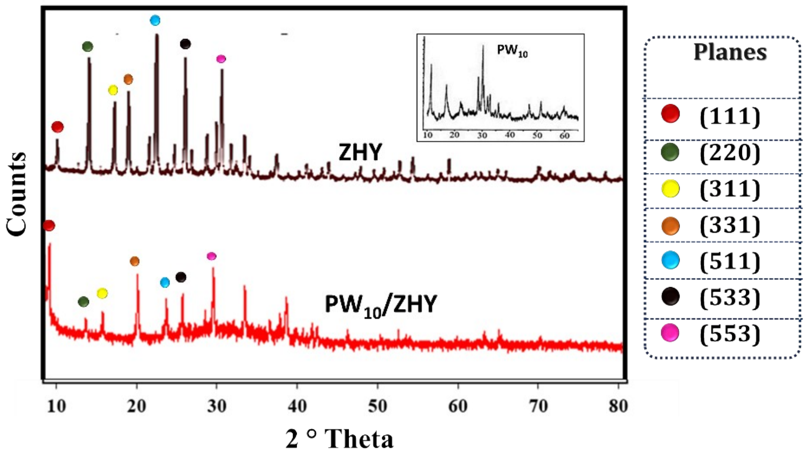
2.5 Catalytic activity

In a typical procedure, levulinic acid (10 mmol), H_2O_2 (20 mmol), and a catalyst were taken in a double-neck round-bottom flask, equipped with a water condenser. The condenser prevents the evaporation loss of volatile intermediates and preserves reactant stoichiometry throughout the reaction. The mixture was stirred continuously at a desired temperature and a desired time. After the reaction was completed, the mixture was cooled to room temperature. The solid catalyst was separated by centrifugation, and the clear supernatant was collected. The reaction mixture was then diluted with methanol to ensure complete dissolution of organic components. Prior to solvent removal, the reaction mixture was maintained under mild conditions to ensure decomposition of residual hydrogen peroxide. This quenching step is vital to avoid uncontrolled over-oxidation reactions during the heating/distillation stage, ensuring accurate data. The clear supernatant was carefully decanted and evaporated under reduced pressure at 60 °C using a rotary evaporator, yielding a dense, white semi-solid residue.

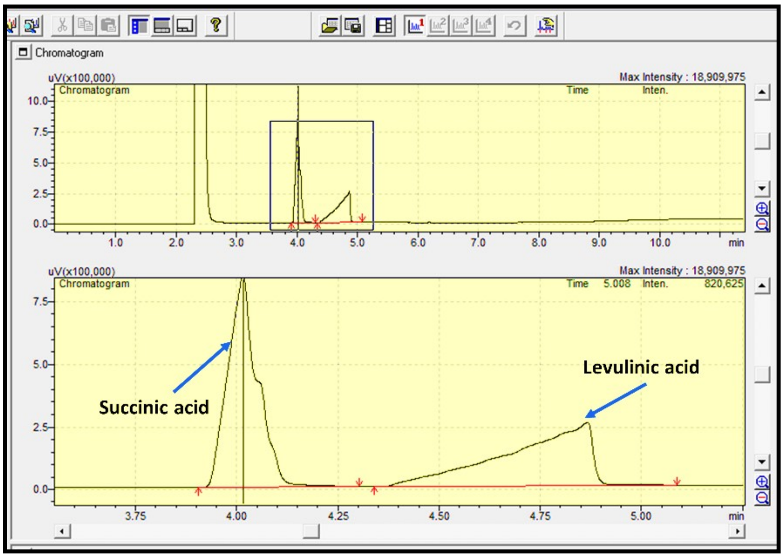
This residue was redissolved in methanol, and the resulting clear supernatant was analyzed by GC. All GC analyses were performed immediately after redissolution to avoid any post-reaction changes or equilibrium shifts in the solution over time. To confirm products, the standards of levulinic acid and succinic acid were injected under identical GC conditions. The programming was carried in which the temperature range was 35 to 300 ^{0}C. The hold time for ramp rate was initially 2 min at 80 ^{0}C (equilibration time = 1.0 min) and then the rate increased by 25 up to 300 ^{0}C with a hold time of 5 min. These parameters, pressure = 69.4 kPa, total flow = 10.1 ml/min, column flow = 0.74 ml/min, linear velocity = 21.9 cm/sec and purge flow = 3.0 ml/min were set. Further, the product was confirmed via GC-MS analysis.



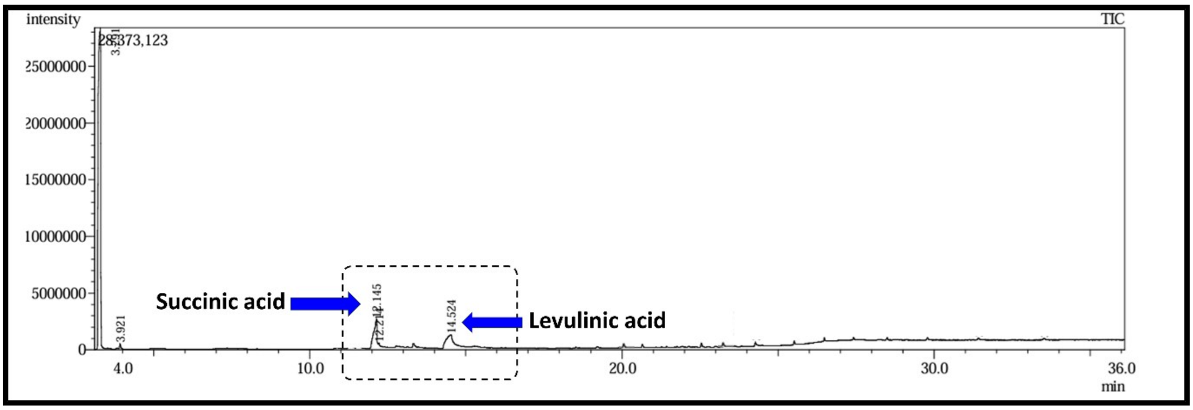
Supplementary Figure 1. FTIR of ZHY



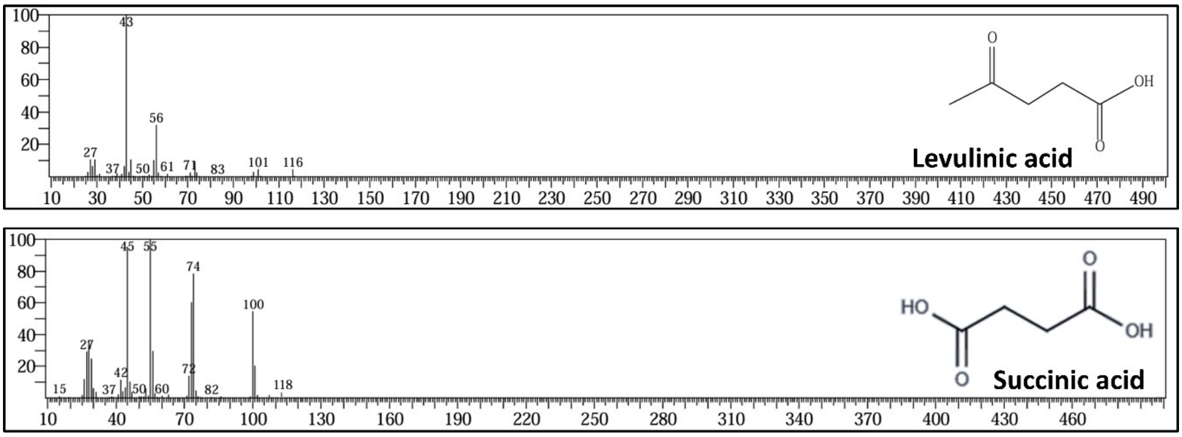
Supplementary Figure 2. XRD of PW_{10}, ZHY and PW_{10}/ZHY



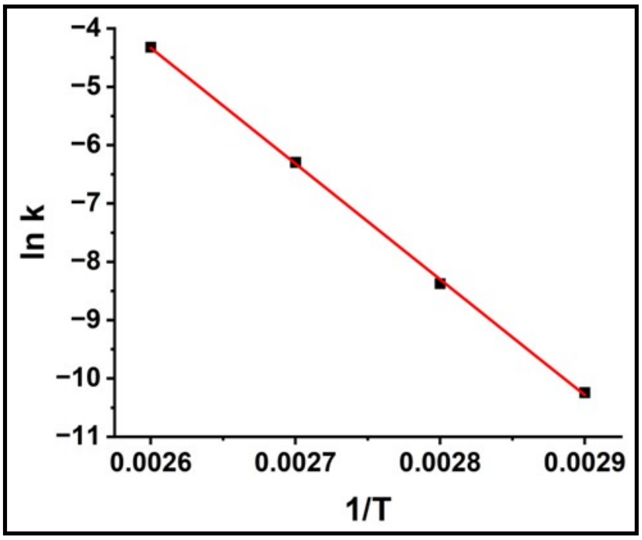
Supplementary Figure 3. GC profile



Supplementary Figure 4a. GC-MS profile



Supplementary Figure 4b. Mass profile



Supplementary Figure 5. lnk vs 1/T plot for activation Energy