Supplementary Material (ESI) for Chemical Science

Electronic Supplementary Information (ESI)

Surface synergism of Ag-Ni-ZrO_2 nanocomposite for catalytic transfer hydrogenation of bio-derived platform molecules

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Catalyst Characterization

BET surface area

BET surface area of the Ag, Ni, Ag-Ni and Ru supported on ZrO_2 catalysts was measured by means of N_2 adsorption at 77 K preformed on Autoabsorb 3100 instrument.

X-ray diffraction (XRD) analysis

X-ray diffraction patterns were recorded on a PAnalytical PXRD Model X-Pert PRO-1712, using Ni filtered Cu Kα radiation (λ = 0.154 nm) as a source (current intensity, 30 mA; voltage, 40 kV) and X-celerator detector. The samples were scanned in the 2θ range of 20–80^0.

The crystallite size was determined by Scherrer equation.

$$D = k\lambda/\beta \cos\theta$$

Transmission electron microscopy (TEM)

The particle size and morphology were studied using transmission electron microscope (HR-TEM), model JEOL 1200 EX. A small amount of the solid sample was sonicated in 2- propanol for 1 min. A drop of prepared suspension was deposited on a Cu grid coated with carbon layer and grid was dried at room temperature before analysis.

ICP Analysis

The sample analysis of metal leaching experiments was carried out by using instrument ICP-OES (Perkin Elmer), the supernatant liquid was evaporated and made up to 25 mL by distilled water.

DR-UV study

The UV–vis diffuse reflectance (DRUV–vis) spectra of the solid samples were recorded in the region 200–800 nm using a spectrophotometer (Shimadzu UV2101 model) with $BaSO_4$ as the reference material.

H_2-Temprature programmed reduction (H_2-TPR)

TPR experiments of prepared Copper catalysts were also performed on a Chemisoft TPx (Micromertics-2720) In the TPR experiment, a U-tube (Quartz tube) was filled with solid catalyst. This sample holder was positioned in a furnace equipped with a temperature control. A thermocouple was placed in the solid for temperature measurement. Equal quantity of fresh vacuum dried catalyst was taken in the U-tube. Initially, flow of inert gas (Argon) was passed through U-tube to remove the air present in the lines, and heated in Ar atmosphere with a flow rate of 25mL/min to 200^0C for 30 min to remove the moisture and surface impurities present on the sample and then it was cooled to room temperature. Ar was replaced by a mixture of 5% H_2 in Ar gas for the TPR experiment with a heating rate of 10 ^{o}C min^{-1} starting from the room temperature to 700 ^{0}C and a thermal conductivity detector (TCD) measured the hydrogen uptake.

X-ray photoelectron spectroscopy (XPS)

The software program X-Pert High Score Plus was employed to subtract contribution of copper Kα2 line prior to data analysis. X-ray photoelectron spectra were recorded using an ESCA-3000 (VG Scientific Ltd. England) with a 9 channeltron CLAM4 analyzer under vacuum better than 1

x 140^{-8} Torr, using MgKα radiation (1253.6 eV) and a constant pass energy of 50 eV. The binding energy values were charge-corrected to the C1s signal (284.6 eV).

Table 1. Surface area of all zirconia supported catalysts

Sr.No	Catalyst	Surface Area (m^2/gm)
1	10% Ag-ZrO2	37
2	20% Ni-ZrO_2	31
3	10%Ag-20% Ni-ZrO_2 [Fresh]	34
4	10%Ag-20% Ni-ZrO_2 [Used]	36
5	5% Ru/ZrO_2	29

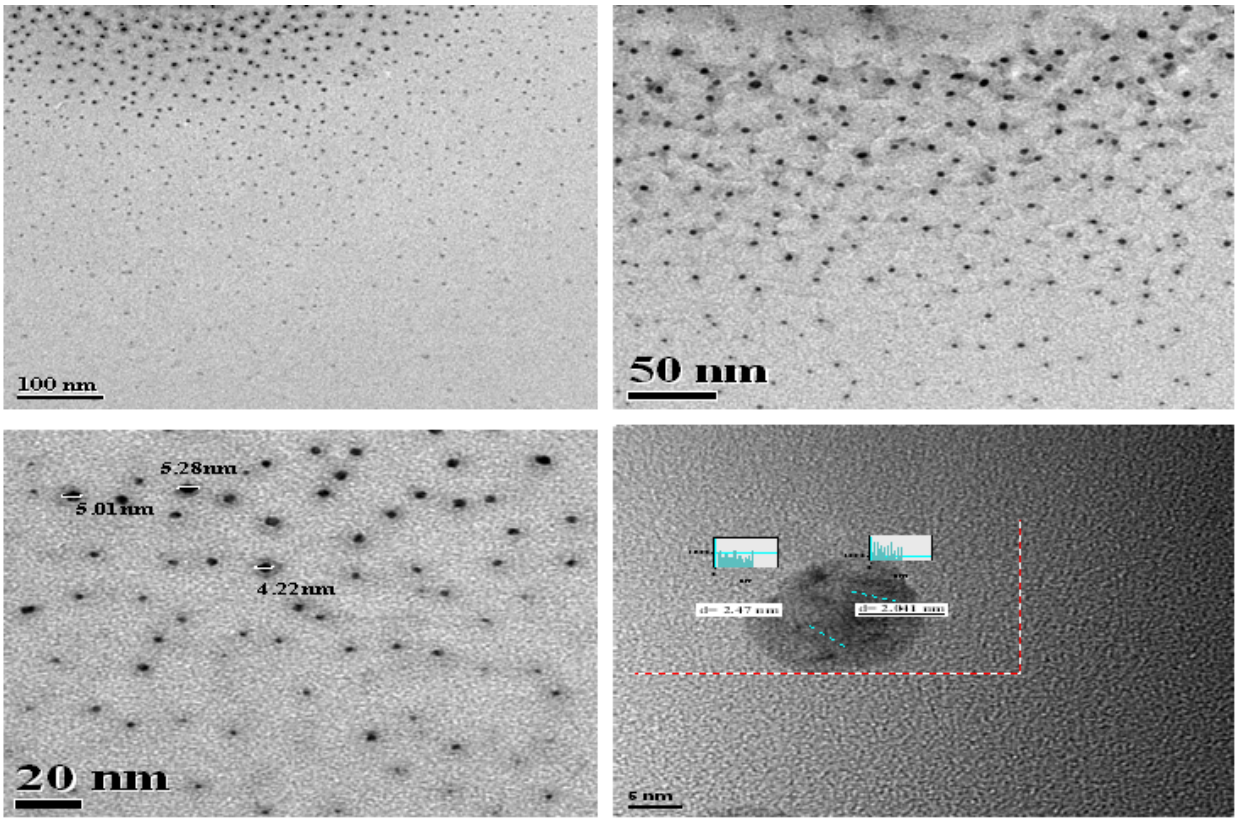

Fig S 1.HR- TEM images of Ag-Ni-ZrO_2

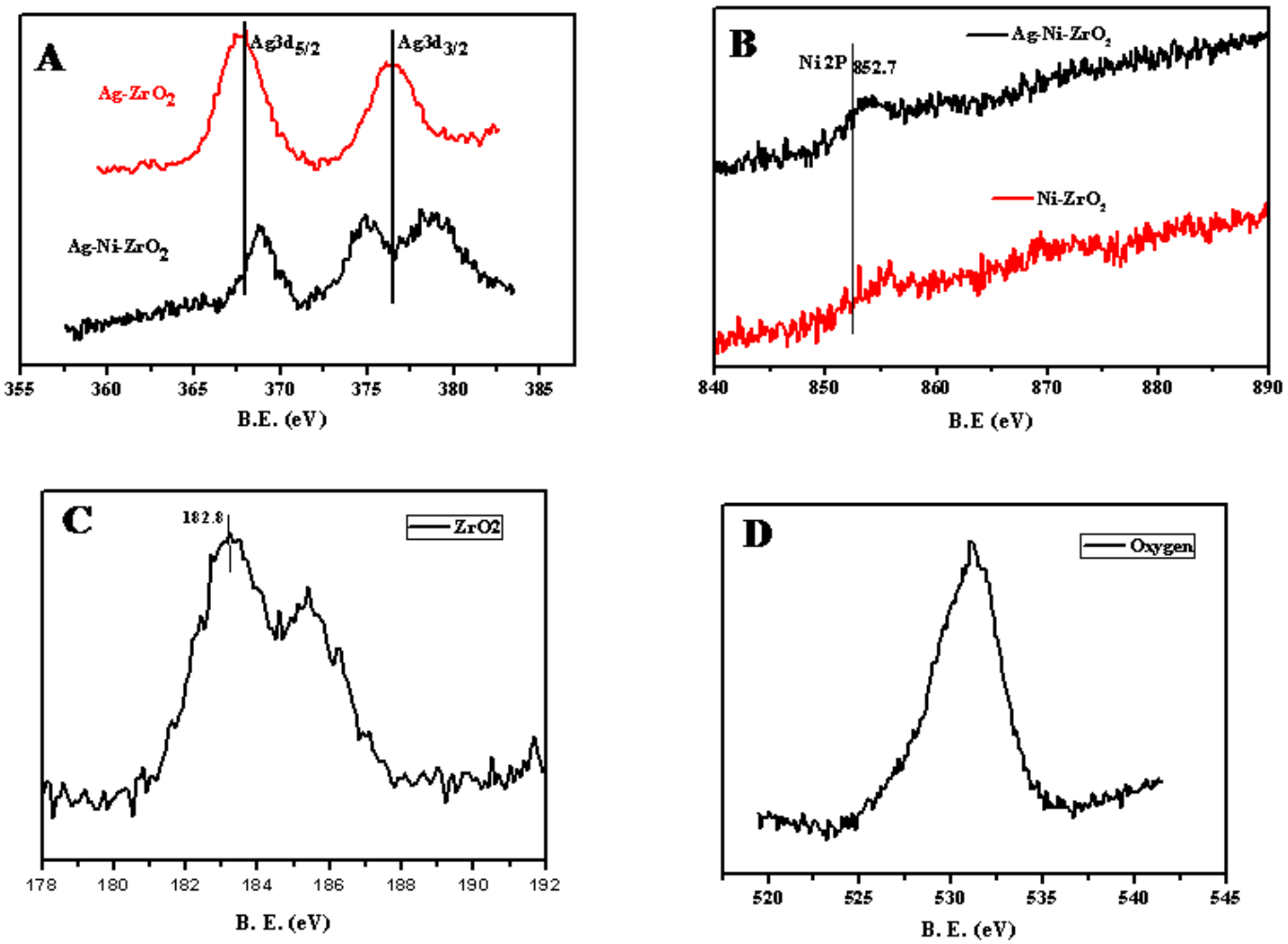

Fig S 2.XPS study of Ag, Ni, Zr and O in a) Ag in Ag-ZrO_2 and Ag-Ni-ZrO_2 b) Ni in Ni-ZrO_2 and Ag-Ni-ZrO_2 c) Zr in Ag-Ni-ZrO_2 d) Oxygen in Ag-Ni-ZrO_2

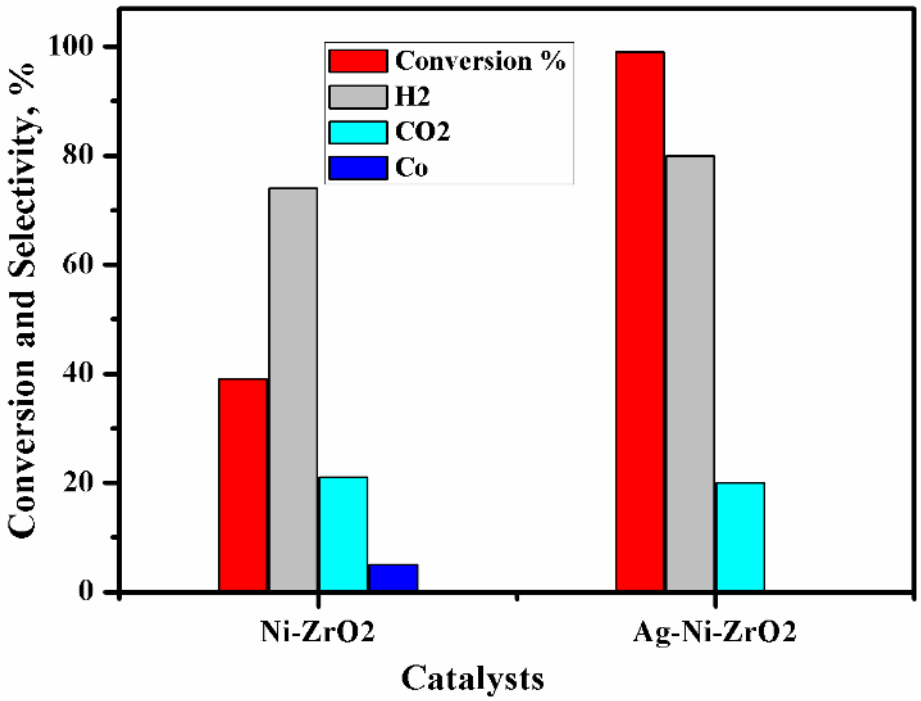

Fig S 3. Conversion and selectivity pattern for decomposition of formic acid over Ni-ZrO_2 and Ag-Ni-ZrO_2

Reaction conditions: formic acid (43 mmol); solvent, water (95 mL); temperature, 493 K; N_2 atm; catalyst, 0.5 g; catalyst:substarte ratio, (1:10) reaction time,5 h.

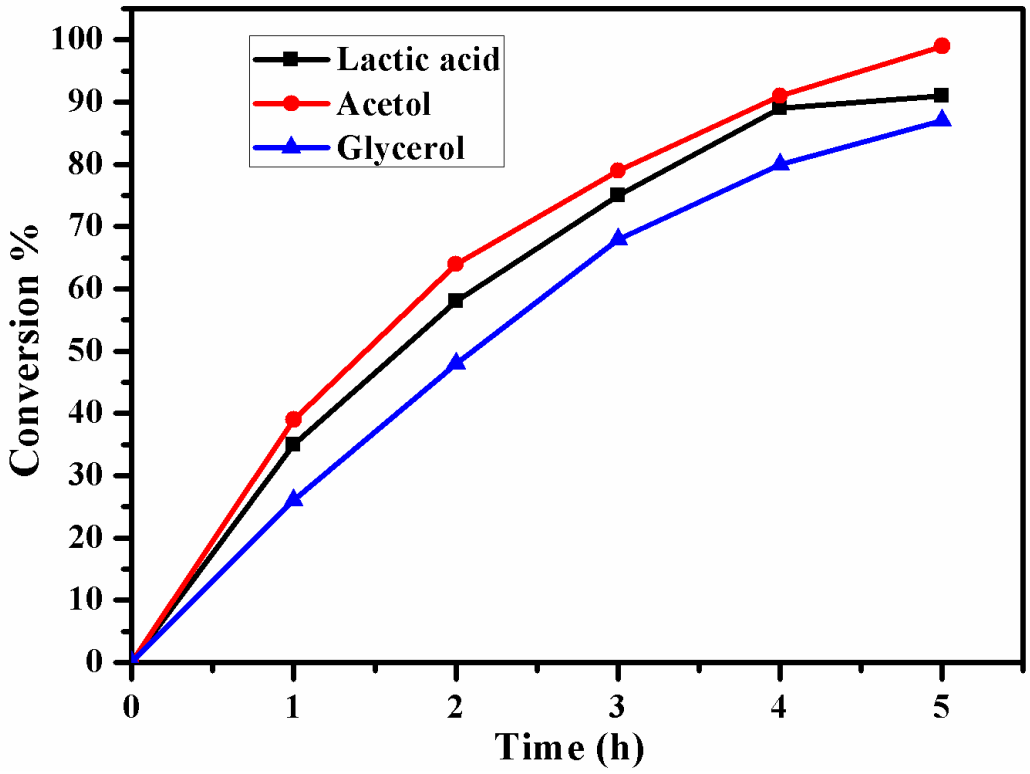

Fig S 4. Conversion Vs Time profile of lactic acid, Acetol and glycerol over Ag-Ni-ZrO_2 catalyst

Reaction conditions: C3 substrates (Lactic acid, Acetol and glycerol) (43 mmol), formic acid; (43 mmol); solvent, water (90 mL); temperature, 493 K; N_2 atm; catalyst, 0.5 g; catalyst:substarte ratio, (1:10) reaction time,5 h.

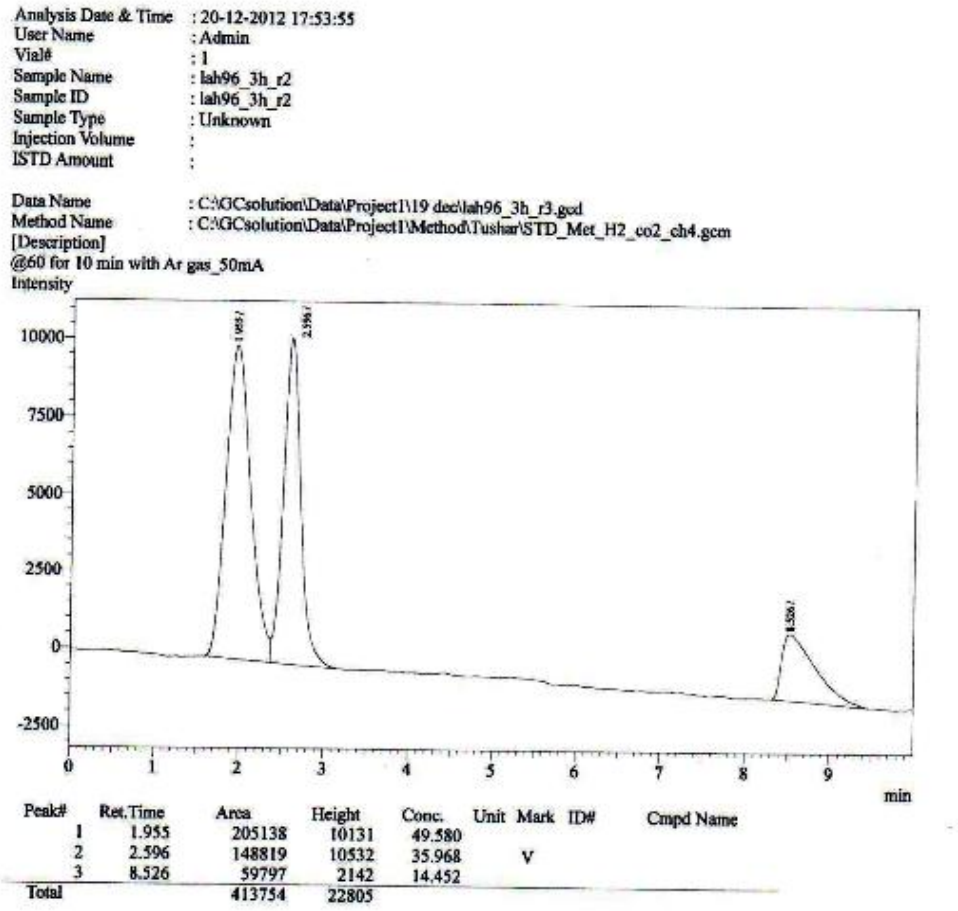

Fig S 5. GC analysis over Ag-Ni-ZrO_2 catalyst

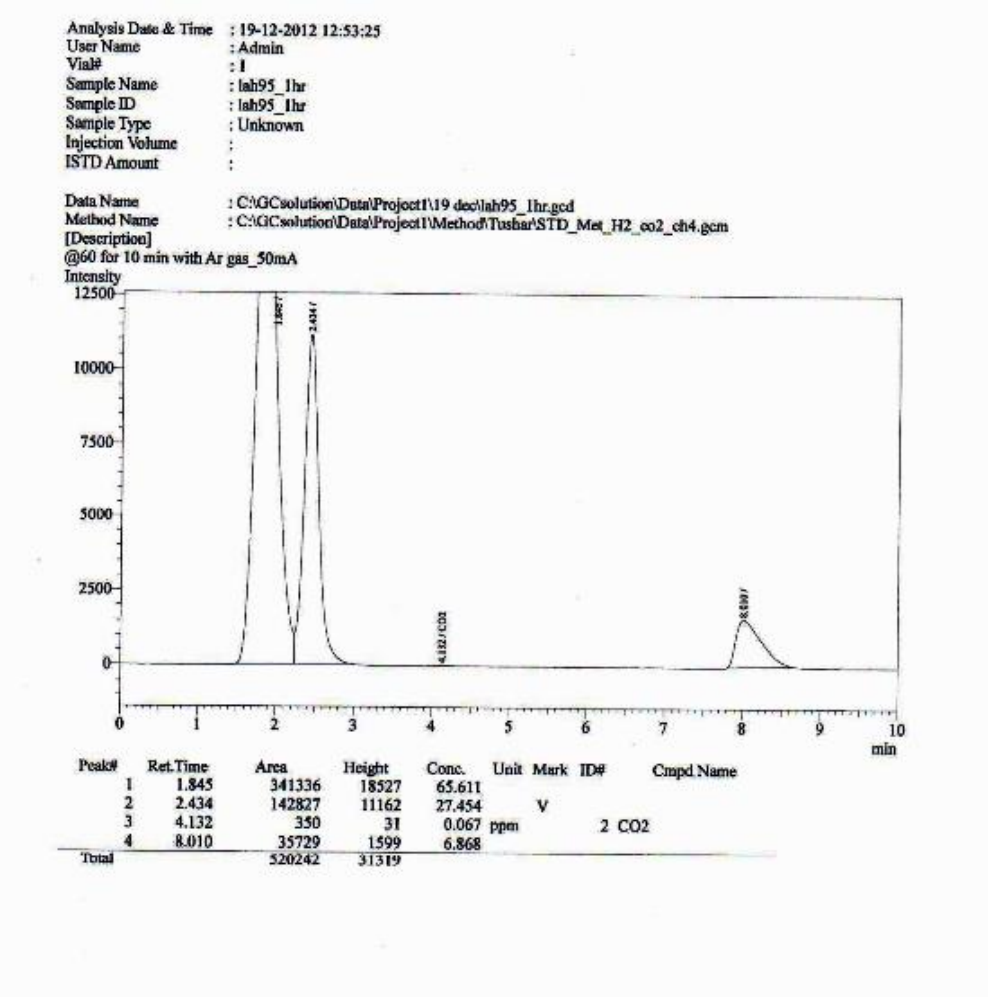

Fig S 6. GC analysis over Ni-ZrO_2 catalyst