

Electronic Supplementary Information

Carbonized glycerol nano tubes as efficient catalyst for biofuel Production†

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1. Synthesis of glycerol carbonized nano tubes

In the present method, the carbonization of the glycerol has been conducted in presence of con. sulphuric acid. A typical synthesis method involves simple procedure of drop-by-drop addition 60 gm of 36N sulphuric acid (98% pure, Merk) to 20 gm of glycerol (anhydrous, 99% pure, Merk) followed by treatment at 373 K for 24 h. Then the temperature was increased up to 573 K. The resultant mixture appeared as a gel type material was allowed to dry at 573 K temperature under nitrogen atmosphere to facilitate the decomposition and transformation of the glycerol to hydrophobic carbon residue bearing sulfonyl groups. The prepared material is washed thoroughly with ample amount of boiling water followed by cold water. The black powder form of material obtained weighs ~ 6.2 g (inclusive of –all the functional groups) which is about 77 wt% to the carbon content of the substrate glycerol taken.

2. Characterization

The element Carbon, Hydrogen and Sulfur of the synthesized material determined by the CHNS Analyser. Model No: Vario Micro Cube 15131010, made in Germany. The total acidity of the sample is measured by acid-base titration method, where, known amount of oxalic acid was mixed with known amount of catalyst. The resultant mixture was titrated against base, sodium hydroxide. The value of consumed NaOH measured the NaOH required to neutralize the

total acidic sites of catalyst plus the acidity of the known amount of oxalic acid added to the catalyst. Subtracting the acidity of the oxalic acid from the total acidity value gives the actual acidity of the catalyst. The amount of S measured by elemental analysis (CHNS analyzer) has been used for the calculation of the number of acid sites contributed by the $-\text{SO}_3\text{H}$ groups in the catalyst. The total acidity measured by the acid base titration method was always higher than the $-\text{SO}_3\text{H}$ values. Hence the remaining acidity can be attributed to the presence of $-\text{OH}$ and $-\text{COOH}$ groups on the sulphonated glycerol material.

XPS spectra were attained using X-ray photoemission spectroscopy (XPS) (Omicron Nanotechnology, Germany) with a monochromatic Al K_{α} radiation ($h\nu = 1486.6 \text{ eV}$) working at 15 kV, 20 mA. Obtained XPS spectra were deconvoluted to individual components using Gaussian Lorentzian function in Casa XPS software (Casa Software Ltd). The binding energies of the obtained spectra were calibrated with respect to the adventitious C 1 s peak at 284.6 eV.

3. Reaction Studies

The synthesized solid material of nano tubes possessing good acidic property has been applied for solvent free liquid phase reaction, where the material exhibited excellent activity to produce bio-fuels in Parr reactor at mild conditions of 343 K within half an hour reaction time. Two reactions we studied are acetalization of glycerol to produce solketal and the esterification of levulinic acid with butanol to give butyl levulinate. The products obtained in the reaction have been analyzed by GC and GC-mass equipments. The studies indeed indicated the promising catalytic functionality of the synthesized material, where, the catalyst exhibited as high as 90 % conversion of glycerol to produce solketal with 100 % selectivity. We have also applied the synthesized material for solvent free liquid phase reaction in parr reactor for esterification of Levulinic acid. The esterification of Levulinic acid is carried out in presence of n-Butanol as a solvent at different reaction temperatures and at different reactant molar ratios to optimize the product yields. At 343k and 1:1 molar ratio, 0.65 gm catalyst exhibited 70% conversion of Levulinic acid with 100% product selectivity to Butyl-Levulinate. Further, the conversion was successfully increased to as high as 90% at 373k temperature and 8 h reaction time at similar reaction conditions to give 100% selectivity to Butyl-Levulinate.

Supporting Figures :

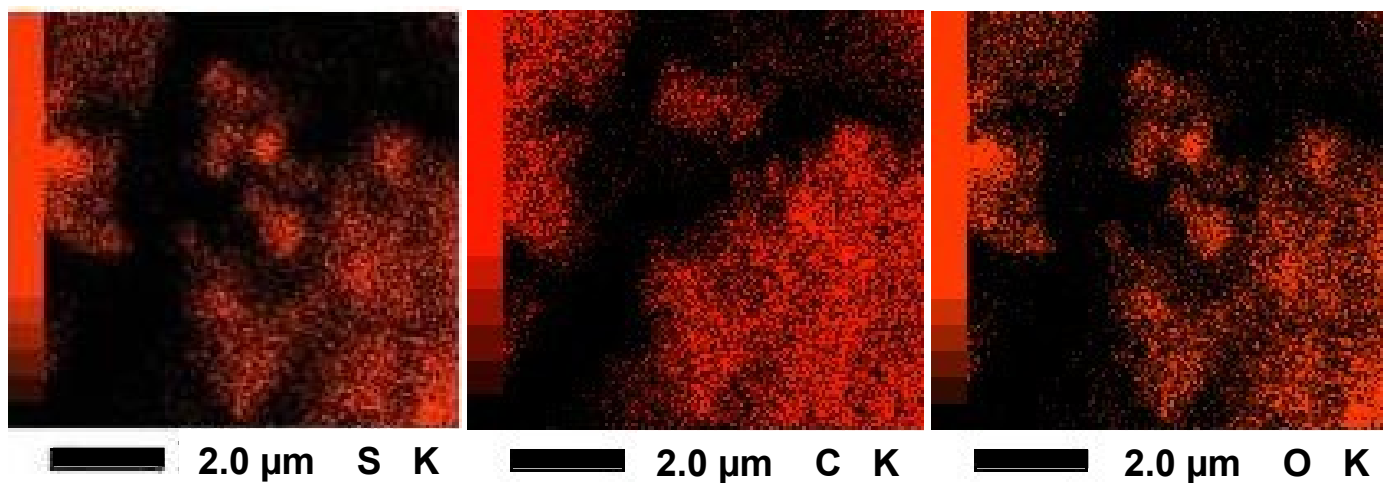
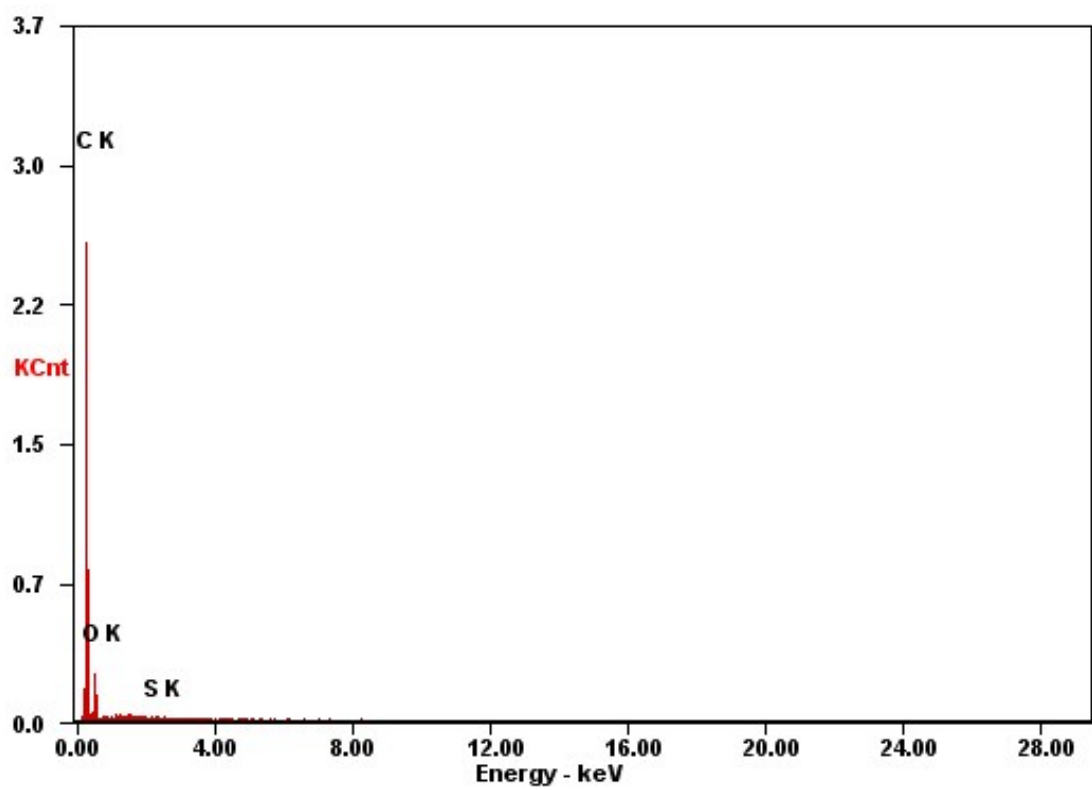


Figure S1. EDX analysis of the synthesized material

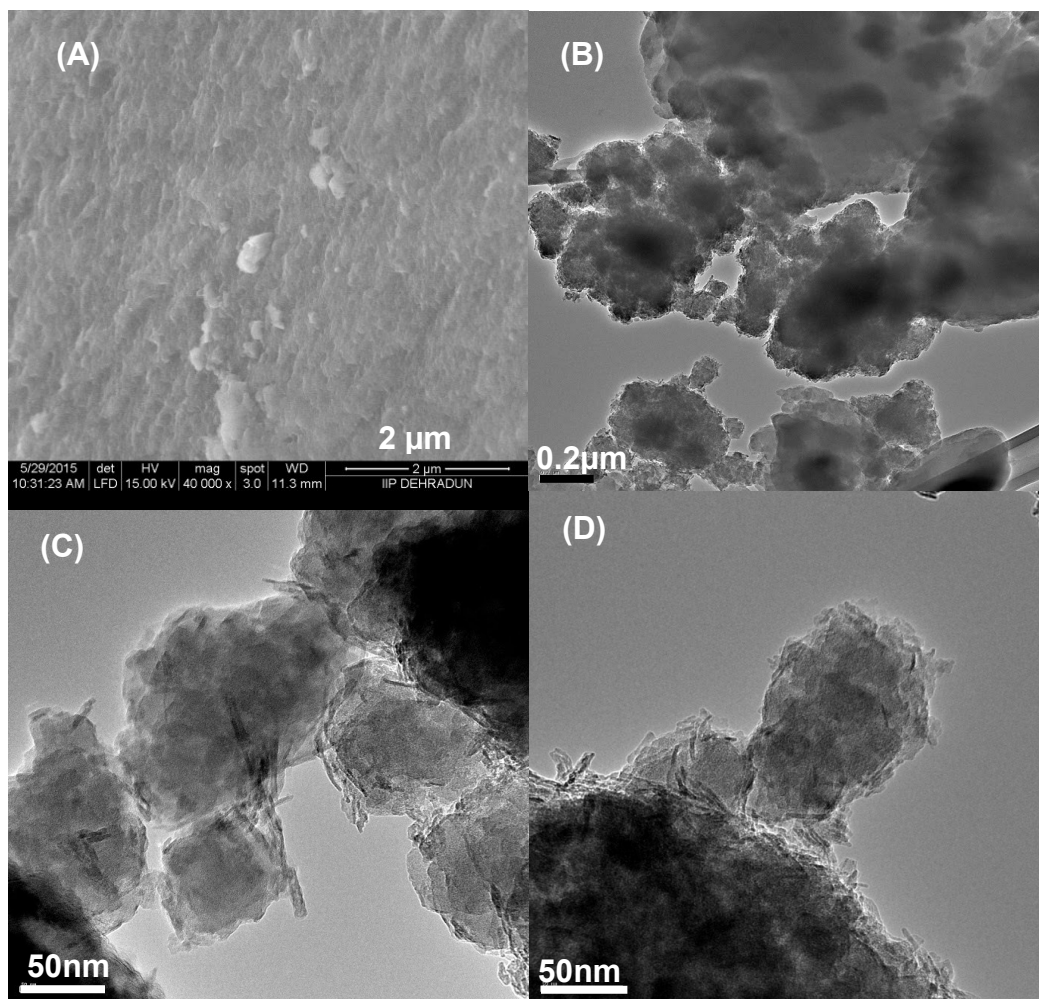


Figure S2. SEM (A) and TEM (B-D) images of the carbonized glycerol

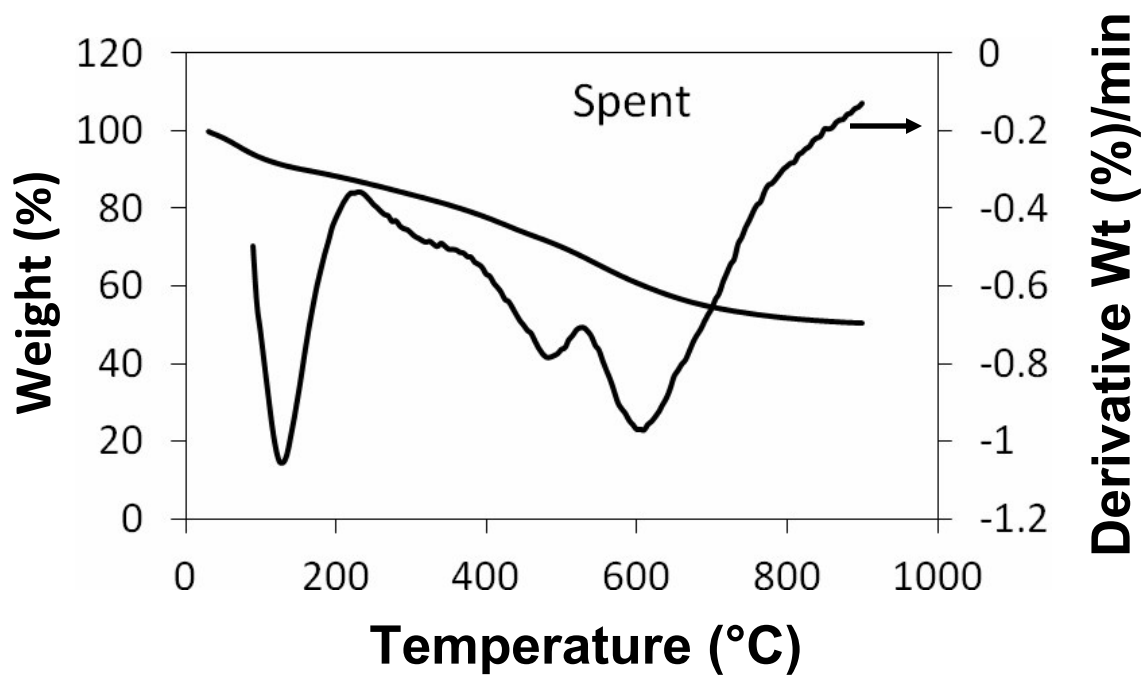
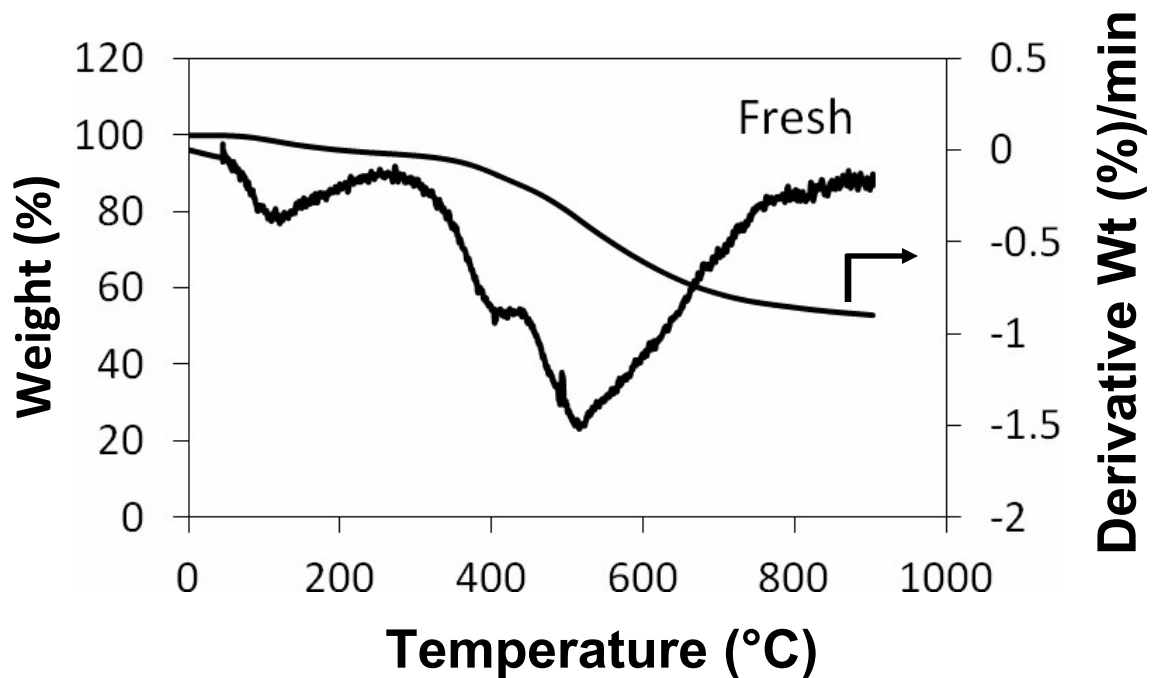


Figure S3. TGA-DTA spectra of fresh and spent carbonized glycerol

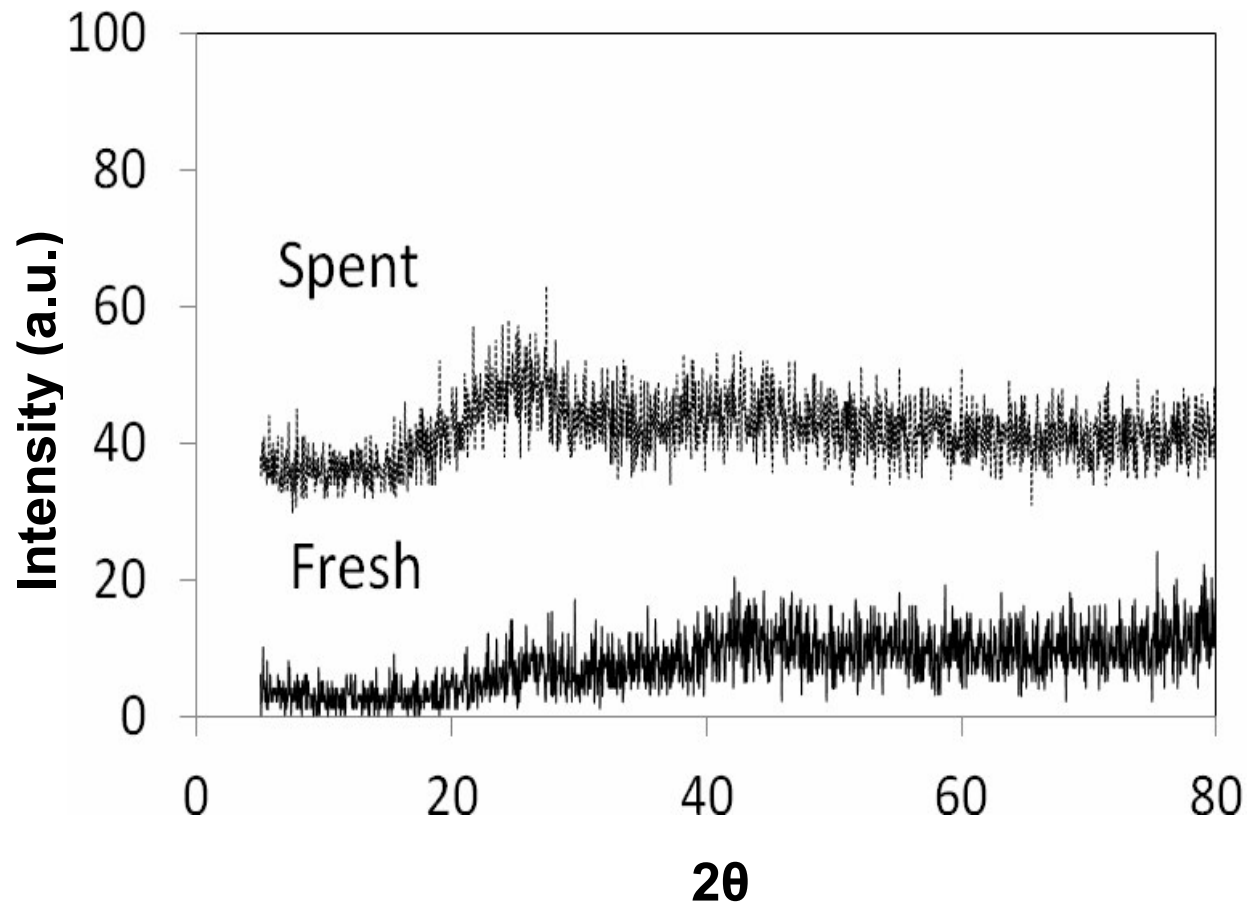


Figure S4. XRD spectra of fresh and spent carbonized glycerol

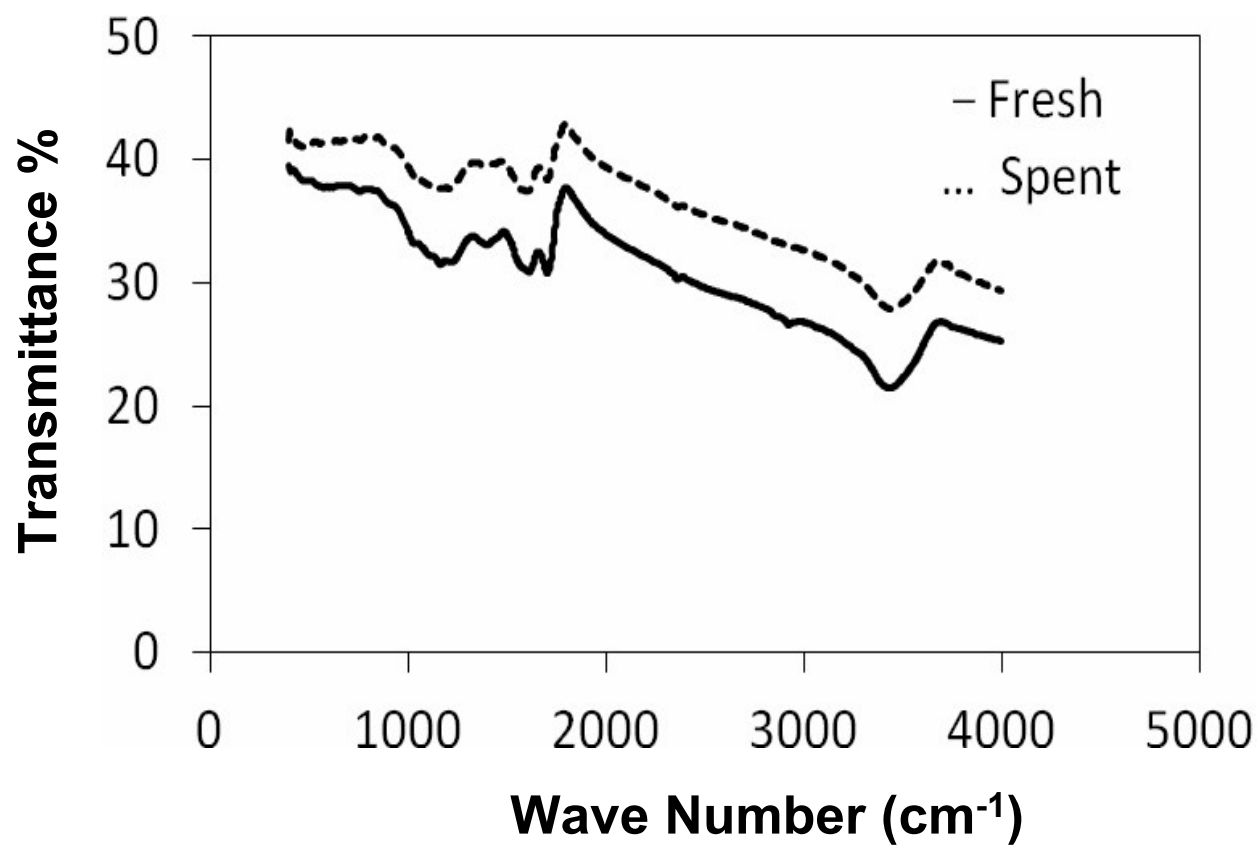


Figure S5. FTIR analysis of fresh and spent carbonized glycerol

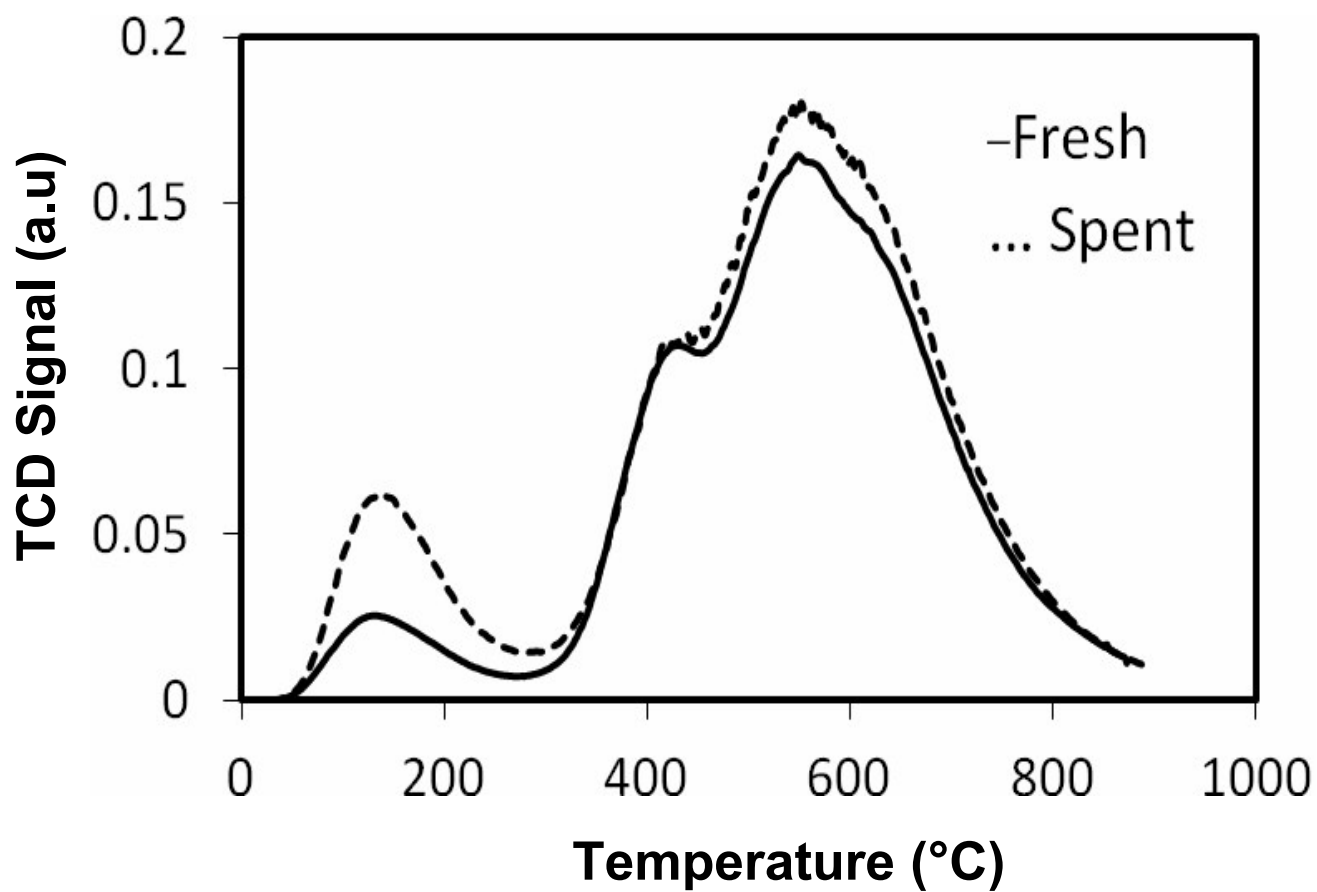


Figure S6. TPD spectra of fresh and spent carbonized glycerol catalyst

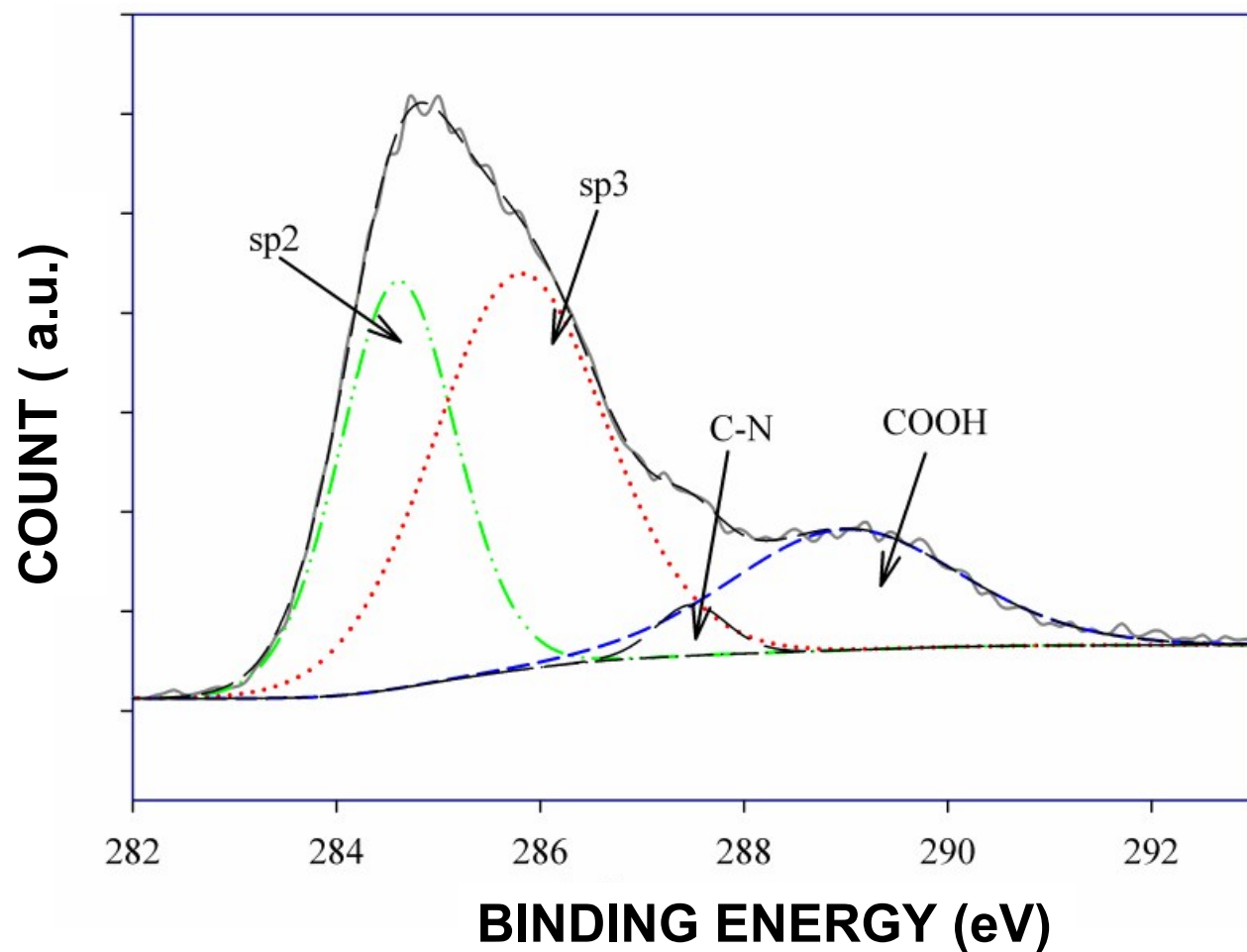


Figure S7. XPS analysis of spent catalyst