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Electronic Supplementary Information (ESI)

Ni/apatite-type lanthanum silicate supported catalyst in glycerol steam reforming reaction

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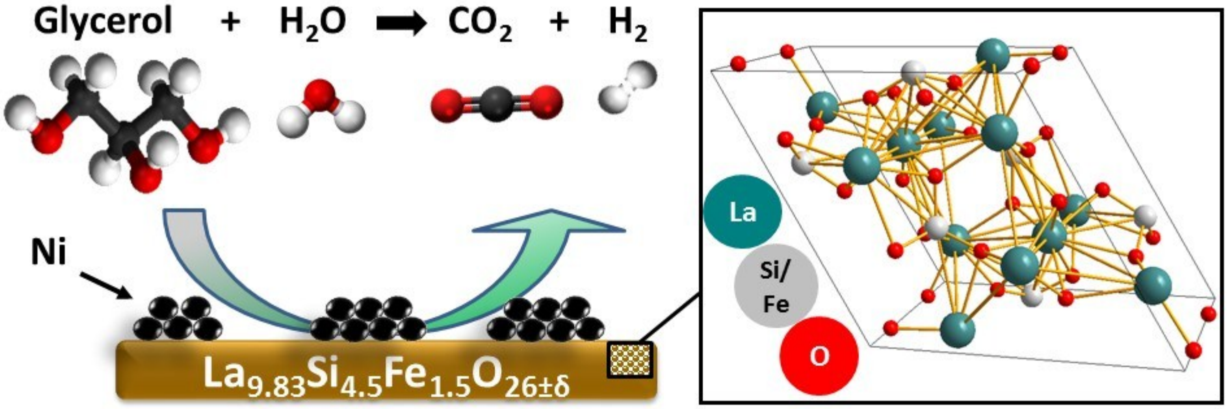

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Contents

Preparation of $La_{9.83}Si_{4.5}Fe_{1.5}O_{26\pm\delta}$ (LFSO) supports and catalysts

LFSO sample was prepared by solid state reaction [1,2]. Stoichiometric amounts of metal oxides were mixed, grinded and annealed at 1000°C for 2h with a heating and cooling rate of $3K\cdot min^{-1}$. Subsequently, the powder was mechanically milled to a mean particle size under 50μm, uniaxially pressed at 18MPa into pellets and sintered at 1500°C for 1h. Pellets were crashed, milled to the final material. This powder was agglomerated by uniaxial pressing to form catalytic pellets by a thermal treatment at 1400 °C. Finally, the agglomerated sample was crashed and sieved into the desired fraction between -425μm and +350μm. The as prepared LFSO catalytic support particles had a porosity of 26% as measured by Archimedes method.

The Ni catalysts were prepared by the wet impregnation method on the supports using $Ni(NO_3)_2$??™$6H_2O$ aqueous solutions to a final loading of Ni equal to 5% wt. After the impregnation, the catalysts with the support material were air-dried overnight and calcined at 800°C for 4 hours providing the materials for the experimental procedures (Ni-LFSO and Ni-ALO - fresh catalysts). Reduced samples were produced under 100ml/min of pure hydrogen (H_2) flow for 1 hour at 800°C (Ni-LFSOr and Ni-ALOr– r: reduced). The catalysts after the experimental procedures are noted as Ni-LFSOu and Ni-ALOu.

Characterization of catalysts

Determination of Ni in the samples, blank and standard solutions was carried out by ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometer) by Perkin Elmer (Optima 4300 Dual View model). An appropriate amount of the catalyst was weighted in a Teflon beaker. The exact weight of the sample was recorded to the nearest 0.0001 g. Typical sample preparation procedure was used as described elsewhere [3,4].

All LFSO and alumina based catalysts were observed by means of Scanning Electron Microscopy (SEM) using a JEOL6380LV unit at 20kV after gold sputtering of samples.

The specific surface area (m^2/g) of the samples was determined by N_2 porosimetry at 77 K using a FISONS SORPTOMATIC 1900 volumetric adsorption/desorption apparatus. Prior measurement the samples were outgassed at 250 °C under vacuum (5×10^{-2} mbar) for 10 h. The specific surface area of the samples was determined by applying the BET equation using the linear part ($0.05 < P/Po < 0.35$) of the adsorption isotherm and assuming a close-packed BET monolayer with am (N2) = 0.162 nm^2 at 77 K [5,6].

Ni-LFSO, Ni-LFSOr, Ni-ALO and Ni-ALOr were characterized by means of XRD on a SIEMENS D5000 Diffractometer using CuKα radiation (λ = 1.5406 Å) and 2θ range from 10° to 75° with scan step of 0.01°. The Scherrer equation, where applicable, was employed to determine the particle size of different phases based on their most intense diffraction peaks. Thermogravimetric (TGA) and differential thermal analysis (DTA) were performed by a SETARAM TGA 92 system in air environment from 25°C to 900°C with a $10K\ min^{-1}$ rate at fresh and used catalyst samples in order to investigate carbon accumulation (coking).

Main properties of materials can be found in Table 1S.

XRD Results

According to the powder XRD results (Fig.1S) over LFSO, Ni-LFSO and Ni-LFSOr, no other than apatite phase and Ni or NiO were detected. Single phase hexagonal apatite structure (space group P36/m-176) PDF# 00-049-0443 was identified in all samples. No solid state phenomena between Ni and ATLS were observed. In the case of the Ni-ALO and Ni-ALOr samples, nickel aluminate crystal phase ($NiAl_2O_4$) was detected due to the calcination temperature of 800°C. However NiO is only observed in traces , either due to its small crystallite sizes, smaller than the XRD detection limit or their nearly amorphous structure. The main differences between the XRD patterns of the fresh and reduced Ni-ALO catalyst, are the decreasing intensities of Al_2O_3 and $NiAl_2O_4$ peaks and the development of metallic nickel trace peaks.

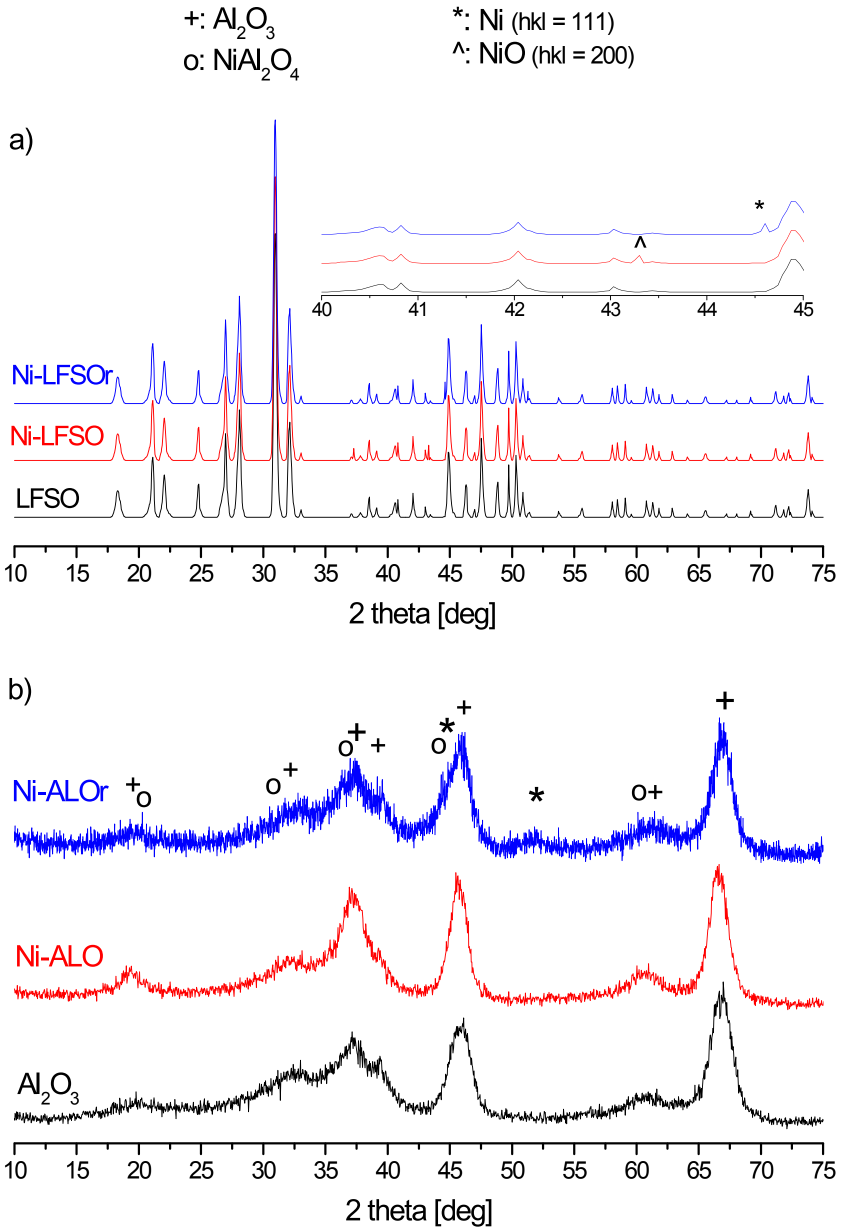

Figure 1S. XRD for a) LFSO, Ni-LFSO, Ni-LFSOr (top), and b) ALO, Ni-ALO, Ni- ALOr (bottom) samples

Materials’ Properties

Table 1S. Materials properties

Material/Catalyst	SSA ($m^2 g^{-1}$)	Ni^0 wt%	Ni^0 species (nm)*
LFSO	<2	-	-
ALO	281	-	-
Ni-LFSO	<2	5.03	105
Ni-ALO	195	4.99	13

* calculated by Scherrer Equation calculated from (111) plane

Thermogravimetric results

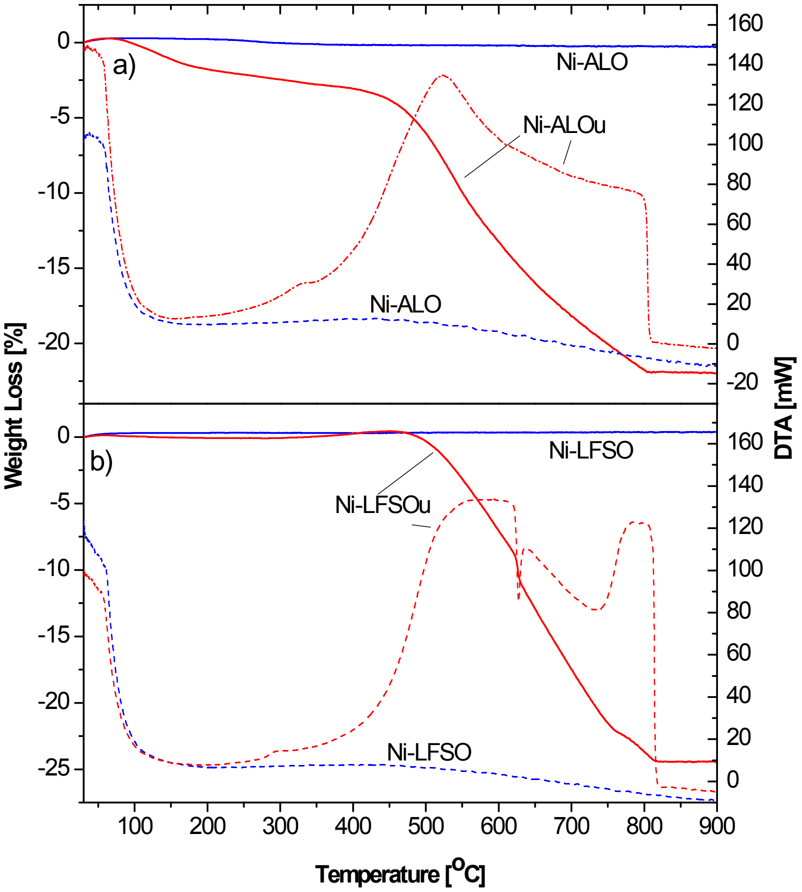

Figure 2S. TGA-DTA results showing the decomposition profile of volatile species a) Ni-ALO (blue) and Ni-ALOu (red) and b) Ni-LFSO (blue), Ni-LFSOu (red) samples. TGA: Solid lines; DTA: dashed lines.

SEM Results

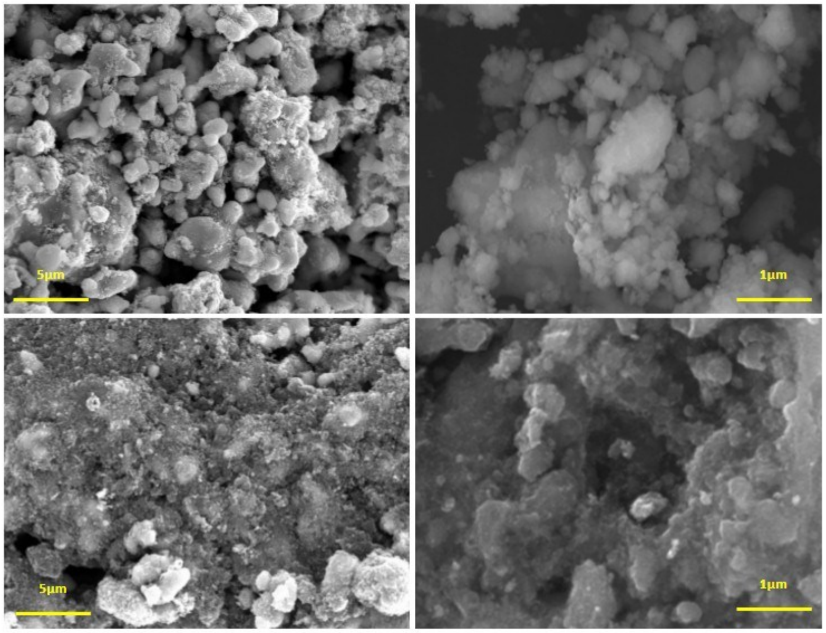

Figure 3S. SEM images of the microstructure of Ni-LFSO (top left), Ni-LFSOu (bottom left), Ni-ALO (top right) and Ni-ALOu (bottom right) samples

Catalytic experiments

Catalytic performance was studied in a fixed bed reactor in order to investigate the effect of the reaction temperature on (i) glycerol conversion, (ii) glycerol conversion into gaseous products, (iii) hydrogen yield and selectivity, (iv) H_2/CO molar ratio, and (v) gas and liquid products selectivity or concentration of the produced gas mixtures at the outlet of the reactor. The catalytic samples after the GSR testing are noted as Ni-LFSOu, (–u: used). ATLS Ni free supports were also tested for comparison purposes.

The glycerol steam reforming reaction was carried out at atmospheric pressure, in a continuous flow, fixed-bed, single pass, tubular stainless steel reactor, with an inner diameter of 14 mm, at temperature ranging from 400-750^{o}C (Fig. 4S). The experimental set up used allowed the feeding of both liquid and gaseous streams, having two vaporizers and a pre-heater before the reactor and a condenser after it. The vaporizers, pre-heater and reactor were placed into electrical ovens and regulated with programmed-temperature controllers. Prior to catalytic testing, 200 mg of undiluted catalyst (the catalyst bed was supported by quartz wool) was reduced in situ under a flow of 100 v/v % hydrogen (100 mL min^{-1}) at 800 ^{o}C for 1 h. The catalyst was then purged with helium for 45 min, the temperature was lowered to 750 ^{o}C and the reaction feed was introduced into the catalyst bed. In order to ensure operation at steady state conditions, the catalyst was left for approximately 50 minutes at each step. Liquid products were obtained at the end of this 50 min period.

The reaction feed consisted of the liquid stream - an aqueous solution of 20:80 wt. % $C_3H_8O_3$ and H_2O (20:1 steam/glycerol molar ratio), with a total liquid flow rate of 0.12 mL min^{-1}, which was kept under continuous stirring at room temperature - and the gas stream (Helium 5.0, 38 mL min^{-1}). The glycerol used had 99.5% purity and was obtained from Sigma Aldrich. The water / glycerol mixture was fed with a HPLC pump (Series I) into the evaporator and was first vaporized at 350 ^{o}C before it was mixed with helium. To prevent overpressure phenomena, pressure controllers were placed before and after the inlet and outlet gas, respectively. The gas feed at the reactor's inlet consisted of a gas mixture of 73% H_2O, 4% glycerol and 23% helium, corresponding to a Weight Hourly Space Velocity (WHSV) of 50,000 mL g^{-1} h^{-1}.

The reactor's outlet gases passed through a cold trap for liquid products capture. The gaseous products were analyzed on-line by a gas chromatographer (Agilent 7890A), with two columns in parallel, HP-Plot-Q (19095-Q04, 30 m length, 0.530 mm I.D.) and HP-Molesieve (19095P-MSO, 30 m length, 0.530 mm I.D.), equipped with TCD and FID detectors. Liquid products were analyzed via a combination of Gas Chromatography (Agilent 7890A, with a 5MS column, equipped with an FID detector) and Mass Spectroscopy (Agilent 5975C).

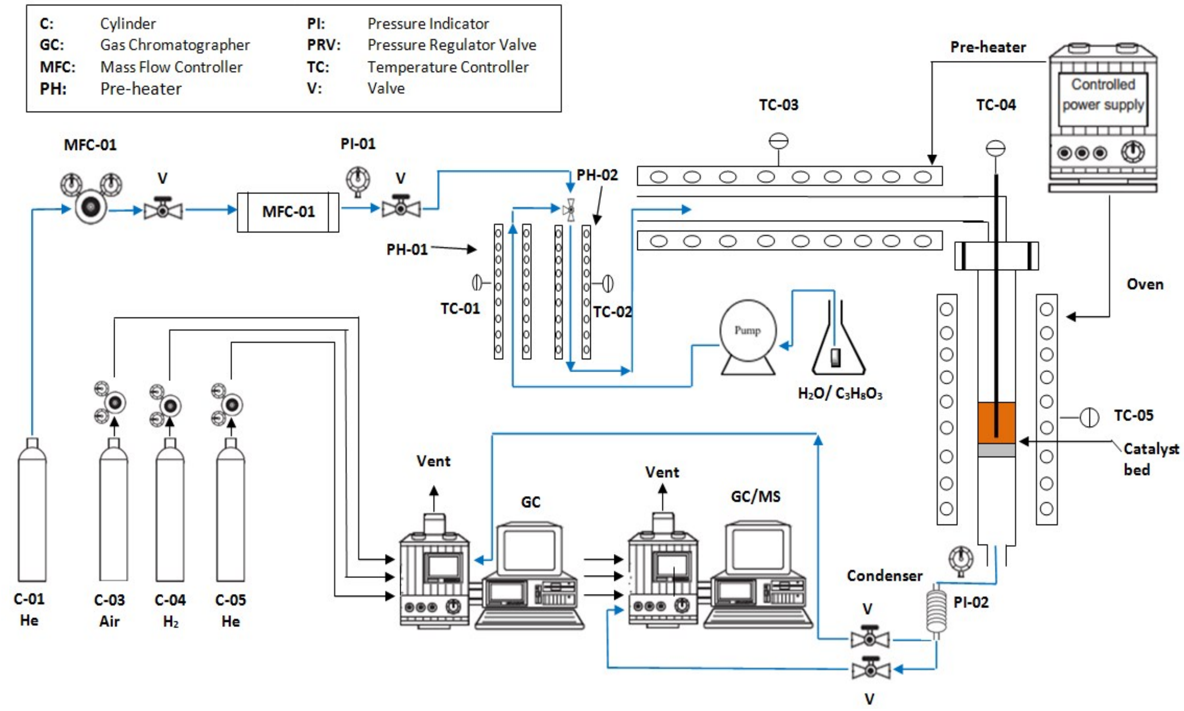

Figure 4S. Experimental Setup

Equations used for calculations

The performance of the catalysts in the gas phase is reported in terms of H_2 yield, H_2, CO, CH_4 and CO_2 selectivity, glycerol conversion into gaseous products, and total glycerol conversion (global conversion). Moreover, the performance of the catalysts in the liquid phase is reported in terms of acetol ($C_3H_6O_2$), acetone [$(CH_3)_2CO$], allyl alcohol ($CH_2=CHCH_2OH$), acetaldehyde (C_2H_4O) and acetic acid (C_2H_4O) selectivity. Performance parameters were calculated based on the following equations:

$$\%glycerol\ conversion_{(global\ conversion)} = \left(\frac{Glycerol_{in} - Glycerol_{out}}{Glycerol_{in}}\right) \times 100 \qquad \text{[Eq.1S]}$$

$$\%glycerol\ conversion_{(gaseous\ products)} = \left(\frac{C\ atoms\ in\ the\ gas\ products}{total\ C\ atoms\ in\ the\ feedstock}\right) \times 100 \qquad \text{[Eq.2S]}$$

$$H_2\ yield = \frac{H_2\ moles\ produced}{moles\ of\ glycerol\ in\ the\ feedstock} \qquad \text{[Eq.3S]}$$

$$\%H_2\ selectivity = \left(\frac{H_2\ moles\ produced}{C\ atoms\ produced\ in\ the\ gas\ phase}\right)\times\left(\frac{1}{RR}\right)\times 100 \qquad \text{[Eq.4S]}$$

where, RR is the Reforming Ratio (7/3), defined as the ratio of moles of H_2 to CO_2 formed.

$$\%\ selectivity\ of\ i = \left(\frac{C\ atoms\ in\ species\ i}{C\ atoms\ produced\ in\ the\ gas\ phase}\right)\times 100 \qquad \text{[Eq.5S]}$$

where, species i refers to CO, CO_2 and CH_4.

$$\%\ selectivity\ of\ i' = \left(\frac{C\ atoms\ in\ species\ i'}{C\ atoms\ produced\ in\ the\ liquid\ phase}\right)\times 100 \qquad \text{[Eq.6S]}$$

where, species i' refers to acetol, acetone, allyl alcohol, acetaldehyde and acetic acid.

Reaction Pathways

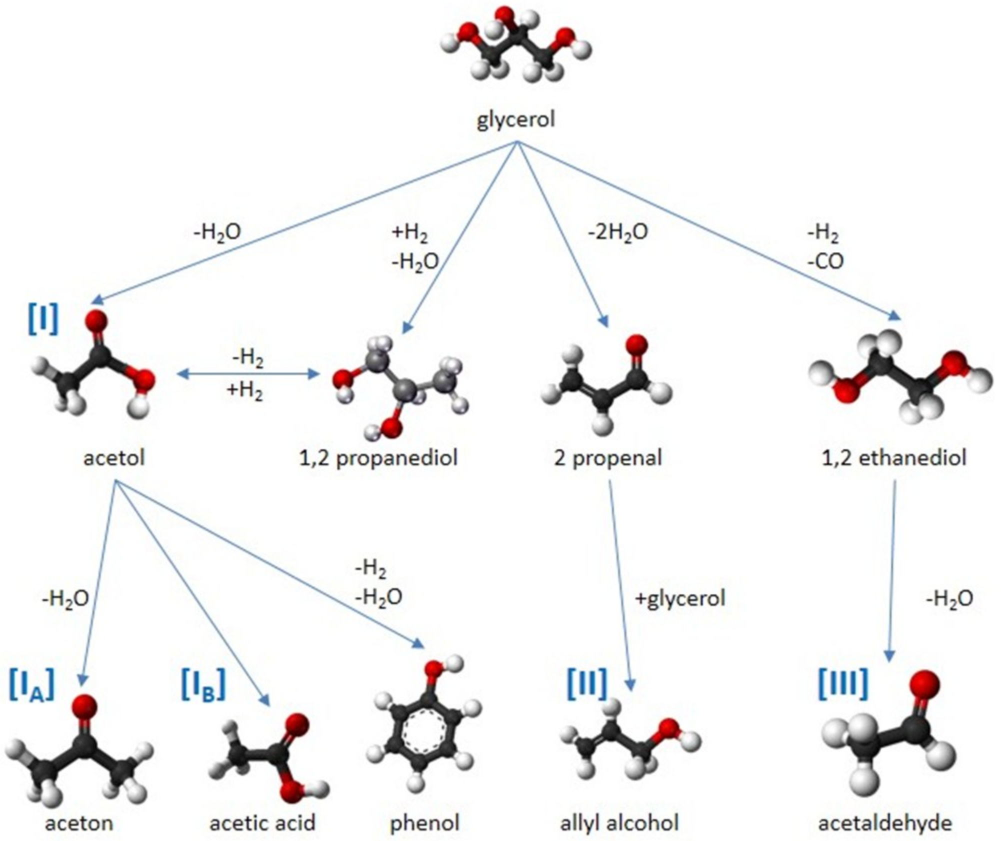

Figure 5S. GSR reaction pathways [I], [I_A], [I_B] [II], [III]

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