Supporting Information

Oxidation of Acid-Whey Derived Glucose-Galactose Syrup to Gluconic and Galactonic Acid with Selective Precipitation

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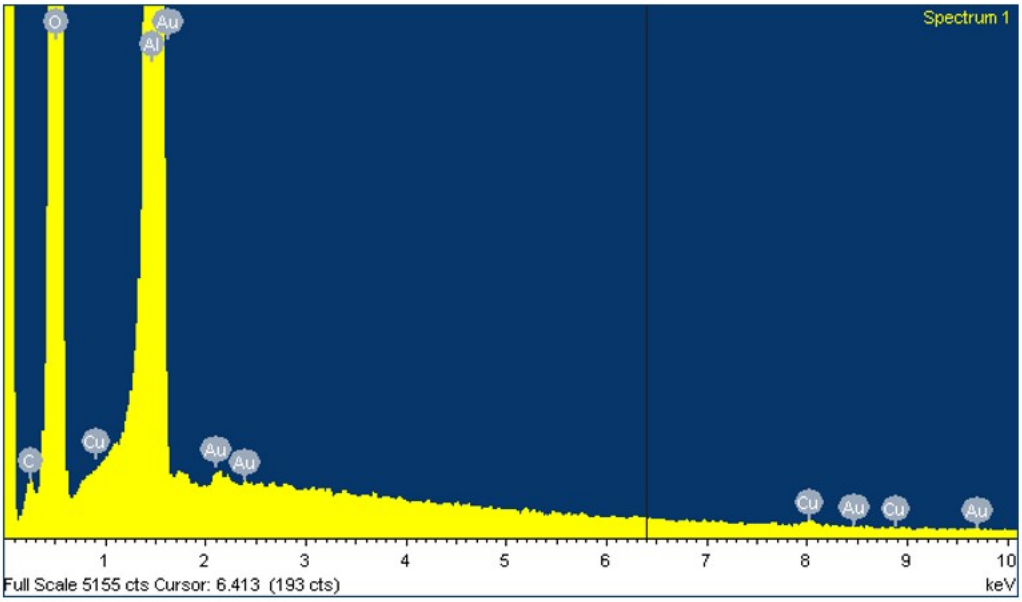


Figure S1 EDS Spectrum of Au/Al_2O_3 measured on Oxford INCA 350 energy-dispersive X-ray microanalysis system

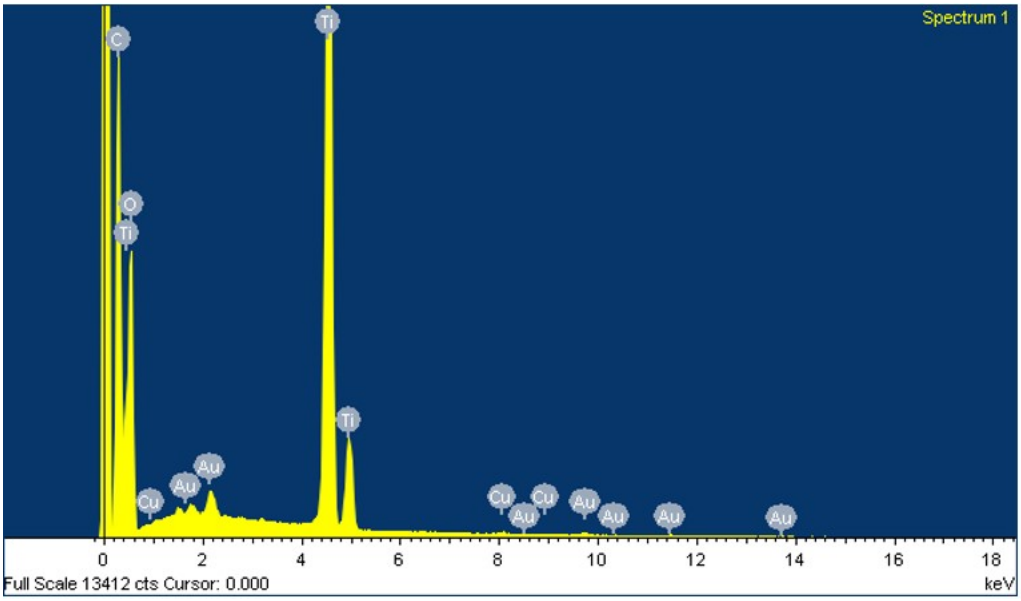


Figure S2 EDS Spectrum of Au/TiO_2 measured on Oxford INCA 350 energy-dispersive X-ray microanalysis system

General Oxidation Experimental Procedure

A simulation feed of the GGS syrup was prepared in situ to ensure that accurate quantifications could be obtained, 90mg glucose, 90mg galactose, 30mg of lactose and 18mg of the selected catalyst were loaded into the 45mL Parr reactor with 10 mL of water added. If O_2 was the required oxidant the reactor was purged 3 times before charging to desired pressure, if H_2O_2 was used then a N_2 atmosphere was obtained by purging in an identical manner. The reaction temperature was raised to 80°C as under constant heating power and then maintained for the desired reaction time. After completion the reaction was cooled then returned to atmospheric pressure. The reaction mixture was centrifuged to separate catalyst and a sample was obtained for HPLC analysis. Standard of sodium gluconate (>99% purity, TCI Chemicals), D-galactonic acid calcium salt (99% purity, Sigma Aldrich) and calcium D-saccharate tetra-hydrate (98.5% purity, Sigma Aldrich) were passed through an ion-exchanger to acidify before creating an external calibration curve for quantifying gluconic, galactonic and glucaric acid in the product mixtures.

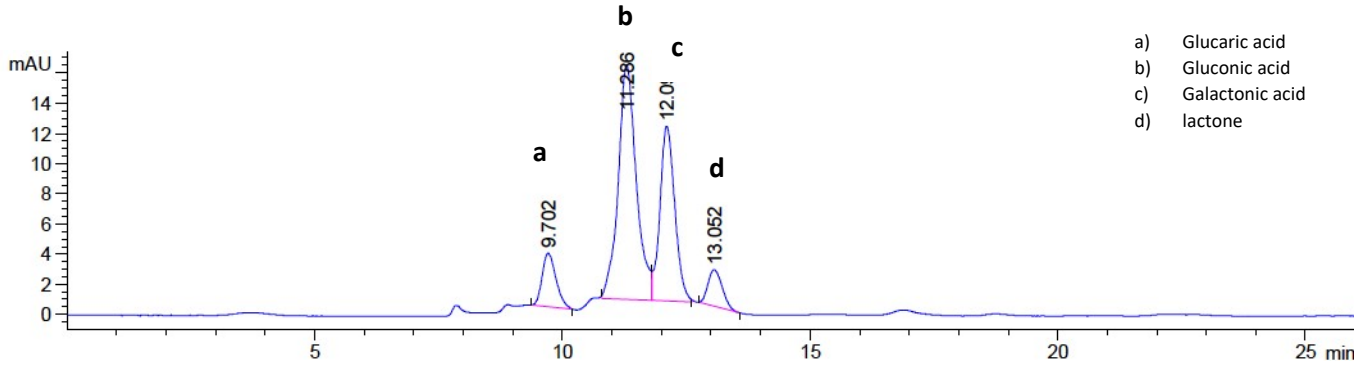


Figure S3 Sample HPLC Chromatogram of GGS oxidation reaction mixture using the UV Detector (210nm).

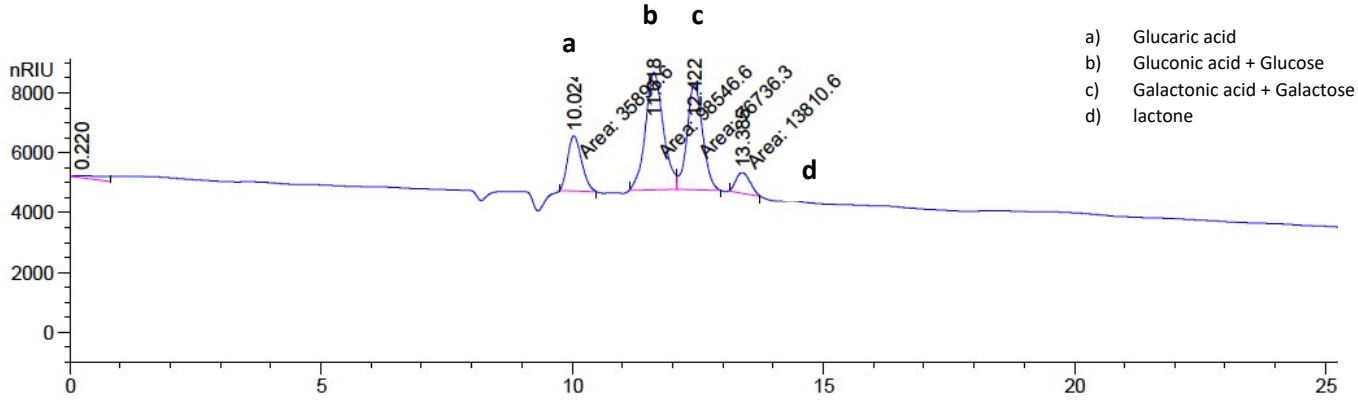


Figure S4 HPLC Chromatogram of GGS oxidation reaction mixture using the RID Detector (Positive Mode)

$$Conversion\ of\ glucose: \frac{mol\ of\ glucose\ in\ GGS\ solution}{mol\ of\ glucose\ in\ product\ mixture} \times 100 \quad \textbf{(1)}$$

$$Conversion\ of\ galactose: \frac{mol\ of\ galactose\ in\ GGS\ solution}{mol\ of\ galactose\ in\ product\ mixture} \times 100 \quad \textbf{(2)}$$

$$Selectivity\ of\ Gluconic\ Acid: \frac{mol\ of\ glucose\ converted\ in\ GGS}{mol\ of\ gluconic\ acid\ in\ product\ mixture} \times 100 \quad \textbf{(3)}$$

$$Selectivity\ of\ Galactonic\ Acid: \frac{mol\ of\ galactose\ covnerted\ in\ GGS}{mol\ of\ galactonic\ in\ product\ mixture} \times 100 \quad \textbf{(4)}$$

Table S1 Yields and Conversions for Oxidation of GGS using H_2O_2 and O_2 as oxidant. . Reaction Conditions: 90mg Glucose, 90mg Galactose, 30mg Lactose, 18mg Catalyst, 10mL H_2O at 80°C for 24hr

Oxidant	Gluconic Acid Yield / %	Galactonic Acid Yield / %	Glucaric Acid Yield / %	Glucose Conversion / %	Galactose Conversion / %
H_2O_2 (4 Equiv)	66%	51%	7%	96%	92%
O_2 (2.5 bar)	71%	52%	7%	98%	95%

Oxidant	Mass Glucose Converted / mg	Mass Galactose Converted / mg	Mass of Gluconic Acid / mg	Mass of Galactonic Acid / mg	Mass of Glucaric Acid / mg	Total Mass of Products / mg
H_2O_2 (4 Equiv)	88.6	82.0	66.5	50.2	7.2	124.0
O_2 (2.5bar)	88.5	88.5	70.0	53.0	7.7	130.8

Table S2 Mass of Products for Oxidation of GGS using H_2O_2 and O_2 as oxidants. Reaction Conditions: 90mg Glucose, 90mg Galactose, 30mg Lactose, 18mg Catalyst, 10mL H2O at 80°C for 24hr

Catalyst	Dispersion / %	Time / hr	Temperature / °C	Conversion / %	TOF / h^{-1}
Au/Al_2O_3	16	24	80	96%	285.4
Au/TiO_2	16	24	80	98%	65.3

Table S3 Turnover Frequencies for Prepared Catalysts. Reaction Conditions: 90mg Glucose, 90mg Galactose, 30mg Lactose, 18mg Catalyst, 10mL H2O

$$TOF = \frac{n_{car} \times conv.}{n_{Au} \times D_{Au} \times t} \quad \textbf{(5)}$$

Where n_{car} is total moles of carbohydrate, $conv.$ is conversion of reaction, n_{Au} is the total number of Au moles calculated from weight percentage and mass of catalyst, D_{Au} is the dispersion of Au on the support[1], and t is the time of reaction.

The dispersion was calculated from the particle size distribution for the prepared catalysts and allowed for the turnover frequency (TOF) to be calculated accordingly to the formula 5[1]. For Au/Al_2O_3 it had an increased TOF compared to Au/TiO_2 which is logical as the calculated loading was lower (1 wt% for Au/Al_2O_3 and 3 wt% for Au/TiO_2), marking it as a more efficient catalyst.

Figure S6 Effects of H2O2 Equivalents with respect to carbohydrates glucose and galactose and the selectivity towards gluconic and galactonic acid on the conversion of galactonic acid. Reaction Conditions: 90mg Glucose, 90mg Galactose, 30mg Lactose, 18mg Catalyst, 10mL H_2O at 80°C for 6hr

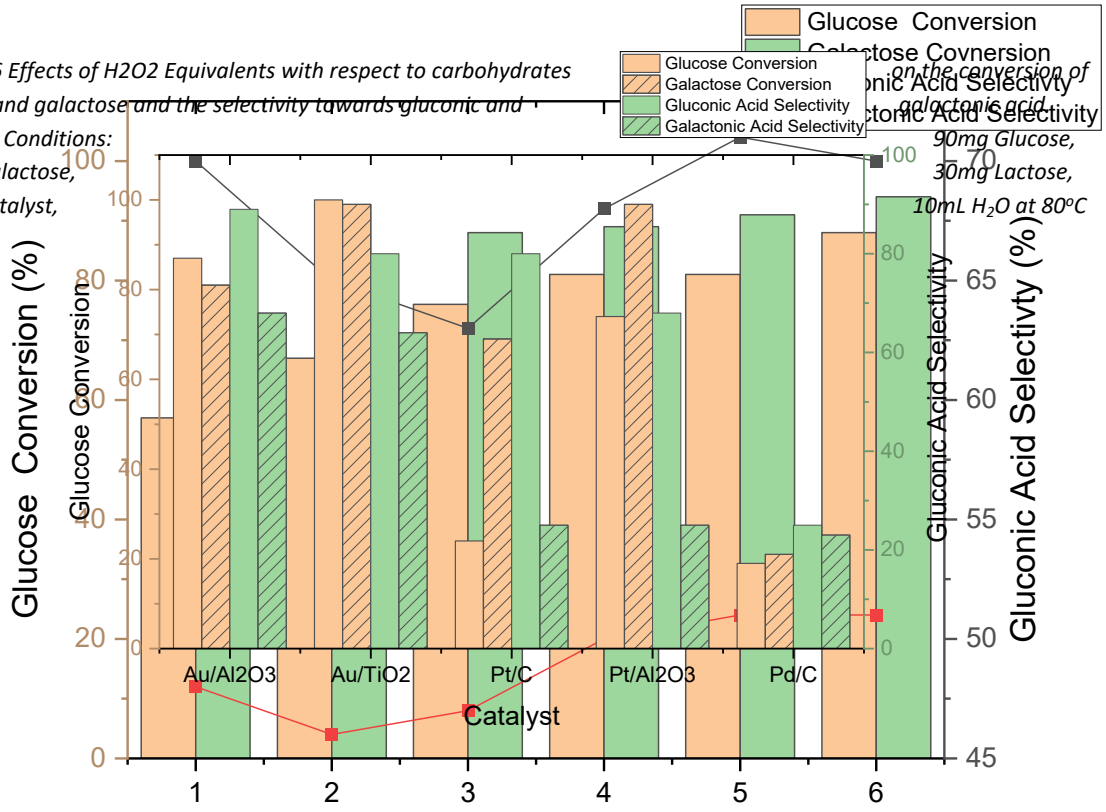


Figure S5 Effect of catalyst on the conversion of glucose and galactose and the selectivity to gluconic and galactonic acid using O_2 as oxidant. Reaction Conditions: 90mg Glucose, 90mg Galactose, 30mg Lactose, 18mg Catalyst, 10mL H_2O with 5.0 bar O_2 at 80°C for 24hr

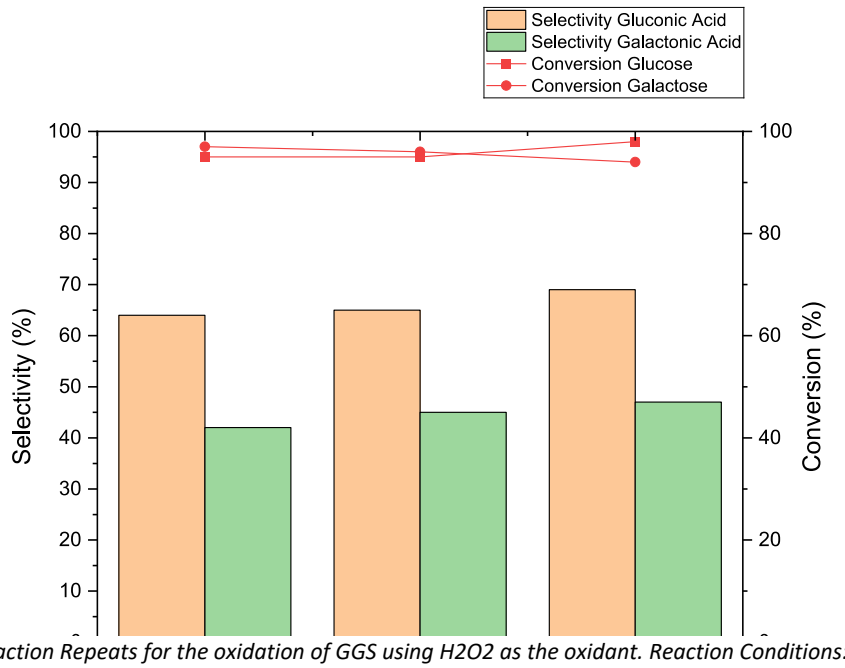


Figure S7 Reaction Repeats for the oxidation of GGS using H2O2 as the oxidant. Reaction Conditions: 90mg Glucose, 90mg Galactose, 30mg Lactose, 18mg Catalyst,4 equiv. H_2O_2, 10mL H_2O at 80°C for 6hr

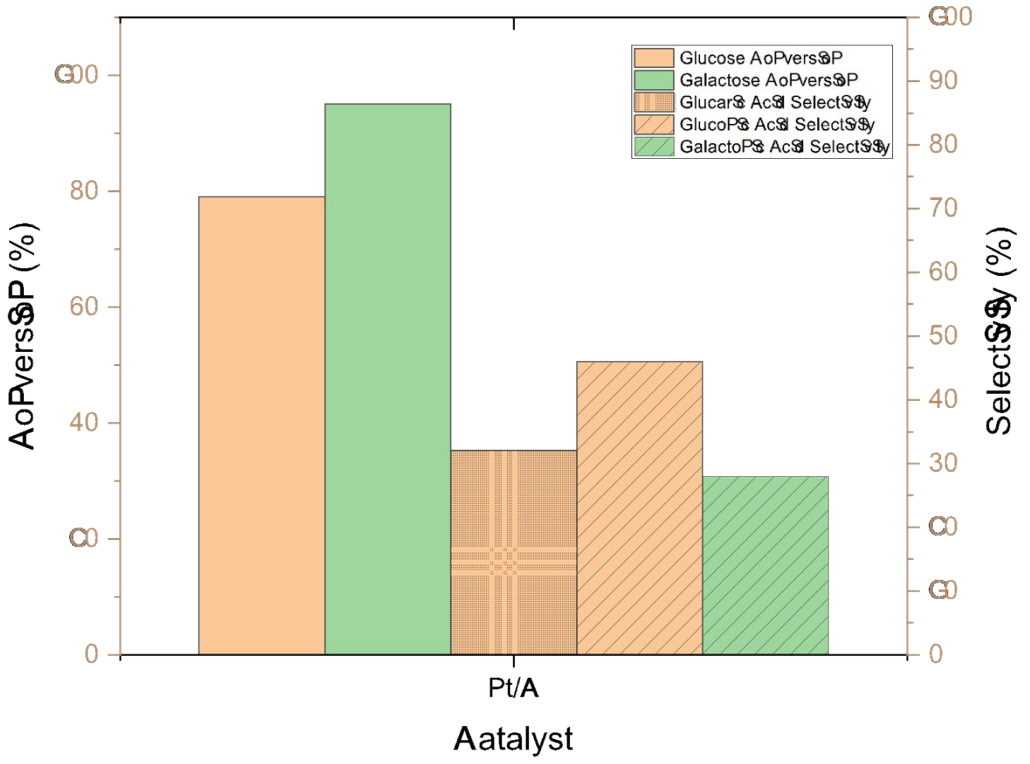


Figure S8 Reaction products when using Pt/C as catalyst. Reaction Conditions: 90mg Glucose, 90mg Galactose, 30mg Lactose, 18mg Catalyst Pt/C, 10mL H_2O with 5.0 bar O_2 at 80°C for 24hr

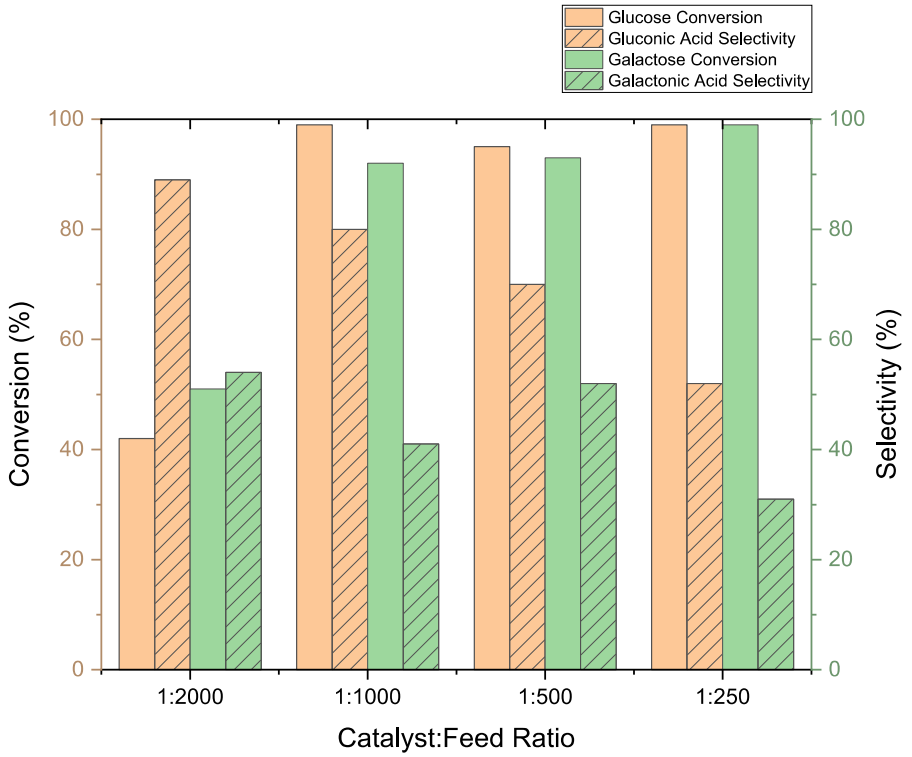


Figure S9 Effect of catalyst:feed on the conversion of glucose and galactose and the selectivity to gluconic and galactonic acid using O_2 as oxidant. Reaction Conditions: 90mg Glucose, 90mg Galactose, 30mg Lactose, 18mg Catalyst, 10mL H_2O with 5.0 bar O_2 at 80°C for 24hr

Table S4 Influence of Catalyst:Feed to the carbon balance and carbon loss of the oxidation of GGS. Reaction Conditions:

Catalyst:Feed	TOTAL C mmol	Total Carbon Mass / mg	Total Carbon ppm	Carbon Balance / %	Recorded C ppm	Total C ppm	% Lost
1:1000	5.23	62.81	6611.71	0.79	84.15	8415.00	0.12
1:500	5.28	63.39	6672.41	0.85	78.42	7842.00	0.18
1:250	3.84	46.12	4854.54	0.67	72.34	7234.00	0.23

90mg Glucose, 90mg Galactose, 30mg Lactose, 18mg Catalyst, 10mL H_2O with 5.0 bar O_2 at 80°C for 24hr

Effect of Al_2O_3 Particle size

When trying to assess the influence of the catalyst support, various particle size Al_2O_3 were sampled for catalyst preparation and their respective activity for the oxidation of GGS. The influence of particle size to conversion and selectivity of GGS are summarised in Table S2. The trend observed was increasing particle size decreases the selectivity to desired products. The particle size will influence the Au particle size as well as the accessibility and structure of the active site for substrates to enter. In addition, the surface area also decreases which may explain the observed reduction in conversion, the surface area intuitively decreases as particle size of support increases.

Al_2O_3 Particle Size (nm)	Glucose Conversion (%)	Galactose Conversion (%)	Selectivity Gluconic Acid (%)	Selectivity Galactonic Acid (%)
20	46	33	75	56
40	48	53	46	32
300	42	36	46	52

Table S5 Influence of Al2O3 Support Particle Size on the conversion & selectivity of GGS oxidations

Separation of GGS oxidation reaction products procedure

After oxidation is completed, the resulting mixture is centrifuged at 5000rpm for 5 mins to separate the solid catalyst from solution where it is recovered. 5 equivalents of $CaCO_3$ are added to the solution and stirred for 2 hrs to form calcium gluconate and calcium galactonate. The slurry is then filtered to remove excess $CaCO_3$. The resulting aqueous solution is evaporated under reduced pressure with the addition of EtOH to promote water removal. Once minimal volume is reached, 200mL EtOH is added to precipitate the calcium carboxylate salts which are recovered by filtration. ^{1}H NMR (400mHz D_2O) is used to establish the ratio of ca-gluconate:ca-galactonate (Figure S11). The salt mixture is then dissolved in minimal H_2O before adding 20mg ca-galactonate to aide crystallisation and cooling to 0^{o}C and allowing to precipitate overnight. The resulting precipitate is ca-galactonate with >99% purity and in solution remains ca-gluconate with minimal ca-galactonate impurities. To recover the ca-gluconate, the solvent amount is reduced before adding EtOH to precipitate out the salts. The purity is then assessed by ^{1}H NMR (Figure S12), with ca-gluconate exhibiting 86% purity with the major impurity being ca-galactonate. Ca-galactonate: ^{1}H NMR (400 MHz, D2O): δ 4.31–4.26 (m, 1H), 4.02–3.94 (m, 2H), 3.74–3.68 (m, 2H), 3.68–3.62 (m, 1H). Ca-gluconate: ^{1}H NMR (400 MHz, D2O): δ 4.19 (d, J = 3.4 Hz, 1H), 4.11–4.05 (m, 1H), 3.87–3.73 (m, 3H), 3.73–3.61 (m, 1H).

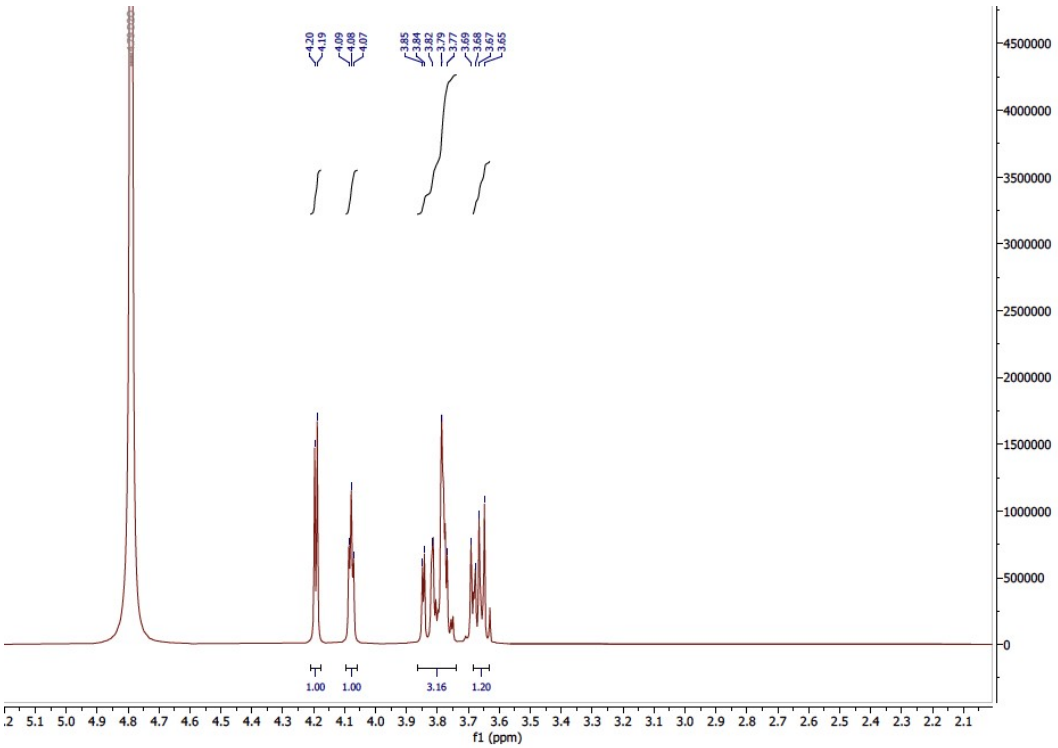


Figure S10 ^{1}H NMR (400 mHz D_2O) of Ca-gluconate standard

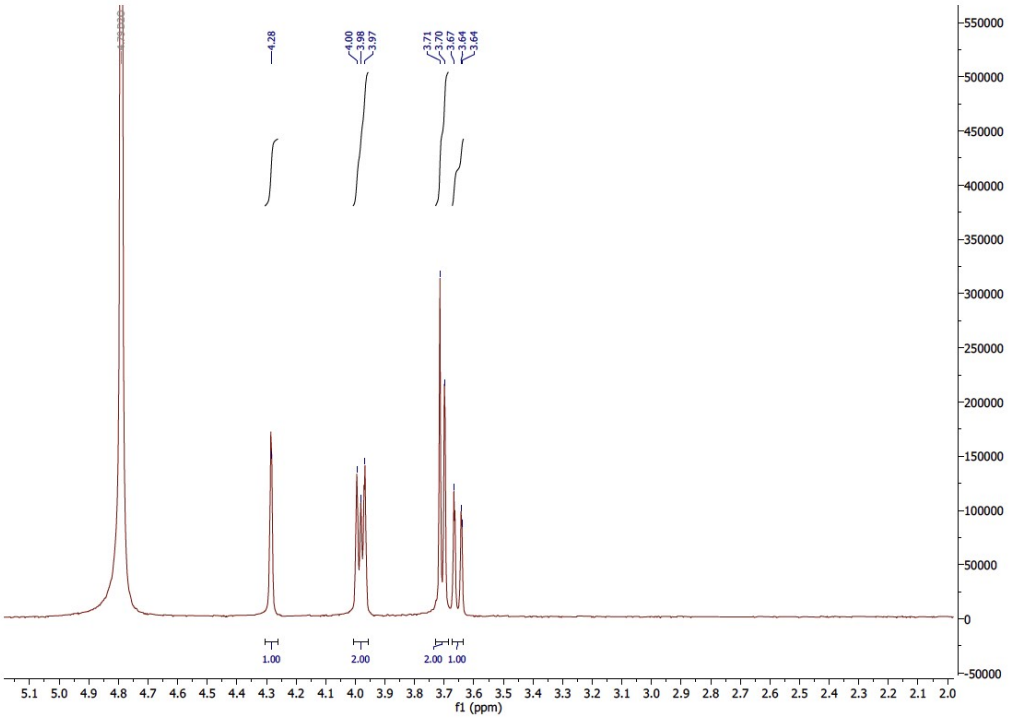


Figure S11 ^{1}H NMR (400 mHz D_2O) of Ca-galactonate standard

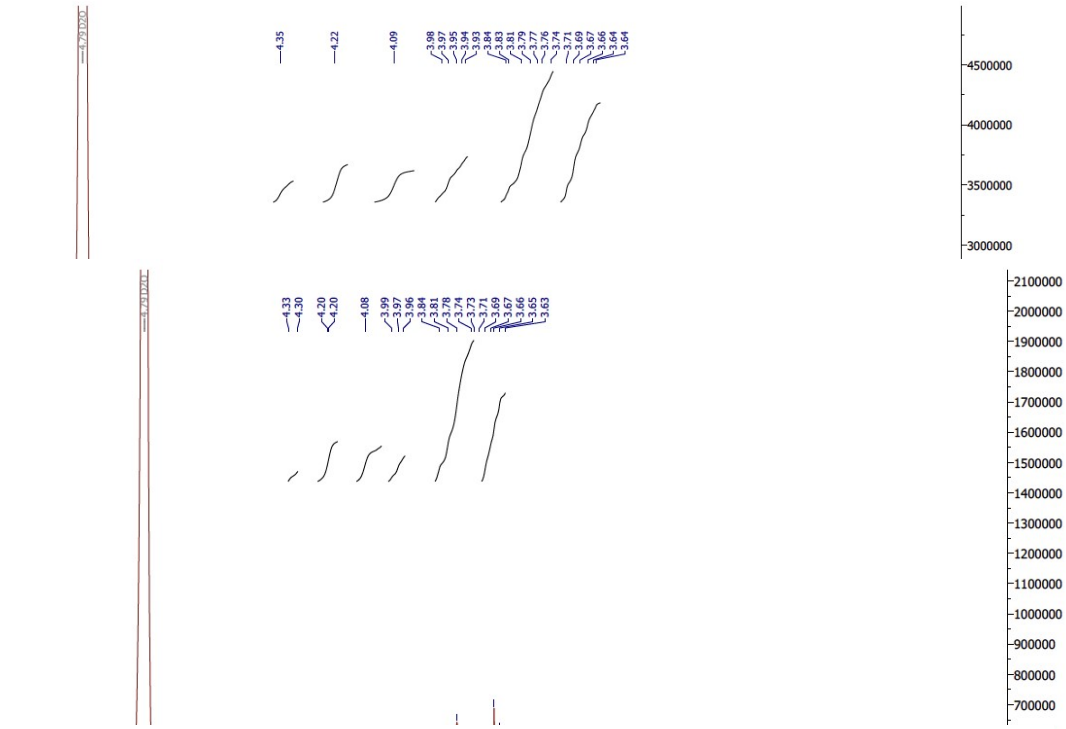
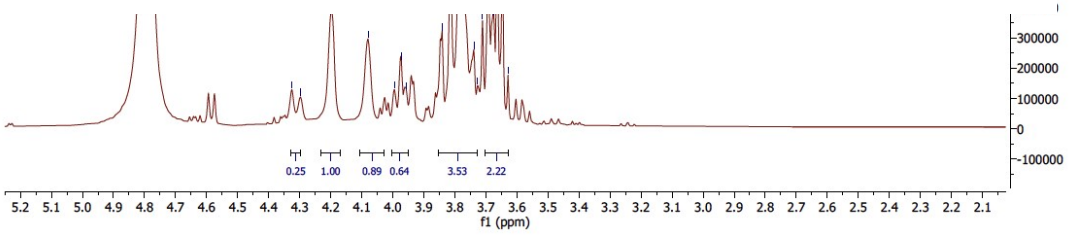


Figure S12 ^{1}H NMR (400 mHz D_2O) of salt mixture of Ca-gluconate and Ca after initial precipitation from reaction mixture



References

1 I. V. Delidovich, B. L. Moroz, O. P. Taran, N. V. Gromov, P. A. Pyrjaev, I. P. Prosvirin, V. I. Bukhtiyarov and V. N. Parmon, *Chemical Engineering Journal*, 2013, **223**, 921–931.