

## Supporting Information

### **The oxidative esterification of glycerol to methyl glycerate in methanol using gold on oxidic supports: An insight in product selectivity**

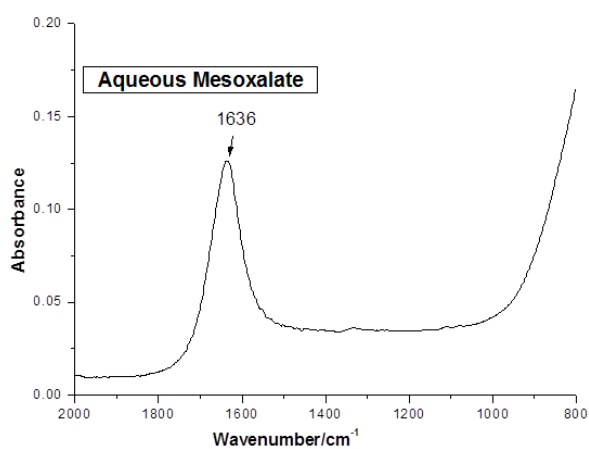
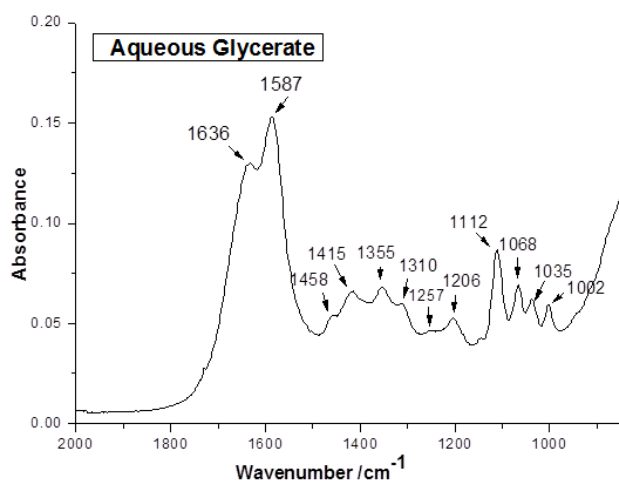
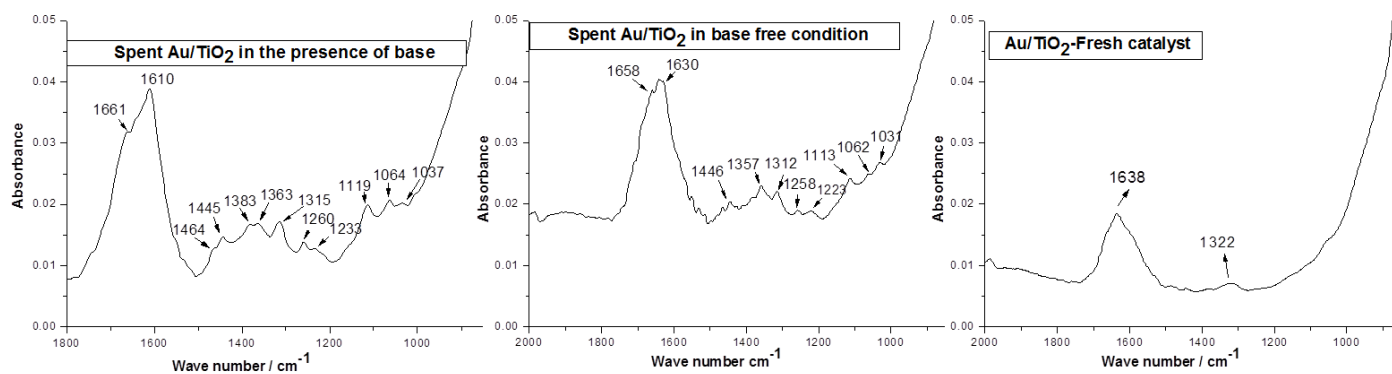
**Rajeesh Kumar Pazhavelikkakath Purushothaman, J. van Haveren, D.S. van Es, I. Melian Cabrera and H.J. Heeres**

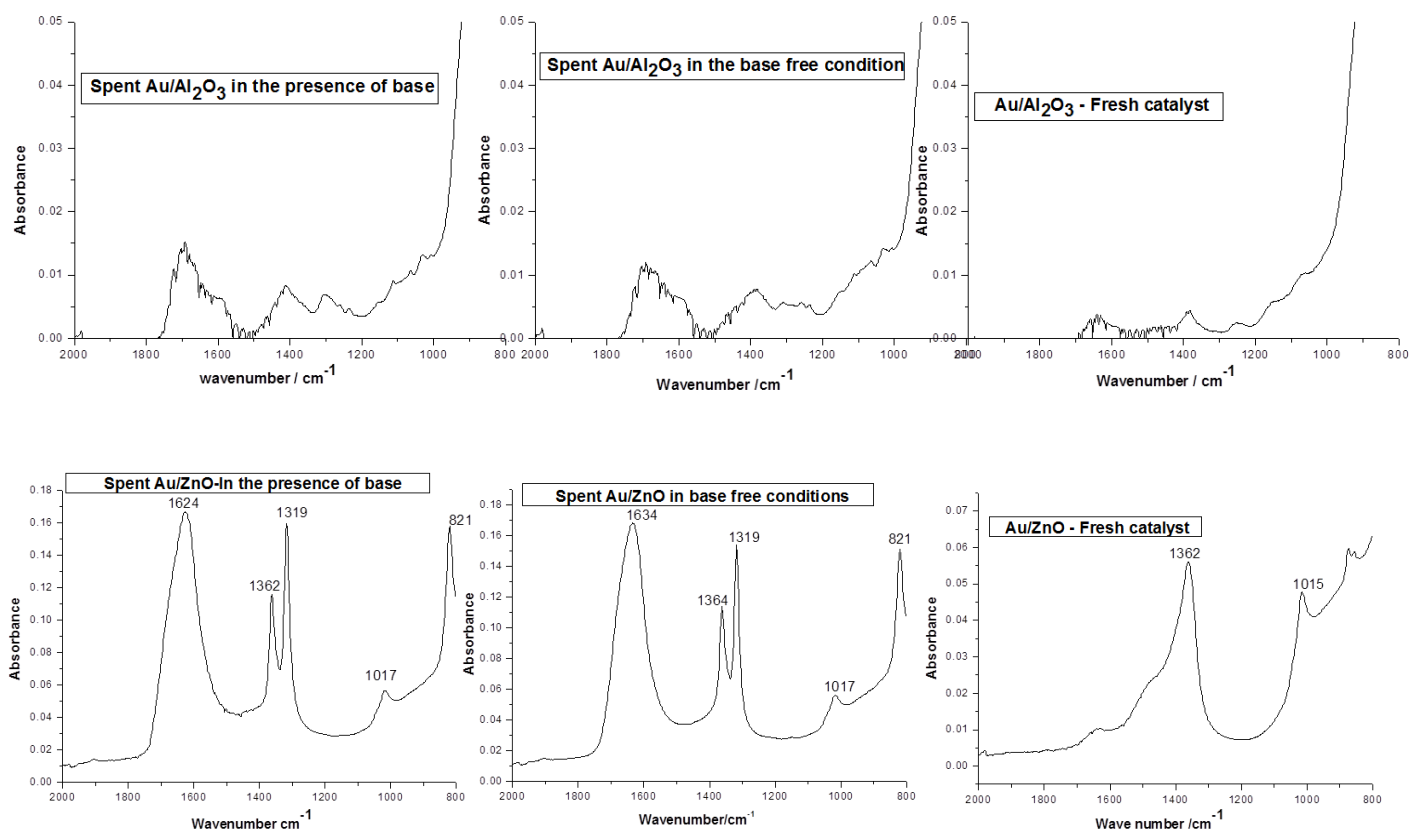
#### **FT-IR measurements on fresh and spent catalysts**

Fourier transform infrared (FT-IR) spectra were obtained on a Varian Scimitar 1000 FT-IR spectrometer equipped with a Pike MIRacle ATR Diamond/ZnSe single reflection plate and a DTGS-detector. The measurement resolution was set at 4 cm<sup>-1</sup>, and the spectra were collected in the range 4000–650 cm<sup>-1</sup> with 64 co-added scans

The spent catalysts were separated by filtration and washed several times with methanol under vacuum. Prior to analyses, the catalysts were dried in a vacuum oven at 50° C for 20 h in the presence of desiccant.

All spectra are provided in Figure S1.

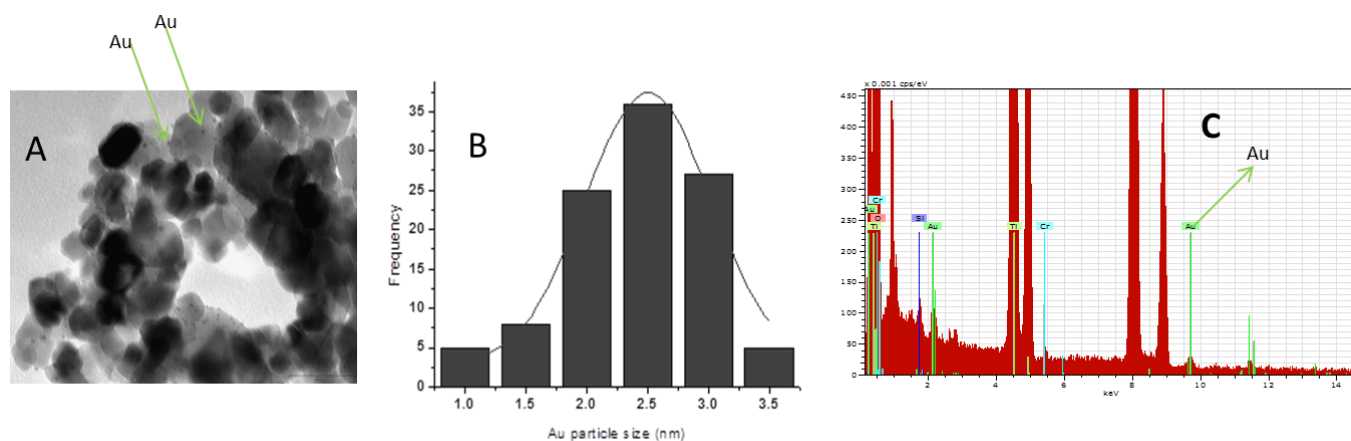




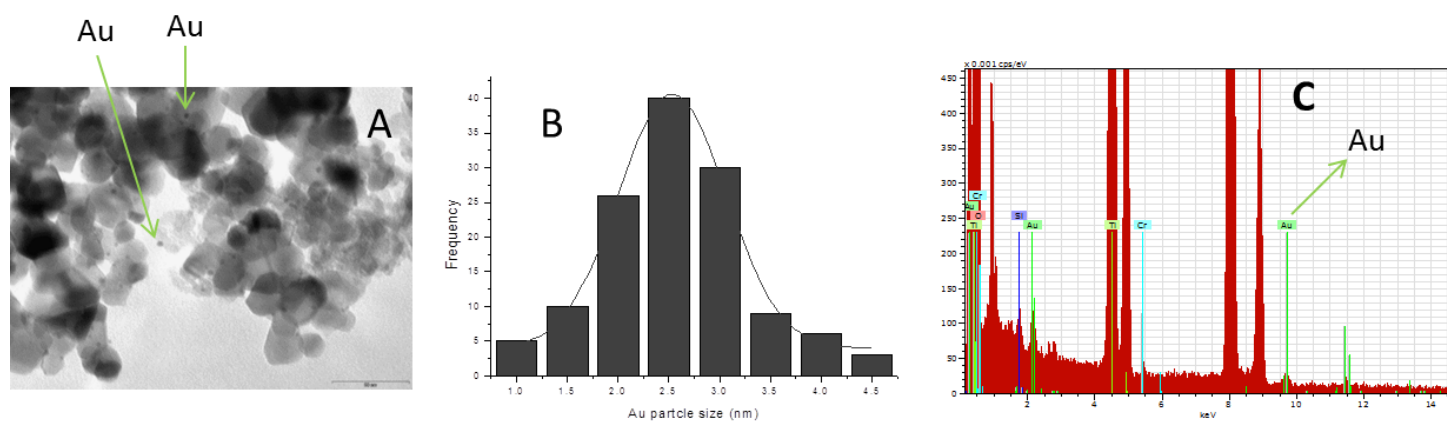
**Figure S1.** FT-IR spectra

### TEM measurements

Transmission Electron Microscopy (TEM) images of the fresh and spent Au/TiO<sub>2</sub> catalyst are given in Figure S2 (Fresh catalyst) and Figure S3 (Spent catalyst, used in the presence of base).



**Figure S2.** (A) TEM image of Au/TiO<sub>2</sub> (Fresh). Scale is 50nm (B) Particle size distribution (C) Representative EDAX spectra taken for a single Au particle



**Figure S3.** TEM image of Au/TiO<sub>2</sub> (Spent) . Scale is 50nm (B) Particle size distribution (c) Representative EDAX spectra taken for a single Au particle

### Recycle studies using the Au/TiO<sub>2</sub> catalyst

After an oxidation experiment (30 h), the Au/TiO<sub>2</sub> catalyst was recovered by filtration under vacuum and washed several times with methanol. Then the catalyst was suspended in methanol-water (200 mL, 1:1 ratio) and heated to 80° C at stirring for 5 h. The catalyst was recovered by a vacuum filtration, washed with methanol several times and dried under vacuum at 323 K in the presence of a desiccant (Phosphorous pentoxide, Sigma-Aldrich) for 20 h. This recycled catalyst was tested for the oxidative esterification of glycerol in the presence of base (Table S1).

**Table S1.** Oxidative esterification of glycerol over Au/TiO<sub>2</sub> catalysts in the presence of 10 mol% base on glycerol

Time (h)	Glycerol conversion (%)	Selectivity (%)						Carbon mass balance closure (%)
		GLA/DHA	MGLY	DMT	DMM	MPYR	MGLYC	
5	45	9	71	2	6	2	2	93
30	69	2	81	0.5	10	1	0.5	95

Reaction conditions: Glycerol: methanol = 1:99, Glycerol/metal = 153, T = 353 K, P (O<sub>2</sub>) = 5 bar

Both fresh and spent catalyst were characterised by TEM, physisorption using nitrogen and ICP-OES. TEM showed no significant sintering of Au particles whereas changes in the Au content (ICP-OES) and the BET surface area are limited (Table S2).

**Table S2.** Characterisation of the Au/TiO<sub>2</sub> catalysts (fresh and spent)

Catalyst	Condition	Au (wt%)	BET, m <sup>2</sup> /g	Pore volume (PV), cm <sup>3</sup> /g	Micropore volume, cm <sup>3</sup> /g	Average pore size (4·PV/BET), nm
Au/TiO <sub>2</sub>	Fresh	1.2	50	0.352	below detection	28.1
Au/TiO <sub>2</sub>	Spent, base	1.1	52	0.320	below detection	24.7
Au/TiO <sub>2</sub>	Spent, base free	1.2	47	0.306	below detection	25.8