ELECTRONIC SUPPLEMENTARY INFORMATION

A reusable magnetic nanocatalyst for bio-fuel additives: The ultrasound-assisted synthesis of solketal

Kalyani Rajkumari,[a] Bishwajit Changmai,[a] Ananta Kumar Meher,[a] Chhangte Vanlalveni,[b] Putla Sudarsanam,[c] Andrew E. H. Wheatley,*[d] Samuel Lalthazuala Rokhum*[a,d]

[a]Department of Chemistry, National Institute of Technology Silchar, Assam-788010, India

[b]Department of Botany, Mizoram University, Tanhril, Aizawl, Mizoram, 796001, India

[c]Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr Homi Bhabha Road, Pune 411008, India

[d]Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

*Corresponding authors. Tel.: +91 3842 242915; fax: +91 3842-224797; Email address: aehw2@cam.ac.uk (AEHW); lr512@cam.ac.uk, rokhum@che.nits.ac.in (SLR)

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1. XPS survey spectrum of FSS MNP catalyst

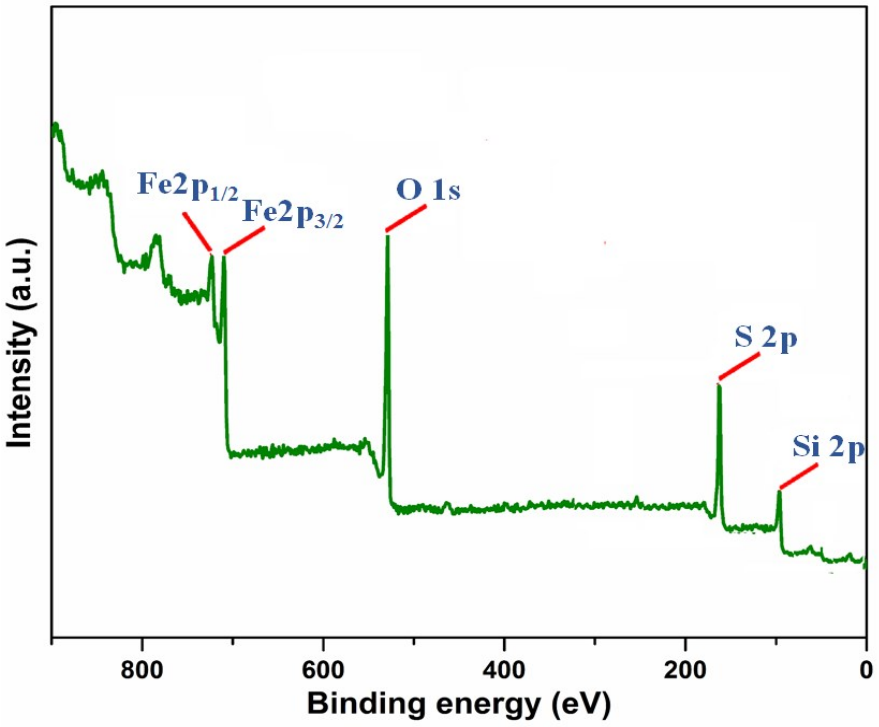


Figure S1: XPS survey spectrum of FSS MNPs.

2. Analytical data for the product of glycerol acetalization by FSS MNP catalyst

In the ^{1}H NMR spectrum of the product of glycerol acetalization (Figure S2a) the two distinct singlets at δ 1.38 and δ 1.45 refer to the six methyl hydrogens of 1,3-dioxolane product while the broad singlet peak for hydroxyl appears at δ 1.75. Peaks in the region δ 3.58-4.28 have a total integration of five and represent the –C*H*$_2$ and –C*H* groups present in the product structure. The ^{13}C NMR spectrum of the solketal product is shown in Figure S2b. The most shielded peaks, at δ 25.3 and δ 26.7, are due to the methyl carbons. The peak at δ 76.1 is due to the –*C*H carbon and the other two peaks at δ 65.6 and 63.0 refer to the two –*C*H$_2$ carbons. The most deshielded peak, at δ 109.4, is due to the ketal carbon. These two spectra clearly provide evidence for the formation of 5-membered solketal product,[1] pointing to it being the sole product, of glycerol acetalization. The absence of NMR peaks due to the previously reported six-membered acetal (2,2-dimethyl-1,3-dioxan-5-ol) argue against the competitive formation of the corresponding 6-membered acetal ring in the reaction.[2] ^{1}H and $\{^{1}H\}^{13}C$ NMR spectra recorded on Bruker Avance II, 400 MHz

spectrometer at 28 °C. Deuterated solvent stored over molecular sieves (3 Å). Chemical shifts (δ ppm) internally referenced to deuterated solvent and calculated relative to TMS.

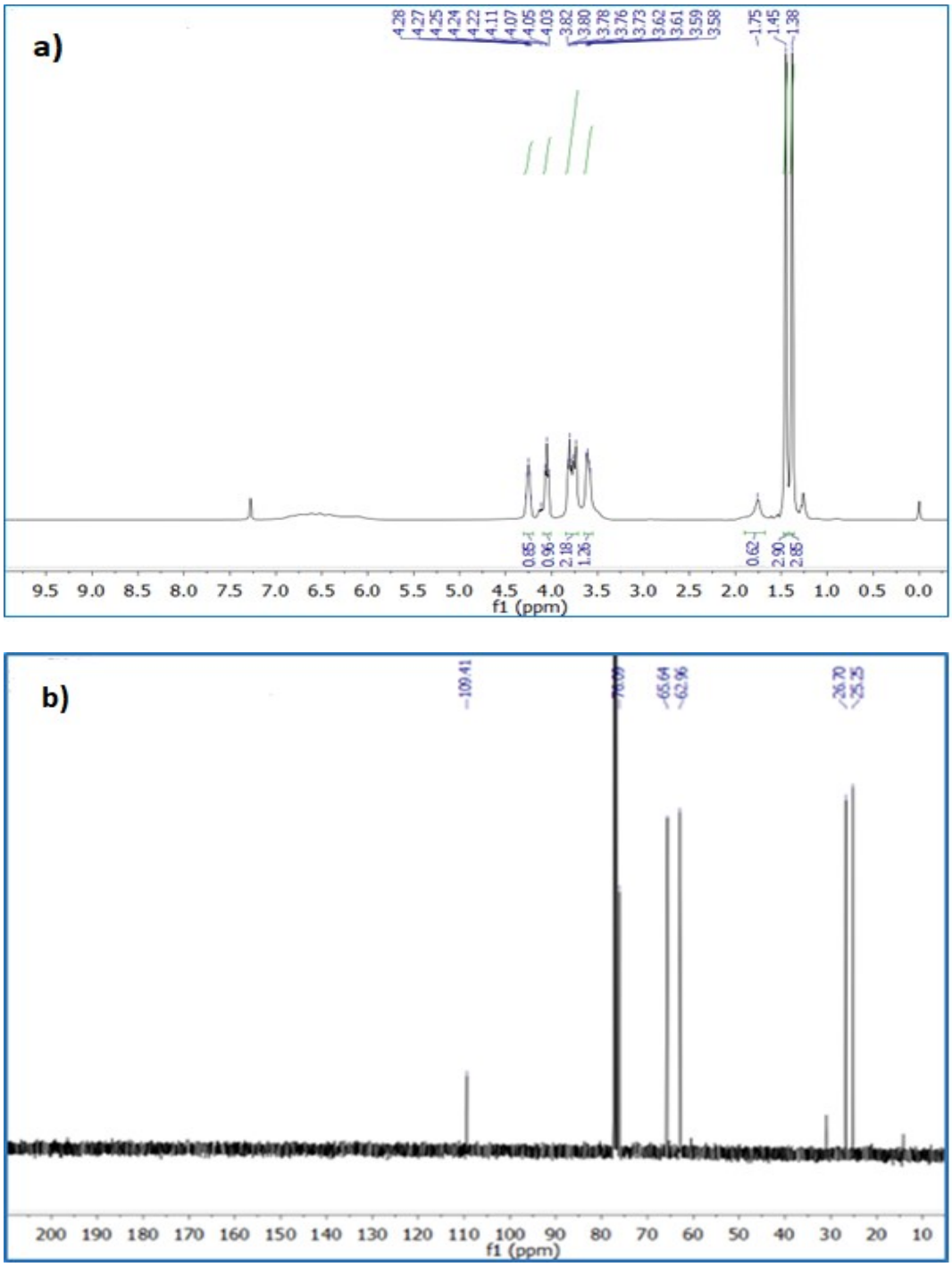


Figure S2: (a) ^{1}H NMR (400 MHz) and (b) $\{^{1}H\}^{13}C$ NMR (100 MHz) spectra in $CDCl_3$ of the product of glycerol acetalization using FSS MNP catalyst.

GC data recorded on an Agilent 7890 fitted with head-space injector mode, a CPSIL 8CB capillary column (30 m × 0.25 mm × 0.25 μm) and GC FID detector. Initial oven temperature 55 °C. This was increased to 230 °C at 10 °C min^{-1}. Temperature of detector and the injector were 300 °C and 250 °C, respectively. Biphenyl used as internal standard.

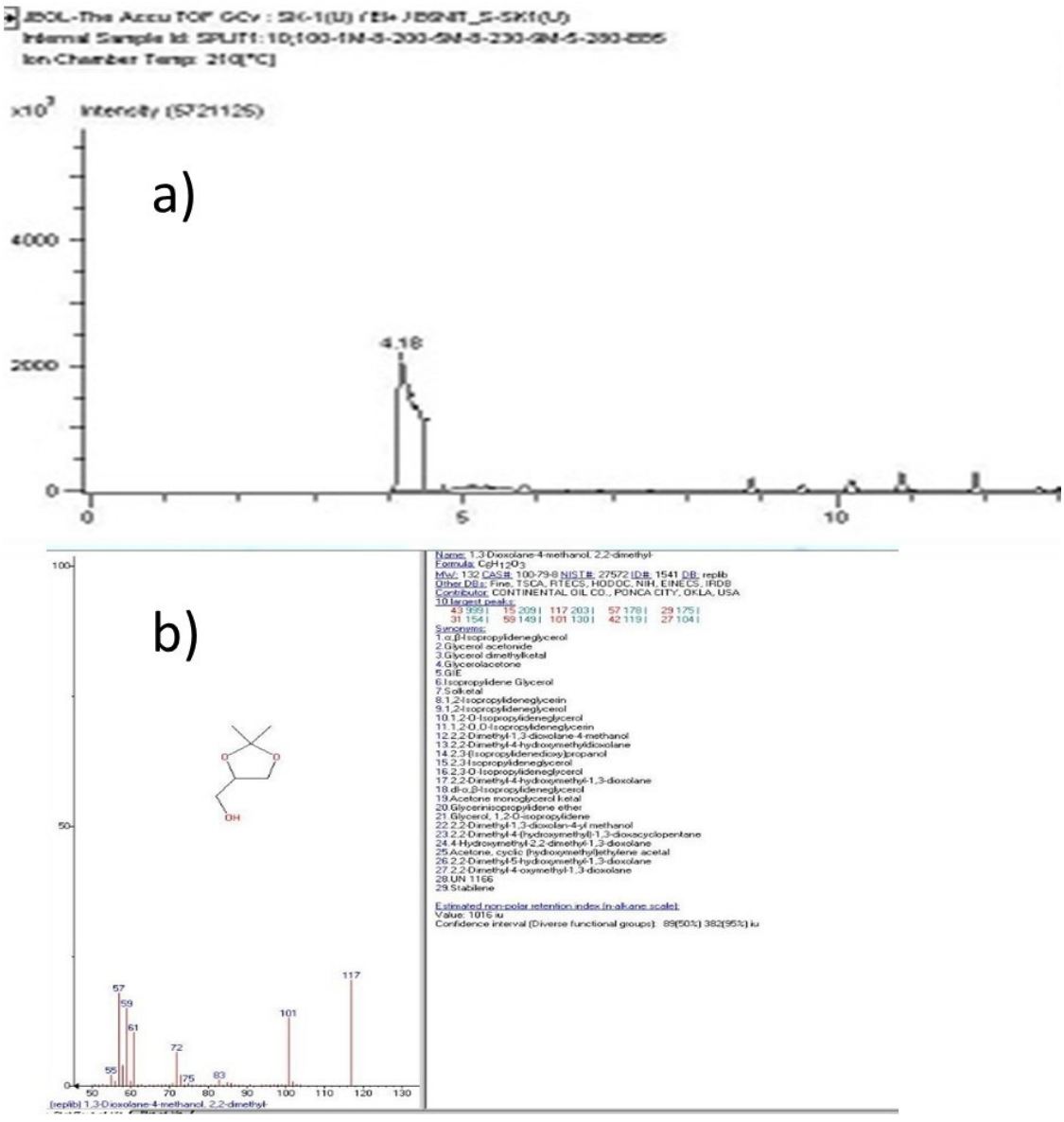
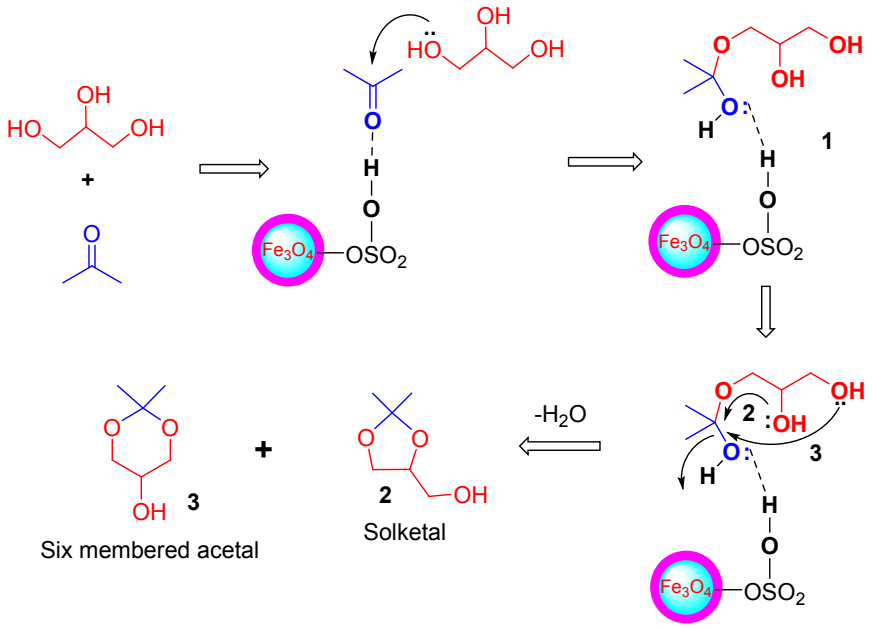


Figure S3: a) GC data for synthesized solketal revealing it's elution at 4.18 min. The potentially competing 6-membered cyclic acetal would be expected at 7 min. Biphenyl internal standard, oven temperature 55-230 °C, ramp rate 10 °C min^{-1}; b) MS spectra of solketal

3. Mechanism of acetalization of glycerol

The usual explanation for the selectivity of acetalization is the ketal mechanism.[2,3,4] It is suggested that in our work the first step of the reaction sees the acetone activated by the acid sites of the FSS catalyst to form **1**. This intermediate would then cyclize to form solketal **2** and/or 6-membered cyclic **3**. It is established that formation of **3** is not favorable kinetically,[3] so reaction normally prefers **2**. In our case, the selectivity for **2** over **3** is 100%, i.e. **2** is made to the complete exclusion of **3**.



Scheme S1: Proposed mechanism of acetalization of glycerol using FSS MNP catalyst.

4. Activation energy data

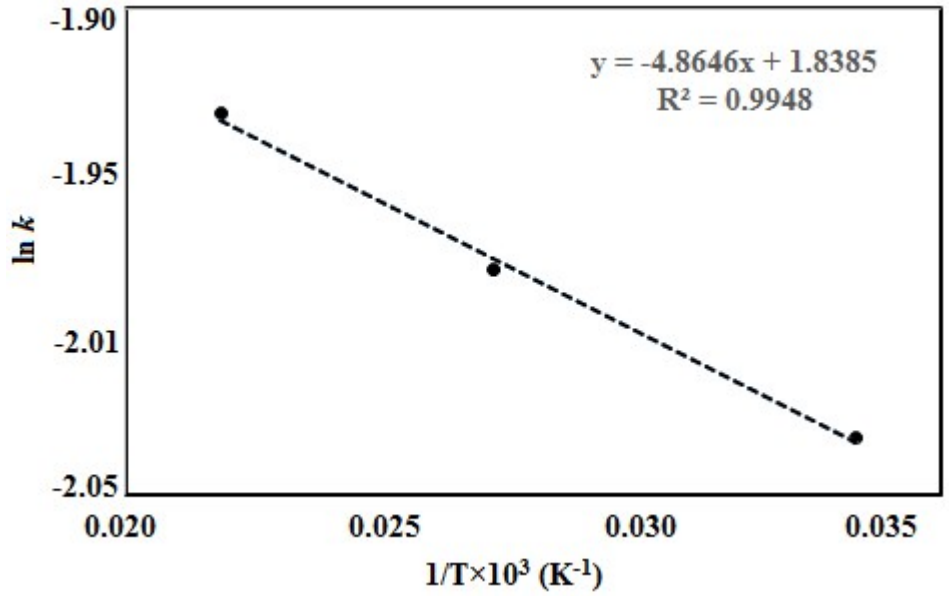


Figure S4: Plot of ln *k vs* 1/T×10^3 (K^{-1}) for the ultrasonic-assisted synthesis of solketal using FSS MNPs. Reaction conditions: 5:1 acetone/glycerol molar ratio, 2 wt. % catalyst loading, 15 min time.

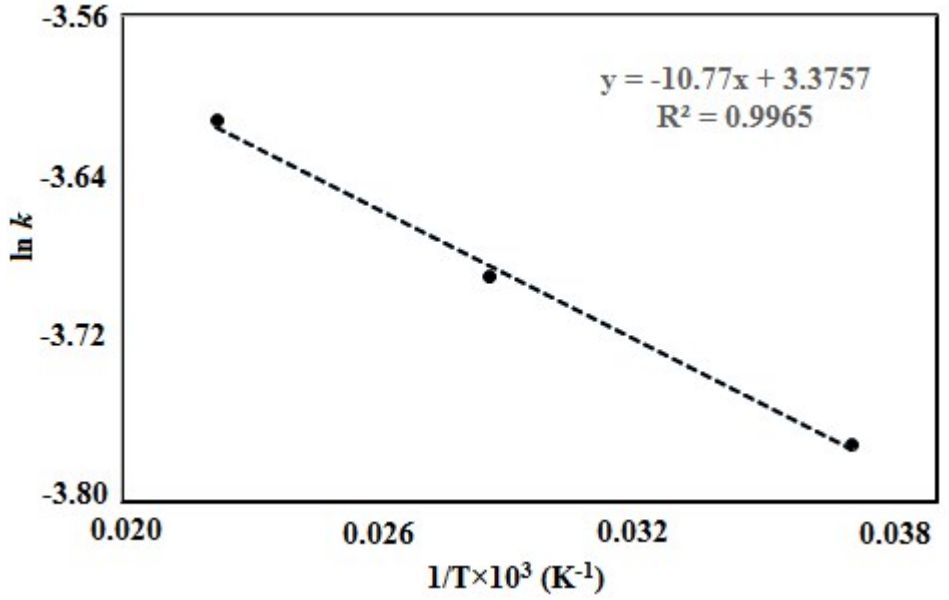


Figure S5: Plot of ln *k vs* 1/T×10^3 (K^{-1}) for the traditional synthesis of solketal using FSS MNPs. Reaction conditions: 5:1 acetone/glycerol molar ratio, 2 wt. % catalyst loading, 60 min time and 1000 rpm.

5. Procedure for the scaled-up acetalization of glycerol

The optimized glycerol acetalization (see main manuscript) was undertaken treating 20 g glycerol (217.3 mmol) and 100 g acetone (1087 mmol) with 1 g of FSS MNP catalyst. Ultrasonication for 15 mins. at 28 °C was followed by catalyst removed using magnetic separation. Centrifugation (3000 rpm for 5 min), removal of excess acetone by rotary evaporation and finally elution of the product (using 8:2 hexane-ethyl acetate solution) in a short alumina column gave solketal (with 100% selectivity) in an isolated yield of 94±1%.

6. Analysis of FSS MNP catalyst after 5 recycling experiments

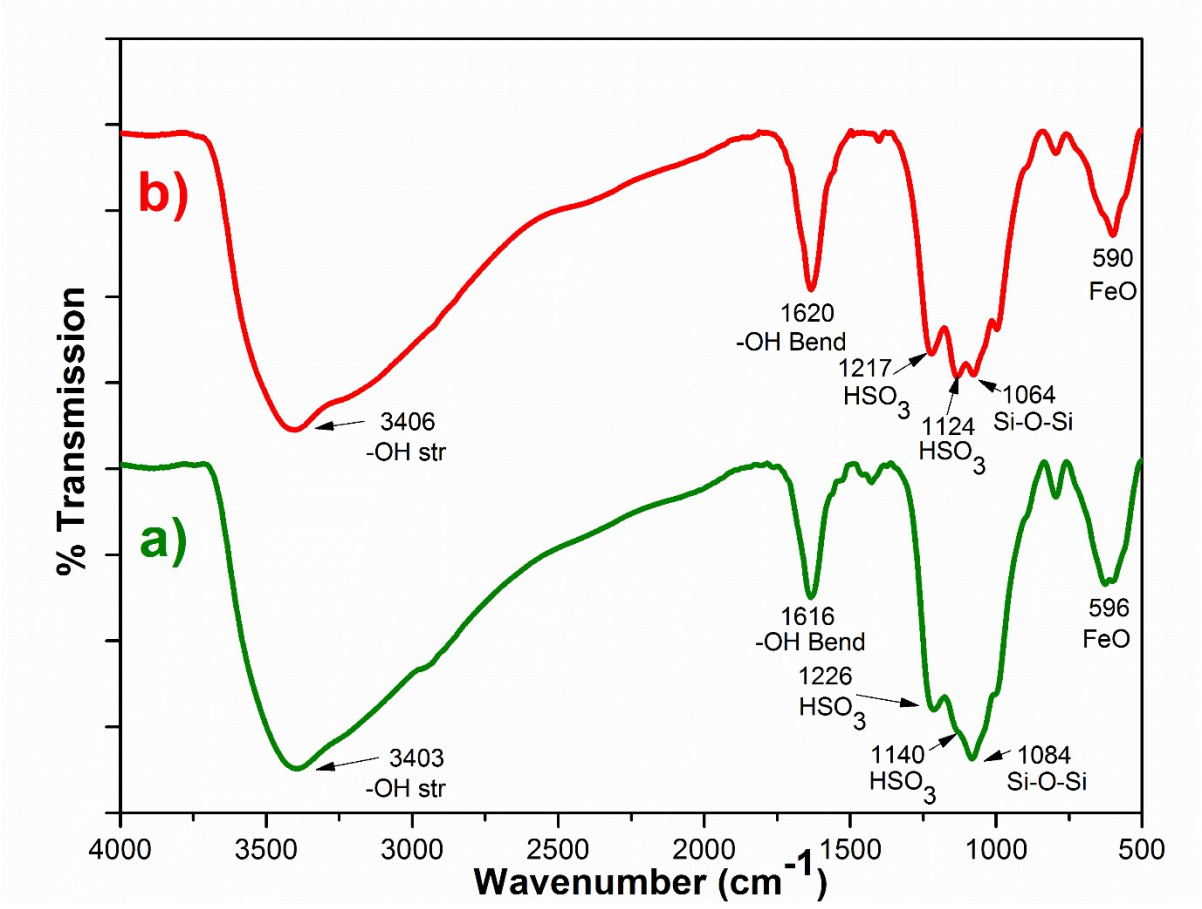


Figure S6: FTIR spectra of a) FSS MNPs recovered after 5 catalytic cycles and b) fresh FSS MNPs

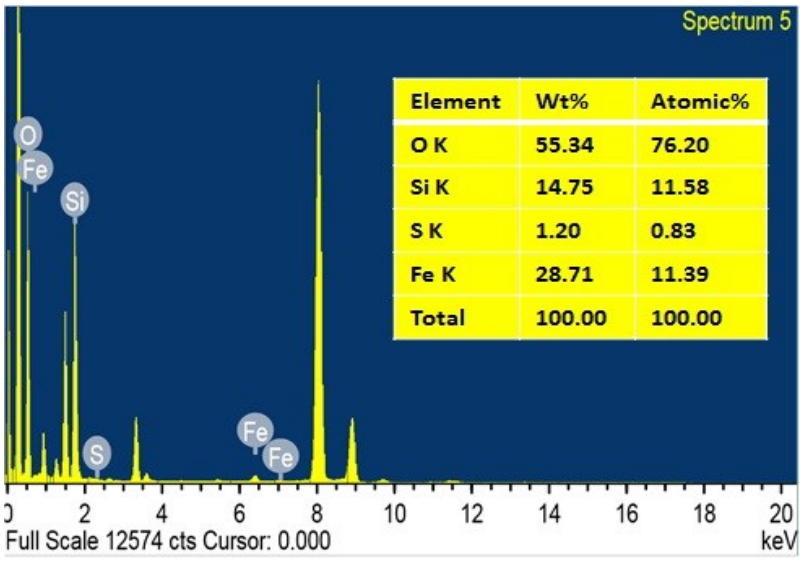


Figure S7: EDX data for FSS MNPs recovered after 5 catalytic cycles. Signals at 8.034 and 8.895 keV are due to the Cu grid

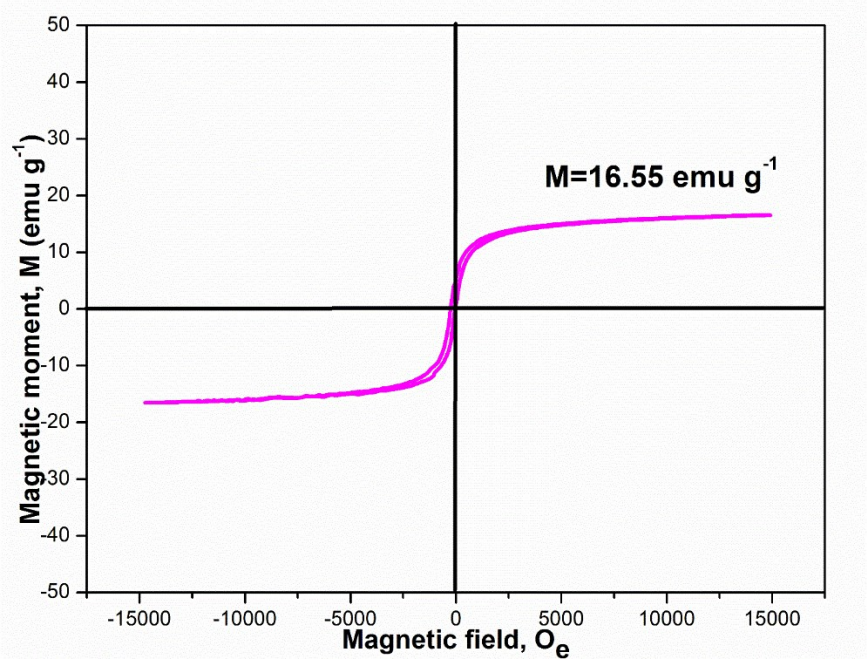


Figure S8: Room temperature magnetization curve of FSS MNPs recovered after 5 catalytic cycles

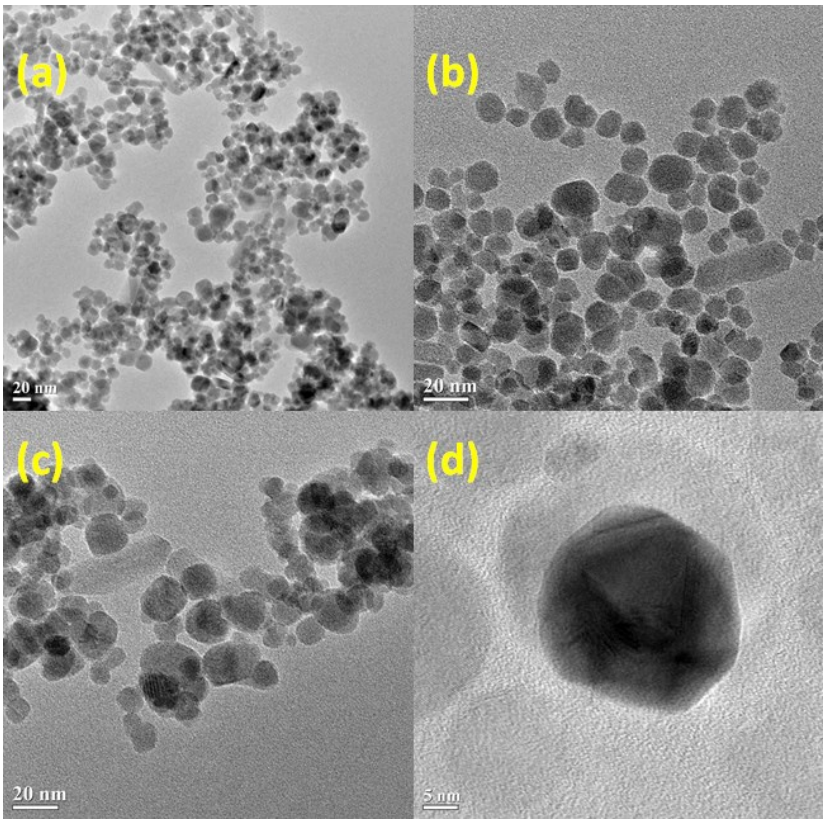


Figure S9: Representative TEM images of FSS MNPs recovered after 5 catalytic cycles. Scale bars 20 nm (a-c) and 5 nm (d)

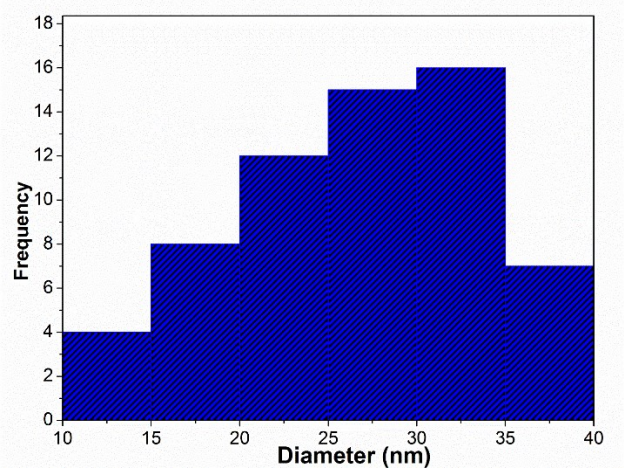


Figure S10: Particle size distribution histogram for FSS MNPs recovered after 5 catalytic cycles (N = 100)

6. Turnover number (TON) and Turnover frequency (TOF) Calculation

TOF = TON/time of reaction

$$\text{TON} = \frac{\%\ Conversion\ of\ glycerol}{(Catalyst\ wt.\%)(Molar\ mass\ glycerol)}$$

$$\text{TOF} = \frac{\%\ Conversion\ of\ glycerol}{(Time)(Catalyst\ wt.\%)(Molar\ mass\ glycerol)}$$

7. References

1. I. B. Laskar, K. Rajkumari, R. Gupta and L. Rokhum, *Energy Fuels*, 2018, **32**, 12567-12576.
2. C. Crotti, E. Farnetti and N. Guidolin, *Green Chem*., 2010, **12**, 2225-2231.
3. B. Mallesham, P. Sudarsanam, G. Raju and B. M. Reddy, *Green Chem*., 2013, **15**, 478-490.
4. A. R. Trifoi, S. P. Agachi and T. Pap, *Renewable Sustainable Energy Rev*., 2016, **62**, 804-814.