Nanocomposite γ-Ferric oxide (γ-Fe_2O_3) mediated, green, solvent free, one pot synthesis of naturally occurring acetate esters.

Chandan P. Amonkar*, Savio S. Dias, Anita S. Tilve

Department Of Chemistry, P.E.S.'s R.S.N. College of Arts & Science, Farmagudi, Ponda - Goa,

Goa, INDIA, 403401 (affiliated to Goa University, Goa, India)

Email: cpamonkar@rediffmail.com

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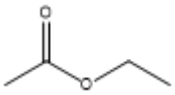
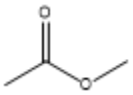
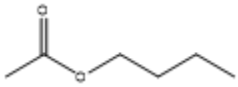
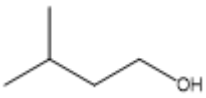
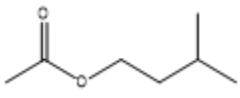
Table S1: Showing structures of starting alcohols and ester products with yields.

Sr. No.	Alcohol	Acetate esters	% Conversion			Isolated Yields (%)	Boiling Points (^{O}C)
			FU	FO	FUO		
1	 a	 b	62	54	50	43	77
2	 a	 b	64	54	40	45	57
3	 a	 b	62	49	49	41	117
4	 a	 b	64	50	49	41	131

(Reaction Conditions: 1 mole of alcohol, 2 moles of acetic acid, 80^{0}C, 4 hours, 10% wt of catalyst)

Table S2: γ-Fe_2O_3 catalysts preparation using molar ratios of $FeCl_3$, urea and oxalic acid.

Catalyst Code	$FeCl_3$ (Ratio of moles)	Urea (Ratio of moles)	Oxalic acid (Ratio of moles)	Crystallite Diameter (nm)
FU	1	1	0	34.5
FO	1	0	1	40.8
FUO	1	1	1	48.1
Catalyst - I				

Table S3: Comparative table of synthesis of Ethyl acetate using various catalysts.

Catalyst	**Weight (g)**	**Temperature (^{0}C)**	**Time (Minutes)**	**% Conversion**	**Reference**
Ti pillared Clay	0.5	95	90	26	[4]
Amberlyst 15	1	70	240	51	[24]
γ-Fe_2O_3					Present work
FUO catalyst –I	0.2	80	240	62	

Figure S1: FTIR spectra of γ-Fe_2O_3

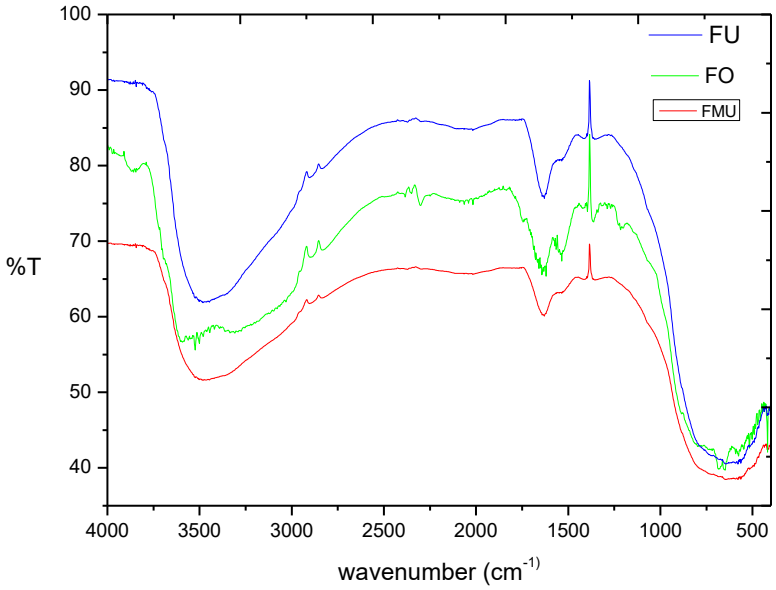


Fig. S1: FTIR spectra of γ-Fe_2O_3

Figure S2: XRD pattern of γ-Fe_2O_3

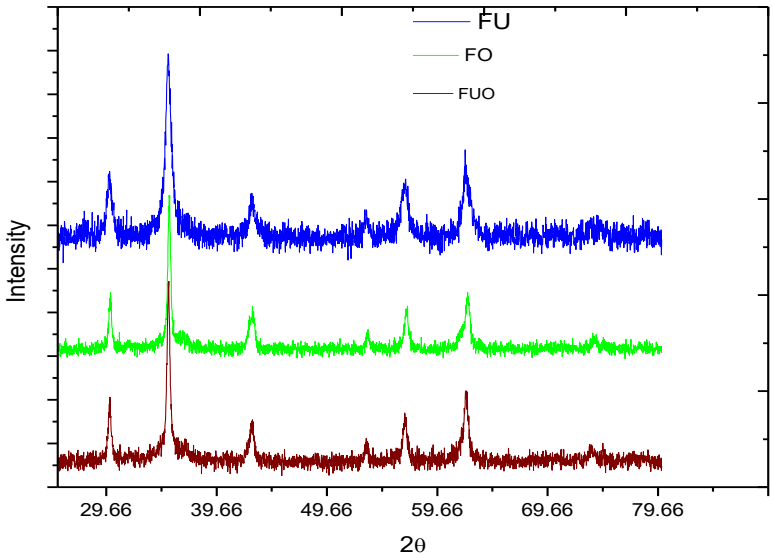
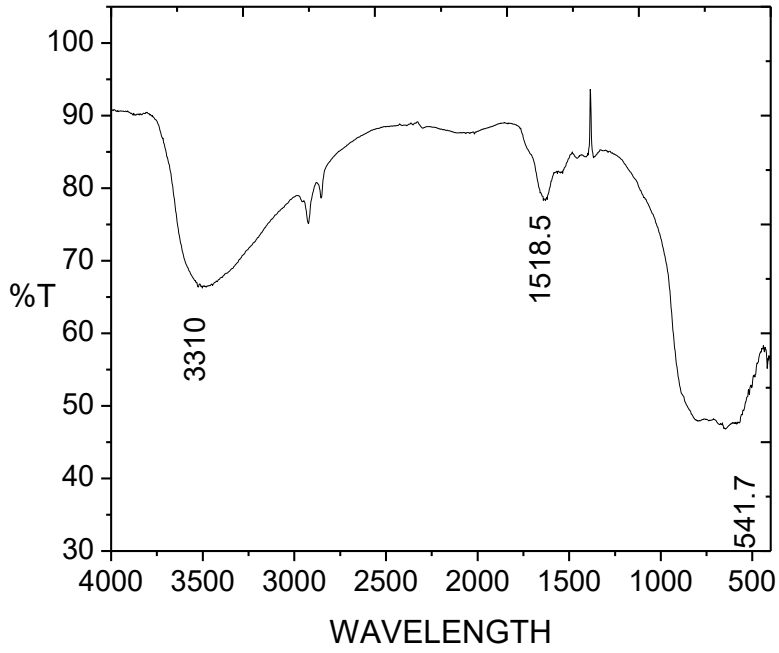


Fig. S2: XRD pattern of γ-Fe_2O_3

FTIR spectrum of catalyst-I

Catalyst characterization: Infra red spectroscopy of Fe_2O_3 catalyst-I: FTIR spectra were recorded using IR Prestige 21 Shimadzu spectrophotometer. FTIR spectra (fig. 1) revealed absorption bands at ~3000-3500 cm^{-1} indicated the presence of O-H stretching. Absorption bands at ~1518 cm^{-1} indicated the presence of O-H bending vibrations. Absorption bands at ~540-788 cm-1 indicated the presence of M-O vibrations.

FTIR spectra of Fe_2O_3 (catalyst-I)



FTIR spectra of Fe_2O_3 (catalyst-I)

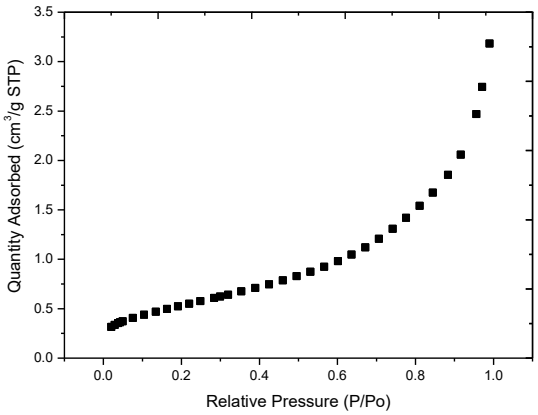
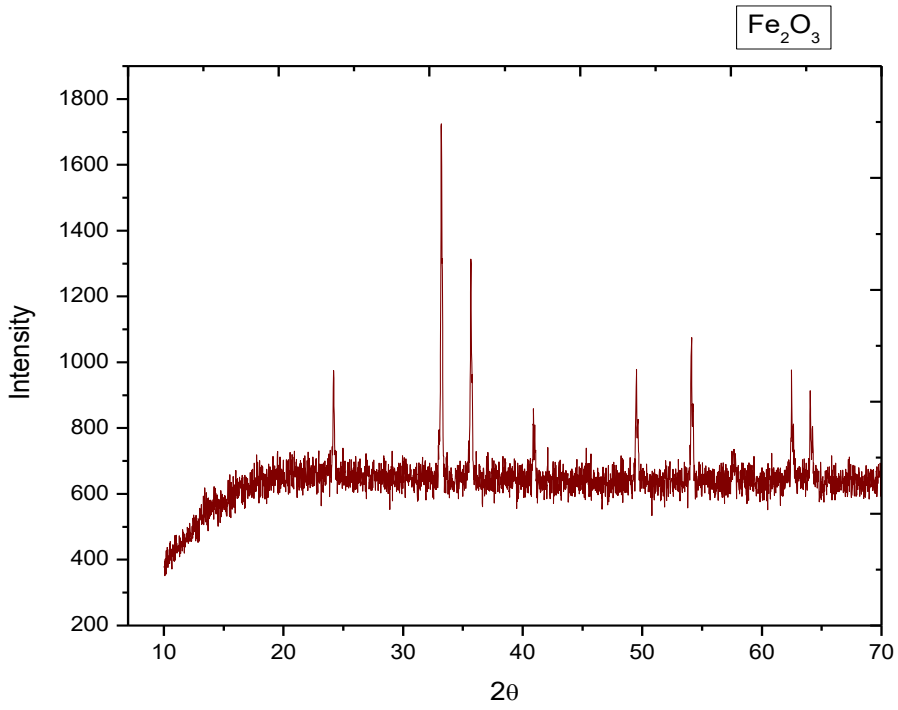


Fig. S3: B. E. T. adsorption isotherm of γ-Fe_2O_3

Nitrogen adsorption – desorption studies were performed to determine the surface area of the γ-Fe_2O_3 and it was found to be 44.265 m^2/g. From the B. E. T. adsorption isotherm, it can be seen that it follows type three curve which is an indication of the formation of a multilayer.

***X- ray diffraction (XRD) of* Fe_2O_3 catalyst-I:** XRD spectra were recorded using ETAL APD 2000 diffractrometer using Cu kα radiation and Ni filter. (λ=1.5406 Angstrom). The scanning Braggs angle was from 10^o to 70^o. The sharp peaks depicts that the sample is crystalline in nature. The crystalline diameter was calculated for catalyst-I by using Debye – Scherer formula and was found to be 34.5nm. As shown in fig 2. XRD pattern of Iron oxide shows 100% relative intensity peak at 34.1^0 which when compared with JCPDS data is found to match with Iron oxide catalyst.

XRD pattern of Fe_2O_3 (catalyst I)



XRD pattern of Fe_2O_3 (catalyst I)

The FTIR spectra of synthesized acetate esters

The IR values of C=O of esters are as follows:

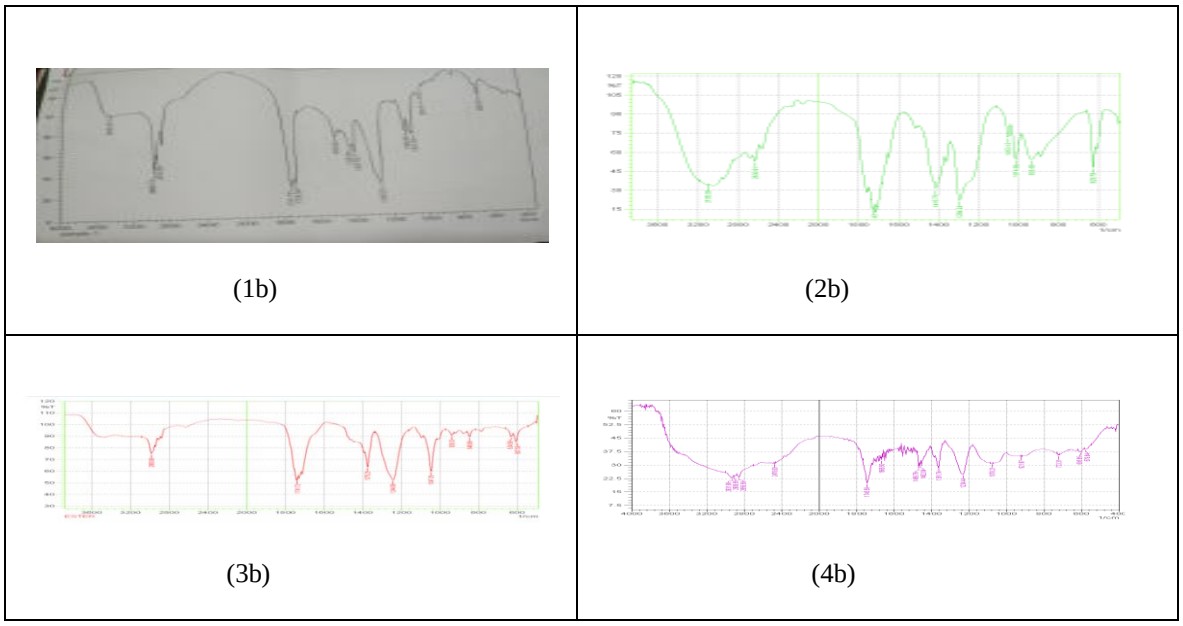
1b: ethyl acetate, 1748 cm^{-1}

2b: methyl acetate, 1750 cm^{-1}

3b: n-butyl acetate 1745 cm^{-1}

4b: isoamyl acetate 1745 cm^{-1}

Fig. S3: FTIR spectra of acetate esters
(1b: ethyl acetate, 2b: methyl acetate, 3b: n-butyl acetate and 4b: isoamyl acetate)

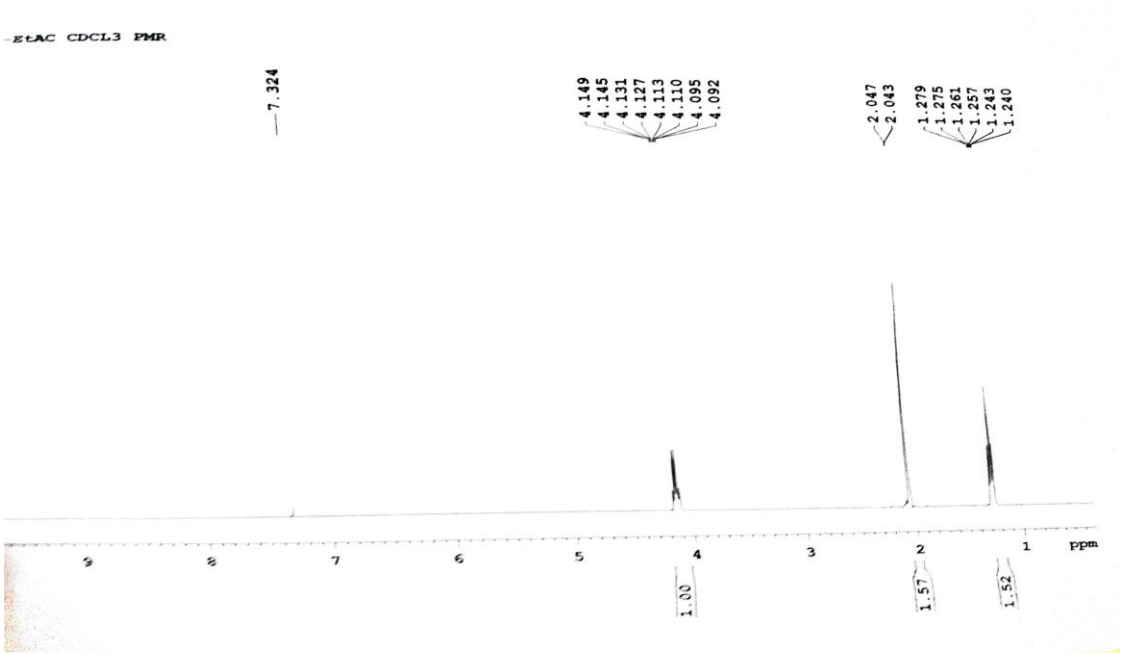


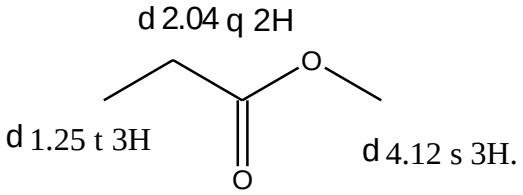
FTIR spectra of acetate esters (1b: ethyl acetate, 2b: methyl acetate, 3b: n-butyl acetate and 4b: isoamyl acetate)

^{1}H NMR data for the products:

(1b) Ethyl acetate: yield = 73%; B.P. = 77°C; IR: 1748 cm^{-1} (C=O of ester);

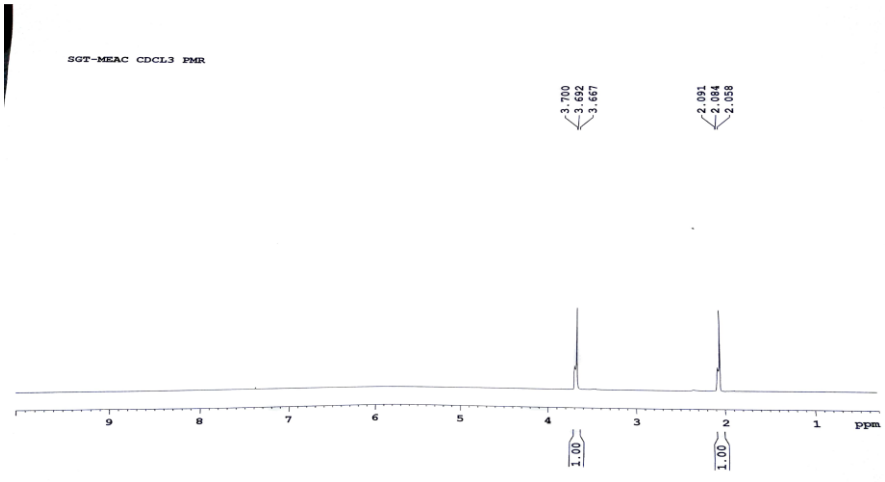
^{1}H NMR (Bruker, 400MHz, $CDCl_3$): □ 1.25 t 3H, 2.04 s 3H, 4.12 q 2H.



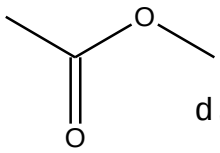


(2b) Methyl acetate: yield = 65%; B.P. = 57°C; IR: 1750 cm^{-1} (C=O of ester);

^{1}H NMR (Bruker, 400MHz, $CDCl_3$): □ 2.08 s 3H, 3.69 s 3H.



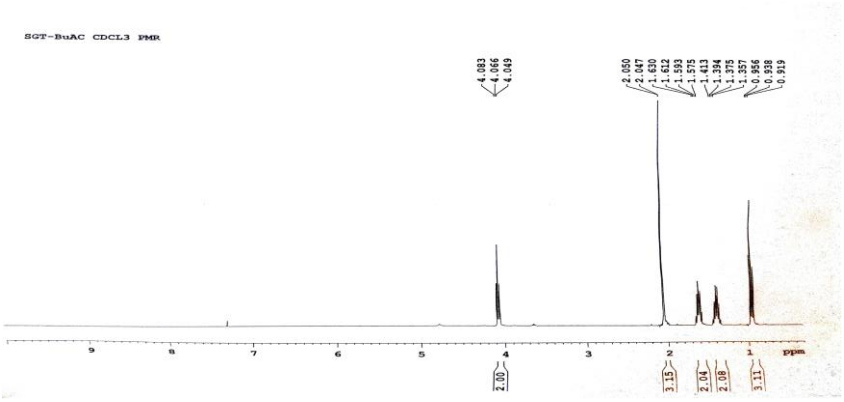
d 2.08 s 3H

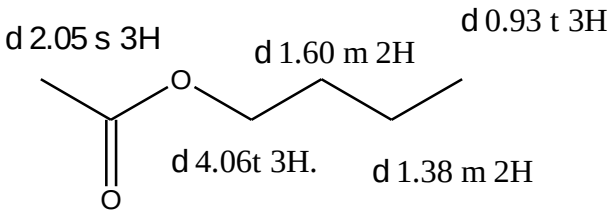


d 3.69 s 3H.

(3b) n-Butyl acetate: yield = 71%; B.P.= 126^{o}C; IR: 1745 cm^{-1} (C=O of ester);

^{1}H NMR (Bruker, 400MHz, $CDCl_3$): □ 0.93 t 3H, 1.38 m 2H, 1.60 m 2H, 2.05 s 3H, 4.06 t 2H.





(4b) Isoamyl acetate: yield = 71%; B.P. =142°C; IR: 1745 cm^{-1} (C=O of ester);

^{1}H NMR (400MHz, $CDCl_3$): □ 0.93 d 6H, 1.52 q 2H, 1.70 m 1H, 2.04 s 3H, 4.09 t 2H.