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

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Nanocomposite ferric oxide, γ-Fe_2O_3 has been synthesized using different structure directing agents by sol-gel method. The synthesized γ-Fe_2O_3 has been characterized by XRD and FT-IR. Using this nano-ferric oxide catalyst, different naturally occurring acetate esters have been synthesized and analyzed using spectroscopic methods. The catalytic activity of the catalyst has been investigated for the green, solvent free, one pot synthesis of naturally occurring acetate esters. It is observed that the γ-Fe_2O_3, synthesized by using urea as structure directing agent shows the highest percent conversion of acetic acid as compared to those synthesized *via* other methods.

Keywords: Nanocomposite Fe_2O_3 catalyst, Green synthesis, Solvent free method, Naturally occurring acetate esters

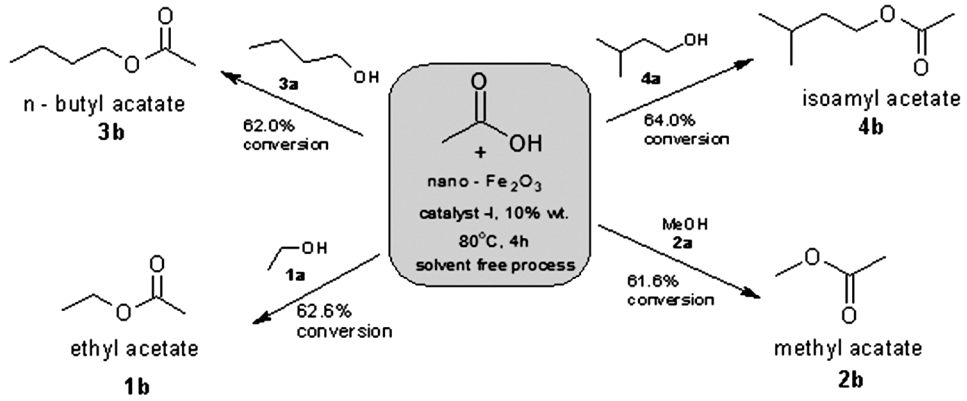
Worldwide there is an increasing need for the green chemical processes. The chemical processes which are clean, safe and energy efficient are normally preferred[1-3]. In order to achieve these requirements for chemical processes which produce minimum chemical waste, minimum energy consumption and minimized chemical utility are preferred[4]. In literature, there are various reports on metal oxide mediated catalytic processes[5-8].

Esterification is an important reaction, which utilizes a catalyst in order to get a considerably better yield[9]. Recently, many green methods have been reported for esterification processes[10,11]. The catalysts used in these esterification reactions can be both homogenous as well as heterogeneous. Homogenous catalysts which are commonly employed are hydrochloric acid, sulphuric acid, hydrofluoric acid, phosphoric acid, *etc*.

Heterogeneous acid catalysts which are commonly being employed are clays, metal oxides, zeolites, *etc*. The drawback of using a homogenous catalyst is that the separation and purification of the products becomes tedious. Most of the times these homogenous catalysts have health hazards too. On the contrary, the advantages of the solid acid catalysts over the homogenous catalysts[4,9] is that they are easy to handle, can be used multiple times, easy purification of the reaction products that are being generated and most important of all is that they are eco-friendly[12]. Due to their most fascinating properties, heterogeneous catalysts are gaining increasing global attention day by day[13]. Esterification is an important process as far as chemical industry is concerned, where acid catalysts like corrosive mineral acids have been used[14,15]. Recently, solid acid catalysts are replacing these commonly used mineral acids[16-18]. Many heterogeneous catalysts such as clay, titanium pillared clay, Al_2O_3-TiO_2, zinc oxide are being used as the solid acid catalysts. Recently synthesis of many esters over solid acid catalysts has been reported in the literature[19]. Esterification of *n*-butanol with acetic acid over ZnO solid acid catalysts is also reported[2]. TiO_2-Al_2O_3 based catalysts are already being used as solid acid catalysts for the esterification reactions[20]. Titanium pillared clay has also been used to carry out esterification of ethanol with acetic acid[4]. In our present investigation, esterification of different alcohols with acetic acid over γ-Fe_2O_3 catalysts has been studied (Scheme 1).

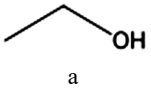
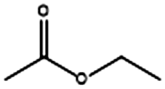
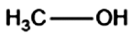
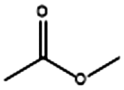
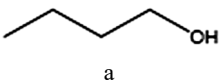
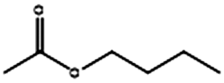
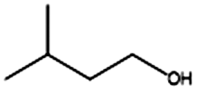
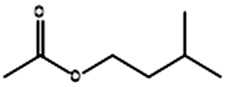
Alcohols studied are ethyl alcohol **1a**, methyl alcohol **2a**, *n*-butyl alcohol **3a** and isoamyl alcohol **4a**, which on esterification with acetic acid produces esters, namely, ethyl acetate **1b**, methyl acetate **2b**,

The authors dedicate this article to Professor Santosh G. Tilve, Department of Chemistry, Schools of Chemical Sciences, Goa University, Goa 403 206, India, on the occasion of his 63rd Birthday.



Scheme 1 — Synthesis of acetate esters using Fe_2O_3 catalyst–I

Table 1 — Showing structures of starting alcohols and ester products with yields

S. No.	Alcohol	Acetate esters	% Conversion			Isolated Yield (%)	b.p. (°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°C, 4 h, 10% wt of catalyst

n-butyl acetate **3b** and isoamyl acetate **4b**. The percentage conversion along with isolated yields are summarized in Table 1.

Esters of acetic acid have various commercial applications as reported in the literature. It is used in artificial fruit essences[21-23].

Results and Discussion

Catalyst synthesis

A series of the γ-Fe_2O_3 were prepared by using sol-gel method. $FeCl_3$ was used as the precursor. First the calculated amount of the precursor was dissolved in minimum quantity of deionized water, followed by addition of the required moles of surface directing agents (SDA) like urea and oxalic acid (Table 2). 10% ammonium hydroxide solution was added to it drop wise under continues stirring till complete precipitation was achieved. The obtained precipitates were dried at 100°C followed by calcination in air at 450°C for 4 h. The catalysts were labeled as FU (γ-Fe_2O_3 with urea), FO (γ-Fe_2O_3 with oxalic acid) and FUO - catalyst-I (γ-Fe_2O_3 with urea and oxalic acid) respectively. The obtained solids were further characterized by XRD and IR spectroscopy and were checked for its catalytic activity.

Catalyst characterization

FTIR spectra were recorded using IR Prestige 21 Shimadzu spectrophotometer. FTIR spectrum (Fig. 1)

Table 2 — 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 Catalyst–I	1	1	1	48.1

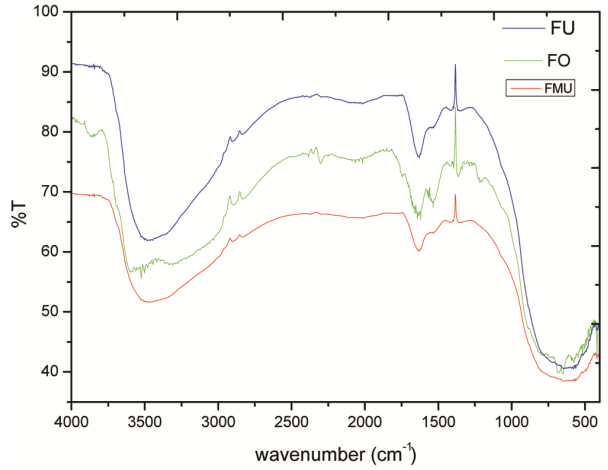


Fig. 1 — FTIR spectra of γ-Fe_2O_3

revealed absorption bands at ~3000-3500 cm^{-1} indicating 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 Fe-O vibrations.

X- ray diffraction (XRD) of Fe_2O_3 catalyst-I

XRD spectra were recorded using ETAL APD 2000 diffractometer using Cu Kα radiation and Ni filter. (λ=1.5406 Å). The sharp peaks depicted that the sample is crystalline in nature. The crystalline diameter was calculated for by using Debye – Scherer formula is as shown in Table 2. XRD pattern (Fig. 2) confirmed the formation of γ-Fe_2O_3 (JCPDS Card No.:#39-1346).

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 (Fig. 3), it can be seen that it follows type three curve which is an indication of the formation of a multilayer.

Experimental Section

Glacial acetic acid (AR grade), ethyl alcohol (AR grade), methyl alcohol (AR grade), *n*-Butyl alcohol (AR grade), isoamyl alcohol (AR grade), and ferric chloride (AR grade), were purchased from Thomas Baker Pvt. Ltd.

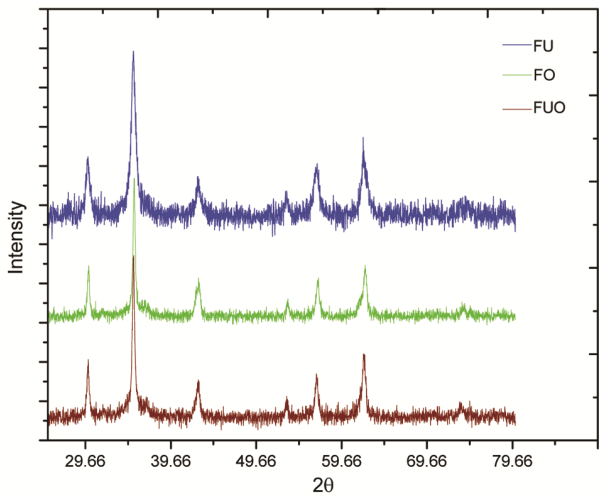


Fig. 2 — XRD pattern of γ-Fe_2O_3

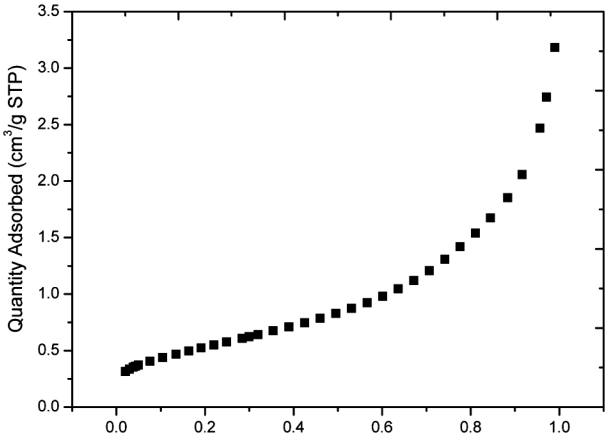


Fig. 3 — B. E. T. adsorption isotherm of γ-Fe_2O_3

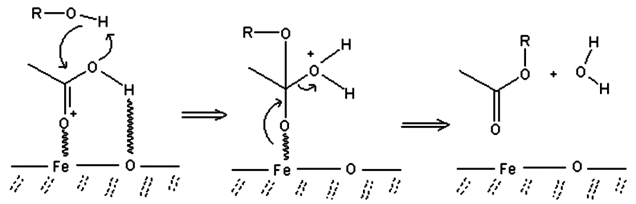
Preparation of ethyl acetate

Acetic acid (2 mol) and 1 mol of ethyl alcohol along with 0.2 g of catalyst were charged in the reaction round bottomed flask. The temperature was maintained at 80°C. After 4 h percent conversion of acetic acid was calculated by using equation 1. The products were purified by distillation. The products were confirmed by recording the boiling points, IR and ^1H NMR spectroscopy.

% conversion of Acetic acid = $[C_i\text{-}C_t/C_i] \times 100$ …equation 1

Table 3 — Comparative table of synthesis of Ethyl acetate using various catalysts

Catalyst	Weight (g)	Temp (°C)	Time (min)	% Conversion	Reference No.
Ti pillared Clay	0.5	95	90	26	[4]
Amberlyst 15	1	70	240	51	[24]
γ-Fe_2O_3 FUO Catalyst–I	0.2	80	240	62	Present work



Scheme 2 — Plausible mechanism for synthesis of acetate esters using Fe_2O_3 catalyst

Where, C_i is the initial concentration of acetic acid and C_t is the concentration at time t.

Characterization of synthesized compounds

Ethyl acetate, 1b: Colorless liquid. Yield 43%. b.p. 77°C. IR: 1748 cm^{-1} (C=O of ester); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 t 3H, 2.04 s 3H, 4.12 q 2H; ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.2, 21.0, 60.4, 171.0. Anal. C, 54.53; H, 9.1; O, 36.32%. MS: M^+ *m/z* 88.

Methyl acetate, 2b: Colorless liquid. Yield 45%. b.p. 57°C. IR: 1750 cm^{-1} (C=O of ester); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 s 3H, 3.69 s 3H; ^{13}C NMR (400 MHz, $CDCl_3$): δ 20.6, 51.6, 171.5. Anal. C, 48.64; H, 8.16; O, 43.19%. MS: M^+ *m/z* 74.

***n*-Butyl acetate, 3b**: Colorless liquid. Yield 41%. b.p.117°C. IR: 1745 cm^{-1} (C=O of ester); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 t 3H, 1.38 m 2H, 1.60 m 2H, 2.05 s 3H, 4.06 t 2H; ^{13}C NMR (400 MHz, $CDCl_3$): δ 13.7, 19.2, 20.9, 30.8, 64.3, 171.1. Anal. C, 62.04; H, 10.41; O, 27.55%. MS: M^+ *m/z* 116.

Isoamyl acetate, 4b: Colorless liquid. Yield 41%. b.p.131°C. IR: 1745 cm^{-1} (C=O of ester); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 d 6H, 1.53 m 2H, 1.70 m 1H, 2.04 s 3H, 4.09 t 2H; ^{13}C NMR (400 MHz, $CDCl_3$): δ 20.9, 22.5, 25.1, 37.4, 63.1, 171.0. Anal. C, 64.58; H, 10.84; O, 24.58%. MS: M^+ *m/z* 130.

Esterification reaction studies

Comparison of esterification reaction studies reveals that FU is more efficient towards the esterification reaction than FO and FUO. The reason for the same can be that the urea serves as a better fuel compared to oxalic acid or in combination with oxalic acid. Furthermore, the crystalline size of FU is smaller than FO and FUO. Thus, FU exhibits a better catalytic activity than FO and FUO. The reaction mechanism of this reaction is according to Eley-Rideal mechanism[4]. The plausible mechanism for the synthesis of acetic acid esters is as shown in Scheme 2.

Conclusion

From our investigation, we can conclude that, the γ-Fe_2O_3 synthesized using urea as SDA is more efficient towards esterification reaction. The comparative study of synthesis of acetate esters using catalysts like titanium pillared clay, Amberlyst 15 and γ-Fe_2O_3 are shown in Table 3. The γ-Fe_2O_3 catalyst provided better percentage conversion of acetate esters compared to the other catalysts. Four acetate esters (**1b**, **2b**, **3b** and **4b**) of commercial importance have been synthesized, using four different alcohols (**1a**, **2a**, **3a** and **4a**) giving good percentage conversion. This may be mainly due to the smaller particle size of the catalyst, which exhibits a greater surface area for the reaction.

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Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

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