



Synthesis Characterization and Esterification of Super acid (SO₄/Fe_{2.04}Co_{1.08}Ni_{0.88}O) and its Tungsten based Super acids Derived from Metal Oxide

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Abstract

In this article, SO₄/Fe_{2.04}Co_{1.08}Ni_{0.88}O₄ and its tungsten-based super acid were synthesized by coprecipitation method. The synthesized SO₄/Fe_{2.04}Co_{1.08}Ni_{0.88}O₄ and its tungsten based solid super acid is analysed by FT-IR spectra, UV-Visible spectra, Raman spectra, TGA, XRD, FE-SEM with EDX and Esterification reaction. FT-IR spectroscopy reveals the predicted functional groups of synthesized nanomaterials. Thermogravimetry analysis of nanomaterials exhibits the loss of water and sulphur dioxide. The XRD reveals that the synthesized nanomaterials are crystal in nature. The synthesized nanomaterials are cubic and spherical, as evidenced by their FESEM. The predicted components are present in the synthesized nanomaterials, as evidenced by their EDX. The amount of acetic acid present in the residual solution using an Acid-Base titration, a greater number of acetic acid molecules are converted as ester molecules when conducting the esterification reaction in the presence of either super acid or sulphate coated nanocomposite than on metal oxide.

Keywords: Nanocomposite; super acid; sulphate coated; activity; esterification; cancer cell.

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1. Introduction:

Most of the chemical reactions are carried out in presence of acid catalyst to increase rate of reaction. The using of conservational acids such as HCl, H₂SO₄, HNO₃, making injury to human body therefore, solid super acids are compiled as catalyst by researchers in chemistry lab and research area. As a result, super acid has been employed in theoretical research as well as synthetic applications such as isomerisation, cracking, dehydration, alkylation, acylation, dehydration and de-alkylation, Friedel-Crafts alkylation, and other new uses [1]. Catalysts are grouped into two types: homogeneous catalysts and heterogeneous catalysts and the heterogeneous catalyst would be solid.

Super acid is a kind of heterogeneous catalyst that can overcome many of the shortcomings of liquid super acid in acid catalysis. Because of their property to catalyse several reactions such as cracking, alkylation, and isomerisation, the intense acidity of super acid has piqued the interest of many researchers [2]. The co-precipitation-impregnation process is a common and widely used preparation method. The co-precipitation approach allows for sulphate assimilation with nanocomposite, which has a substantial impact on the physicochemical properties of nanocomposite. The metals which often used in the literature for the better applications are Iron, Cobalt and Nickel. In which, Cobalt is a hard, grey metal that is similar to iron and nickel. Cobalt is ductile, but it is also malleable. The capacity of metals to be pulled into thin wires is referred to as ductility. Cobalt is a naturally occurring magnetic metal that is malleable, which means it may be hammered into thin sheets. When cobalt is used alone, its magnetic qualities are modest; however, when it is combined with another metal, its magnetic properties are enhanced. As a result, cobalt has been chosen as one of the metal components in the synthesis of nanocompounds in this paper.

The impregnation approach with an aqueous solution of nickel sulphate was used to organise a sequence of NiSO₄ / gamma-Al₂O₃ catalysts. The high catalytic activity of NiSO₄ / gamma-Al₂O₃ for both 2-propanol dehydration and cumene de-alkylation was linked to the rise in acidity and acid strength caused by NiSO₄. Maximum catalytic activity for 2-propanol dehydration and cumene de-alkylation were observed with a 20 wt% - NiSO₄ / gamma-Al₂O₃ calcined at 600 °C [3]. As a result, NiSO₄ was chosen as one of three metals for the production of super acid in this research.

The amalgamation of sulphur ions into nanocomposite leads to alteration of surface physical and chemical properties of the catalyst and endorse electron transfer from the Fe species to H₂O₂ molecules. Therefore, the incorporation of sulphur species into the lattice of Fe₂O₃ might further enhance its activity and make longer the application range in heterogeneous Fenton process [4]. Hence Fe is used as one of the three metals for the synthesis of super acids.

The sulphated mono metallic oxide has more disadvantages such as small specific area consequently limited availability of the acid sites and hence, its catalytic activity will be lower. To progress the catalytic activity of super acid [5] have synthesised sulphated bimetallic oxide (S₂O₈²⁻ / ZrO₂ - Al₂O₃) by doping of ZrO₂ with Al through the impregnation with S₂O₈²⁻.

The surface acidity is greater than before by the amendment of nanocomposite with sulphate anion, which leads to raises in activity of catalyst. Therefore, a strong acidity is generated by the amendment of nanocomposite with sulphate anion and thus acts as super acid catalysts for numerous commercially important reactions. Among an assortment of sulphate reagents available, either dilute sulphuric acid or an aqueous solution of ammonium sulphate has

been commonly used by researchers [6]. Therefore, dilute sulphuric acid is used for modification of nanocomposite in this paper.

Fatty acid esterification processes are carried out in a homogeneously catalysed reaction at the industrial level. The traditional homogeneous catalysts are mineral acids with high reactivity and low cost, like H₂SO₄ and H₃PO₄. However, their use is restricted because leftover catalysts are challenging to remove from the product stream and mineral acids hasten the corrosion of manufacturing equipment. Thus, in order to get rid of the remaining strong acid in the byproducts of homogeneously acid-catalyzed processes, an additional purification step is needed.

The reactions of terephthalic acid with ethylene glycol [7], butanol with propionic acid [8], phthalic anhydride with 2-ethylhexanol [9], and others have all employed SO₄²⁻/M_xO_y (M = Ti, Zr, Fe) as an effective esterification catalyst. Determining the super acid SO₄/Fe_{2.04}Co_{1.08}Ni_{0.88}O₄ by co-precipitation method, as well as its characterisation and investigation of its catalytic activity via esterification process, are covered in this paper.

2. Experimental Method

2.1. Materials and method

In the synthesise of such super acid and sulphate coated nanocomposite, Ferrous sulphate heptahydrate (FeSO₄.7H₂O) from Sigma Aldrich, Cobalt chloride hexahydrate (CoCl₂.6H₂O) from merck, Nickel sulphate hexahydrate (NiSO₄.6H₂O) from merck, sodium tungstate dihydrate (Na₂WO₄.2H₂O) from Sigma Aldrich , De-ionized water, alcohol, aqueous ammonia, Conc. H₂SO₄ solution and pH papers are significantly used. The co-precipitation method is used to create super acids, and the calcinations process is carried out for 6 hours at a constant

temperature of 500 °C. Sulphuric acid is used with sulphating agents in the creation of super acids.

2.2. Instrumentation

The functional group of synthesised nanocomposite ICNO, WCNO, WINO, WICO and its modified nanocomposite (both super acid and sulphate coated nanocomposite) are identified by ALPHA Bruker FT-IR spectroscopy from 4000 cm⁻¹ to 400 cm⁻¹. The ALPHA Bruker 320 UV-Visible spectrophotometer used to determine the absorption bands of synthesised nano materials from 200 cm⁻¹ to 600 cm⁻¹. The Horiba 320 Raman spectrophotometer have used to identify the stretching vibrations of synthesised nano materials and the stretching vibrations of synthesised nano materials has been taken from 100 cm⁻¹ to 1500 cm⁻¹. The thermal studies of synthesised nano materials have recorded using Q 600 SDT instrument and then TGA of nano materials has been taken from 100 cm⁻¹ to 1000 cm⁻¹. The average particle size value is calculated from its XRD data using scherrer equation $D = K\lambda / \beta \cos\theta$. The crystallinity of synthesized nano materials are estimated from its powder XRD data and spectrum respectively using Cu K_α ($\lambda = 1.54060$) radiation in the range of 10 ° - 80 ° in 2θ. The morphology of synthesised nano material by Field Emission Scanning Electron Microscopy (FE-SEM) of synthesised nano materials have carried out using Zeiss FESEM SIGMA VP 03-04 models.

2.3. Catalyst Preparation

2.3.1 Synthesis of nanocomposite

The co-precipitation method was used to create the nanomaterial Fe_{2.04}Co_{1.08}Ni_{0.88}O₄ by adding aqueous ammonia solution slowly to a mixture of FeSO₄.7H₂O, CoCl₂.6H₂O, and NiSO₄.6H₂O solution while maintaining the pH value of 6 - 7. The reaction is carried out on the magnetic stirrer for 4hrs stirring. The precipitate is formed and filtered and then washed by

mixture of alcohol plus water solution. The precipitate is now dried in an oven before being calcined for six hours at $500\text{ }^\circ\text{C}$.

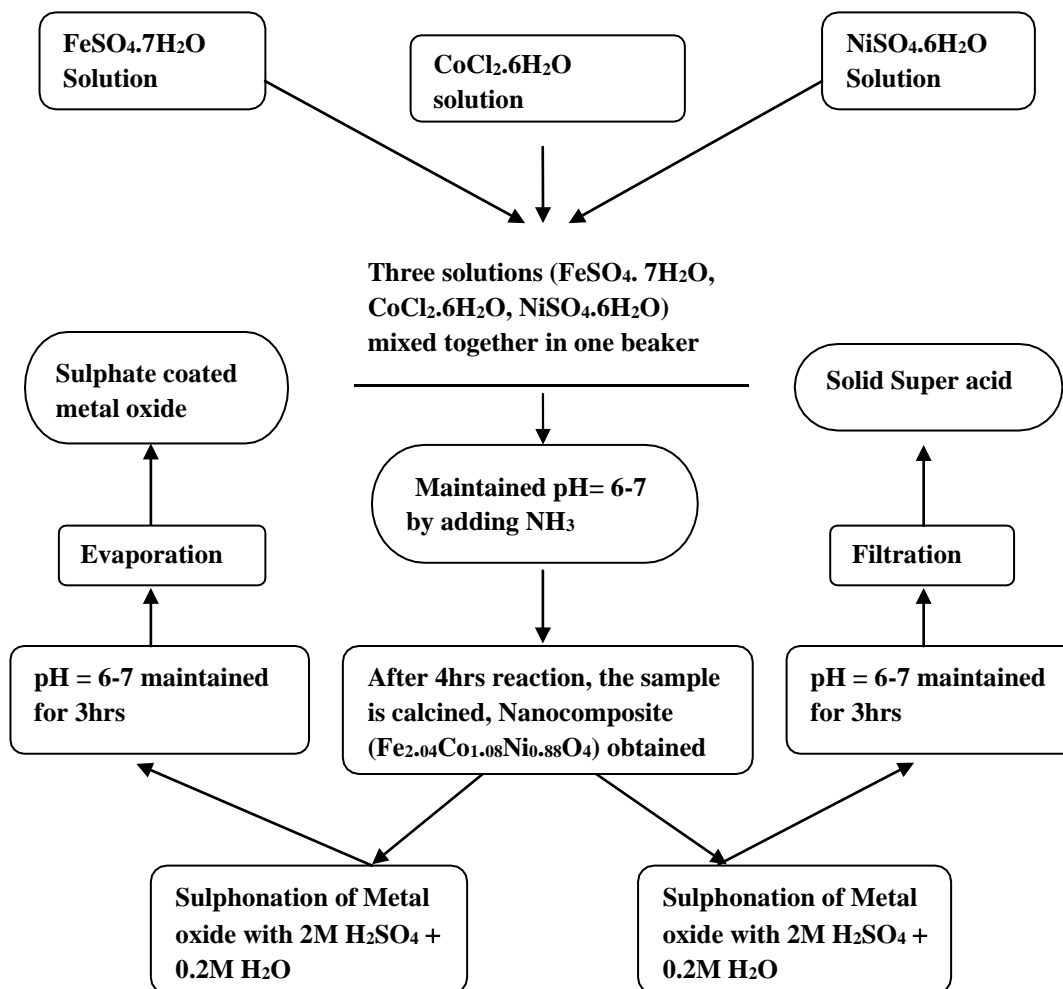


Figure 1: Flow chart of synthesis of nanocomposite and its modifieds.

The calcined sample is grinded in a mortar to create a well-grinded powder sample, which is then referred to as nanocomposite ($\text{Fe}_{2.04}\text{Co}_{1.08}\text{Ni}_{0.88}\text{O}_4$). Similarly, other compounds are obtained by contiguous exchange of tungsten instead of Fe, Co, Ni such as W leading to a compound.

$\text{W}_{2.04}\text{Co}_{0.88}\text{Ni}_{1.08}\text{O}_4$ (WCNO), $\text{W}_{2.04}\text{Fe}_{0.88}\text{Ni}_{1.08}\text{O}_4$ (WINO), $\text{W}_{2.04}\text{Fe}_{0.88}\text{Co}_{1.08}\text{O}_4$ (WICO).

Similar to figure 1 other nanocomposites are synthesised using their corresponding metal compounds.

2.3.2. Synthesis of Super acids

The well-grinded nanocomposite sample (Fe_{2.04}Co_{1.08}Ni_{0.88}O₄) is added to the diluted H₂SO₄ solution (2 M Conc. H₂SO₄ + 0.2 M H₂O), and the mixture is slowly swirled on a magnetic stirrer for just three hours while maintaining a pH of 6 -7. The precipitate is then passed through a filter and cleaned with the same dilute H₂SO₄ solution. The obtained sample is oven-dried before being calcined for six hours at 500 °C. The calcined sample is then grinded into a fine powder and given the name SO₄/Fe_{2.04}Co_{1.08}Ni_{0.88}O₄ (S_F-ICNO). Similarly, other super acids prepared are SO₄/W_{2.04}Co_{0.88}Ni_{1.08}O₄ (S_F-WCNO), SO₄/W_{2.04}Fe_{0.88}Ni_{1.08}O₄ (S_F-WINO), SO₄/W_{2.04}Fe_{0.88}Co_{1.08}O₄ (S_F-WICO).

2.3.3. Synthesis of sulphate coated nanocomposite

The precursor metal oxide, however, is combined with a 2 M Conc.H₂SO₄ + 0.2 M H₂O solution and agitated for three hours while maintaining a pH of 6 to 7. The solution is evaporated using a mantel at a constant temperature of 80 °C after three hours. Finally, sulphate coated nanocomposite **SO₄/Fe_{2.04}Co_{1.08}Ni_{0.88}O₄ (S_C-ICNO)** is formed. Similarly, other compounds synthesised are **SO₄/W_{2.04}Co_{0.88}Ni_{1.08}O₄ (S_C-WCNO)**, **SO₄/W_{2.04}Fe_{0.88}Ni_{1.08}O₄ (S_C-WINO)**, **SO₄/W_{2.04}Fe_{0.88}Co_{1.08}O₄ (S_C-WICO)**

These synthetic nanocomposites and their modifications are examined using the following techniques: FT-IR, UV-Visible, Raman spectroscopy, TGA, XRD, FE-SEM with EDX, and then subjected as catalyst in the esterification reaction.

2.4. Procedure adopted for Esterification reaction

At first, a separate esterification reaction is carried out in a three-neck RB flask using 7 ml glycerol, 22 ml acetic acid, 20 ml toluene, and 0.5 g of synthesized nanocomposite (ICNO) or 0.5 g of super acid (S_F-ICNO) or 0.5 g of sulphate coated nanocomposite (S_C-ICNO). Now, the reaction temperature is increased up to 120 °C and is maintained as constant temperature in the esterification reaction for 6 hrs. During the esterification reaction, The Dean-Starck apparatus and a reflux condenser are alternately attached to the combination of solution that contains Round bottom flask. The magnetic stirrer is used to support the entire setup. The forward and backward reaction is maintained i.e. the equilibrium reaction should be followed otherwise; the ester and water molecules does not produced. Thus obtained water is collected through the Dean-Starck apparatus tap and the strength of acetic acid molecule is determined using reminded residue solution of round bottom flask with the help of Acid-Base titration.

2.4.1.Determination of Residual acid strength by Acid-Base titration

In the Acid-Base titration, 5ml of residual solution is combined with 15 ml of double distilled water. To this, phenolphthalein is added and this solution is titrated against 0.5 N NaOH solutions. Using the end point, the amount of acid molecule, that was lag without converting as ester molecules, as evaluated by its residual solution after the esterification reaction.

3. Result and Discussion

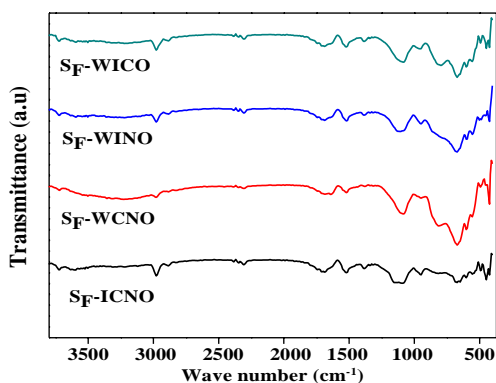
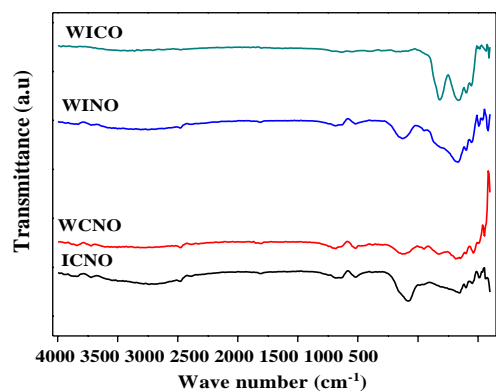
There are four nanocomposite ICNO, WCNO, WINO, and WICO, as well as corresponding super acids, S_F-ICNO, S_F-WCNO, S_F-WINO, and S_F-WICO, were created using the co-precipitation process. On the other hand, the synthetic nanocomposites are coated with sulphuric acid before being transformed into sulphate coated nanocomposites (S_C-ICNO, S_C-

WCNO, S_C-WINO, and S_C-WICO). The formation of the product is evaluated by variable techniques.

3.1.FT-IR Spectroscopy

Table -1. FT-IR value of synthesized nanomaterials

Nanomaterials	W-O	Fe-O	Co-O	Ni-O	SO ₄
ICNO	-	578 cm ⁻¹	507 cm ⁻¹	700 cm ⁻¹	-
S _F -ICNO	-	578 cm ⁻¹	507 cm ⁻¹	700 cm ⁻¹	1100cm ⁻¹
S _C -ICNO	-	578 cm ⁻¹	507 cm ⁻¹	700 cm ⁻¹	1100cm ⁻¹
WCNO	700 cm ⁻¹	-	507 cm ⁻¹	700 cm ⁻¹	-
S _F -WCNO	700 cm ⁻¹	-	507 cm ⁻¹	700 cm ⁻¹	1100cm ⁻¹
S _C -WCNO	700 cm ⁻¹	-	507 cm ⁻¹	700 cm ⁻¹	1100cm ⁻¹
WINO	700 cm ⁻¹	578 cm ⁻¹	-	700 cm ⁻¹	-
S _F -WINO	700 cm ⁻¹	578 cm ⁻¹	-	700 cm ⁻¹	1100cm ⁻¹
S _C -WINO	700 cm ⁻¹	578 cm ⁻¹	-	700 cm ⁻¹	1100cm ⁻¹
WICO	700 cm ⁻¹	578 cm ⁻¹	507 cm ⁻¹	700 cm ⁻¹	-
S _F -WICO	700 cm ⁻¹	578 cm ⁻¹	507 cm ⁻¹	700 cm ⁻¹	1100cm ⁻¹
S _C -WICO	700 cm ⁻¹	578 cm ⁻¹	507 cm ⁻¹	700 cm ⁻¹	1100cm ⁻¹



(a)

(b)

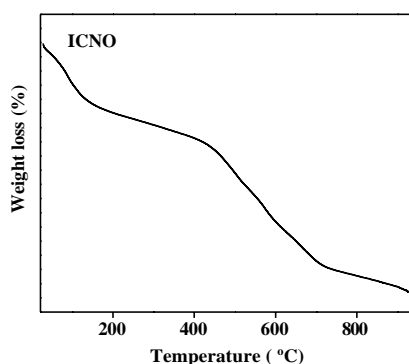
Figure 2. FT-IR Spectra of (a) ICNO, WCNO, WINO, WICO (b) S_F-ICNO, S_F-WCNO, S_F-WINO, S_F-WICO

The synthesised nanocomposites and their modifieds (super acids and sulphate coated nanocomposites) are examined using FT-IR spectroscopy to know its functional groups. Figure 2 (a), 2 (b), and S₁ (a) show the FT-IR spectra of synthesised nanocomposites, super acids, and sulphate coated nanocomposites respectively. The FT-IR spectra of nanocomposites ICNO, WCNO, WINO, and their derivatives show a peak at 700 cm⁻¹, confirming the presence of Ni-O as a stretching vibration [22 - 26]. The FT-IR spectra of nanocomposites ICNO, WCNO, WICO, and their modifications show a peak at 507 cm⁻¹, confirming the presence of Co-O as bending vibrations [10-14]. The FT-IR spectra of nanocomposites ICNO, WINO, WICO, and their modifications reveal a peak at 578 cm⁻¹, confirming the presence of Fe-O as a stretching

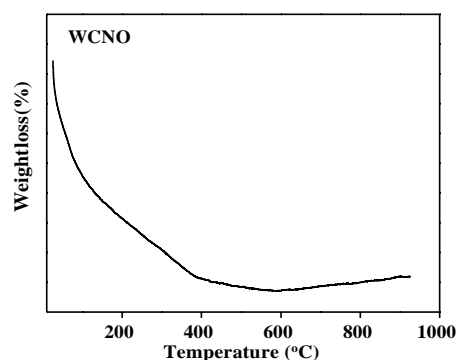
vibration. The existence of a peak around 700 cm⁻¹ in the FT-IR spectra of nanocomposites WCNO, WINO, WICO, and their modified forms shows the presence of W-O [15] as a bending vibration. The emergence of a peak at 1100 cm⁻¹ in the FT-IR spectra of both modified nanocompound demonstrates that the SO₄²⁻ ions are displayed as stretching vibration. The predicted functional groups are presented in the synthesised nanocomposite, super acids, and sulphate coated nanocomposites, according to the overall findings. As a result, the obtained FT-IR values of synthesized nanomaterials are given in table 1.

3.2. Thermo Gravimetry Analysis (TGA)

The following describes four different nanocomposite that have undergone thermal study and their altered materials. Figures 3 (a), 3 (b), 3 (c), and 3 (d) depicts the thermogram of the nanocomposite ICNO, WCNO, WINO, and WICO, respectively. The loss of water is observed in the TGA of such nanocomposites. In the TGA of nanocomposite ICNO, WCNO, WINO and WICO, the loss of weight is observed from 50 °C - 150 °C, 100 °C - 500 °C, 80 °C - 500 °C and 50 °C to 500 °C (assigned to loss of water) [24] respectively.



(a)



(b)

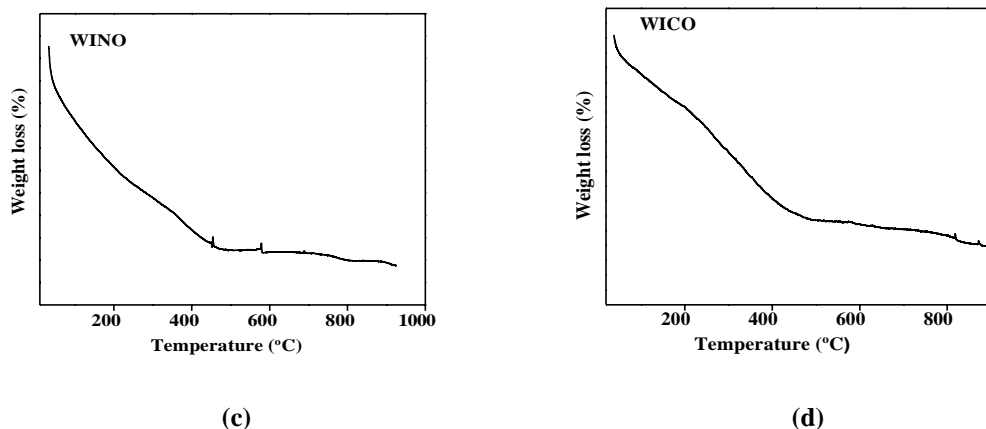


Figure 3 : TGA of (a) ICNO, (b) WCNO, (c) WINO, (d) WICO,

Figure S₂ (a), S₂ (b), S₂ (c) and S₂ (d) shows the TGA of S_F-ICNO, S_F-WCNO, S_F-WINO and S_F-WICO respectively and shows the loss of water and sulphur di-oxide. In the TGA of S_F-ICNO, S_F-WCNO, S_F-WINO and S_F-WICO, the loss of water is observed from 150 °C - 350 °C, 50 °C - 240 °C, 40 °C - 300 °C, 50 °C - 250 °C [24], and the loss of SO₂ is observed from 440 °C - 540 °C, 650 °C - 720 °C, 650 °C - 850 °C, and 750 °C - 900 °C [25] respectively. Similarly, the loss of water and sulphur di-oxide is observed for S_C-ICNO (50 °C -120 °C, 550 °C - 620 °C), for S_C-WCNO (50 °C - 150 °C, 750 °C - 900 °C), for S_C-WINO (50 °C - 150 °C, 610 °C - 900 °C) and for S_C-WINO (50 °C - 150 °C, 600 °C - 900 °C) has been shown in the figure S₂(e), S₂(f), S₂(g), S₂(h) respectively.

3.3. X-Ray Diffraction (XRD) Analysis

X-ray diffraction is a well-known technique for determining the crystalline nature of synthesised nanomaterials. The XRD patterns of nanocomposite ICNO, WCNO, WINO, WICO,

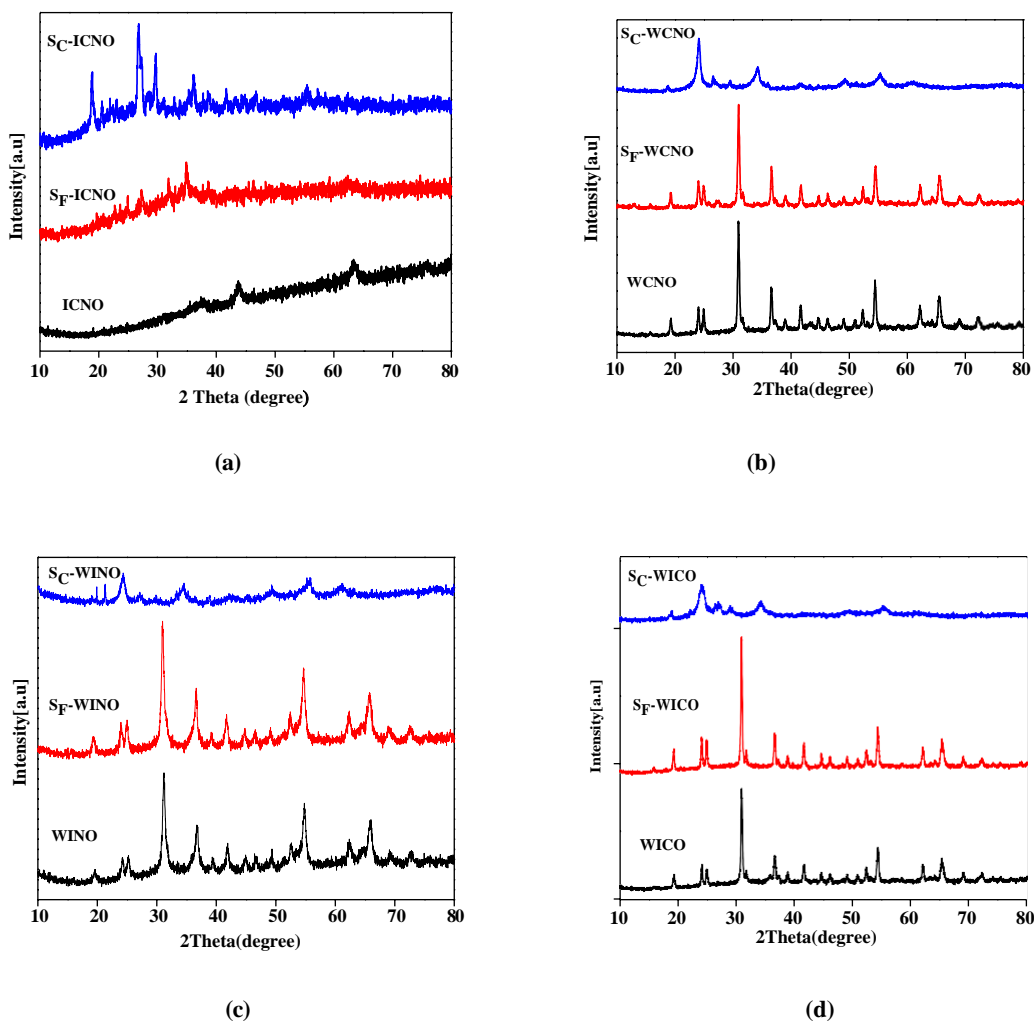


Figure 4: XRD of (a) ICNO, S_F-ICNO, S_C-ICNO, (b) WCNO, S_F-WCNO, S_C-WCNO, (c) WINO, S_F-WINO, S_C-WINO, (d) WICO, S_F-WICO, S_C-WICO.

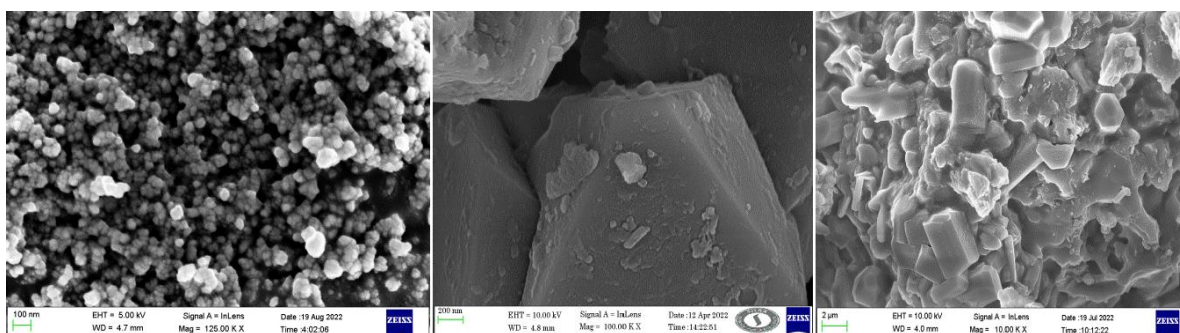
and their modified nanocomposites are shown in Figure 4 (a), 4 (b), 4 (c), and 4 (d). These XRD patterns demonstrate and confirm that each nanocomposite synthesised and its modified nanocomposites were crystal in nature. The average particle size value of nanocomposite ICNO, WCNO, WINO, WICO is 4.6964 nm, 2.2564 nm, 1.7354 nm, 2.4141 nm respectively and the average particle size value of super acid S_F-ICNO, S_F-WCNO, S_F-WINO, S_F-WICO is 5.494 nm, 2.0132 nm, 1.4586 nm, 2.5826 nm respectively and then the average particle size value of sulphate coated nanocomposite S_C-ICNO, S_C-WCNO, S_C-WINO, S_C-WICO is 1.0724 nm,

1.3733 nm, 4.6682 nm, 3.1187 nm respectively. The average particle size values are calculated using scherrer formula.

Since, the XRD pattern of S_C-ICNO, WCNO, S_F-WCNO, WINO, S_F-WINO, WICO and S_F-WICO are highly crystal in nature. Table S₃ (a) shows, the XRD value of some synthesised nano materials.

3.4. Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM) is used to explain the morphology of a synthesised nanomaterial. Figure 5 (a), 5 (d), 5 (g), 5 (j) represent the Field Emission Scanning Electron Microscopy of nanocomposite ICNO, WCNO, WINO, WICO respectively and its morphological structure is sphere in shape. Figure 5 (b), 5 (c), 5 (e), 5 (f)



FESEM of ICNO

(a)

FESEM of Sr-ICNO

(b)

FESEM of Sc-ICNO

(c)

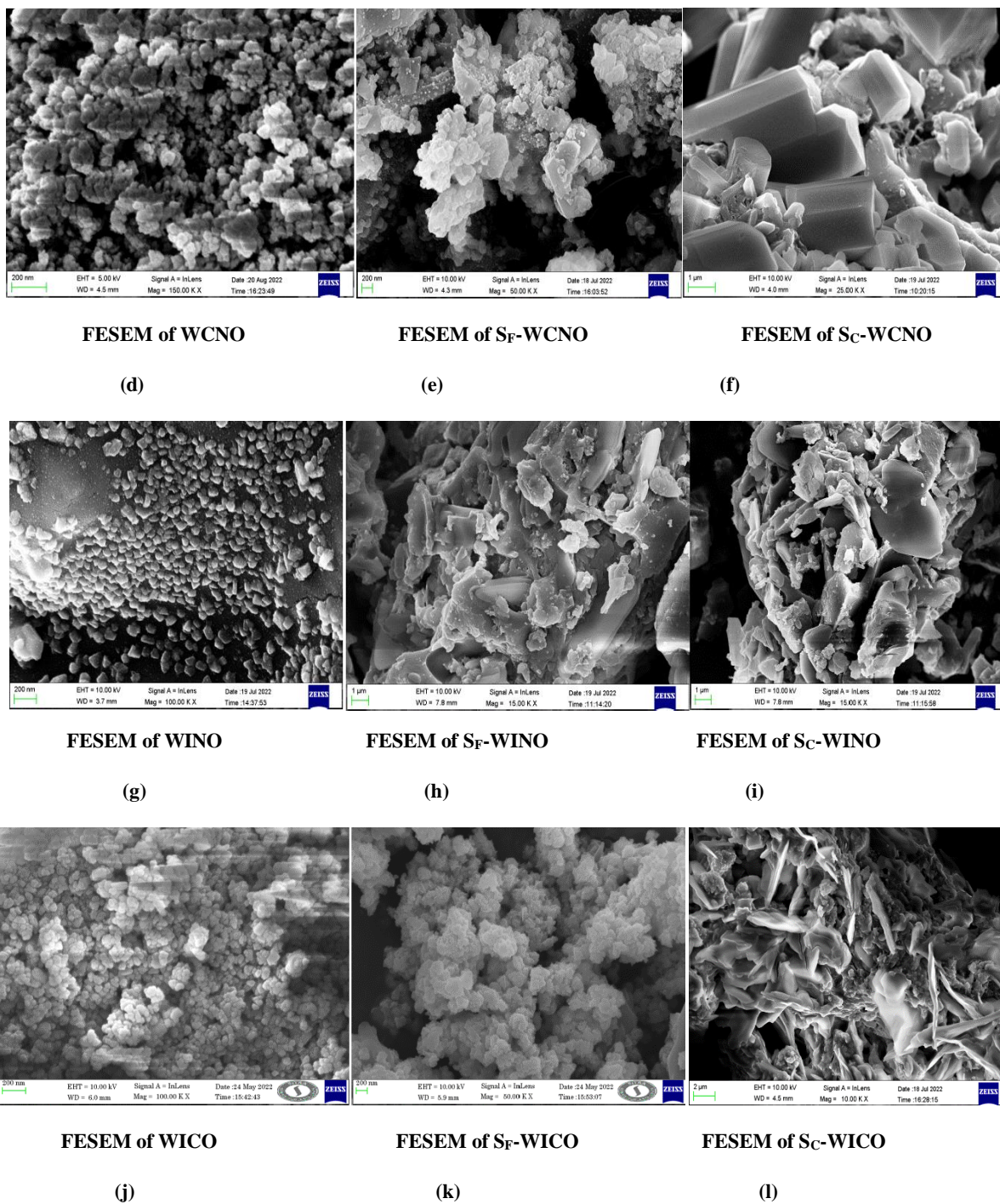


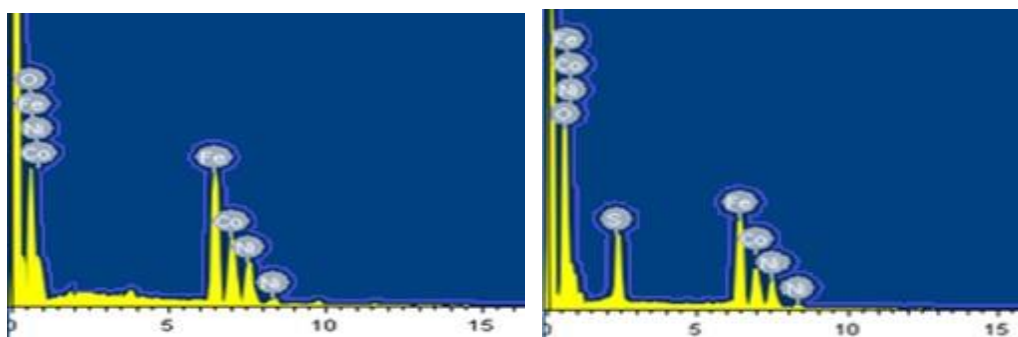
Figure 5: FESEM of (a) ICNO, (b) S_F-ICNO, (c) S_C-ICNO, (d) WCNO, (e) S_F-WCNO, (f) S_C-WCNO, (g) WINO, (h) S_F-WINO, (i) S_C-WINO, (j) WICO, (k) S_F-WICO, (l) S_C-WICO.

exhibits that the FESEM of S_F-ICNO, S_C-ICNO, S_F-WCNO, S_C-WCNO respectively and its morphological structure is being as cubic structure. When analysing the FESEM of S_F-WINO, S_C-WINO and S_C-WICO, its morphological structure is being as flakes and it has been shown in

figure 5 (h), 5 (i) and 5 (l) respectively. Figure 5 (k) indicates that the FESEM of S_F-WICO and on analysing its morphological structure, this is being like as caltrop. Over all, the synthesised nanocomposite is being as spherical in shape but on modifying such nanocomposite using H₂SO₄, its morphological structure is changing from spherical to either cubic or flakes or tack weed.

3.4.1. Energy Dispersive X-ray (EDX) Analysis

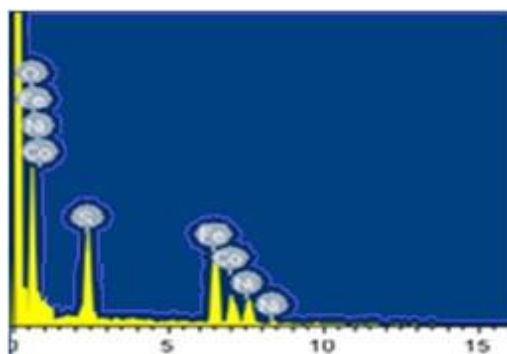
The EDX scale is used to identify and present the components of the synthesised nano compounds. As a result, energy dispersive x-ray analysis is one of the most significant studies for determining whether or not the predicted components are present in the synthesised nano materials. Figures 6 (a), 6 (b), and 6 (c) shows the EDX of nanocomposite ICNO, super acid S_F-ICNO, and sulphate coated nanocomposite S_C-ICNO respectively.



EDX of ICNO

EDX of S_F-ICNO

3.4.1.1. (b)



EDX of S_C-ICNO

(c)

Figure 6: The EDX of (a) ICNO, (b) S_F-ICNO, (c) S_C-ICNO,

The EDX of ICNO, S_F-ICNO and S_C-ICNO shows, the expected components Fe, Co, Ni and O. But, there is one excess component such as “S” in the modified nanocomposites. Similarly, the expected components are presented in the case of other nanocomposites and its modified nanocomposites, they have been shown in the figure S₄ (a), S₄ (b), S₄ (c), S₄ (d), S₄ (e), S₄ (f), S₄ (g), S₄ (h), and S₄ (i). The EDX analysis confirms that the product formed as expected.

3.5. Catalytic Activity of the Synthesised Materials

The synthesised nanomaterials are evaluated as catalyst and their catalytic activity is investigated using the esterification reaction.

3.5.1. Esterification reaction

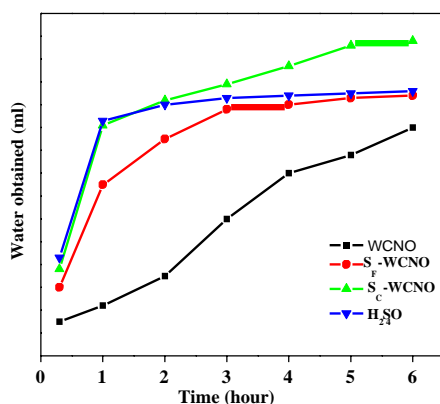
Table 2, 3, S₅ (a), S₅ (b) compares water obtained in presence of sulphuric acid solution to water obtained at various times during the esterification reaction in presence of nanocomposites, super acids, or sulphate coated nanocomposites and is clearly represented as graph in figure 7 (a), 7 (b), S₆ (a) and S₆(b).

Table 2. Water obtained on esterification reaction using WCNO, S_F-WCNO, S_C-WCNO, H₂SO₄.

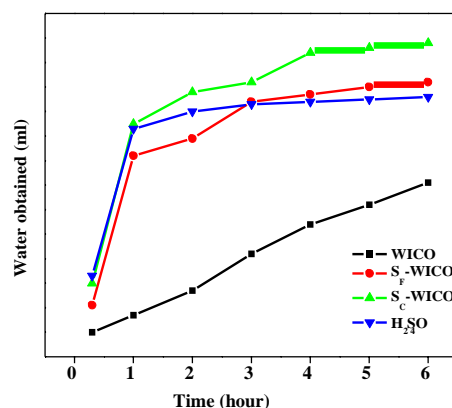
Time	Water Obtained in (ml)						
	30 min	1 hr	2 hr	3 hr	4 hr	5 hr	6 hr
WCNO	0.5	1.2	2.5	5.0	7.0	7.8	9.0
S _F -WCNO	2.0	6.5	8.5	9.8	10.0	10.3	10.4
S _C -WCNO	2.8	9.1	10.2	10.9	11.7	12.6	12.8
H ₂ SO ₄	3.3	9.3	10.0	10.3	10.4	10.5	10.6

Table 3. Water obtained on esterification reaction using WICO, S_F-WICO, S_C-WICO, H₂SO₄.

Time	Water Obtained in (ml)						
	30min	1hr	2 hr	3 hr	4 hr	5 hr	6 hr
WICO	1.0ml	1.7ml	2.7ml	4.2ml	5.4ml	6.2ml	7.1ml
S _F -WICO	2.1ml	8.2ml	8.9ml	10.4ml	10.7ml	11.0ml	11.2ml
S _C -WICO	3.0ml	9.5ml	10.8ml	11.2ml	12.4ml	12.6ml	12.8ml
H ₂ SO ₄	3.3ml	9.3ml	10.0ml	10.3ml	10.4ml	10.5ml	10.6ml



3.5.1.1.



(b)

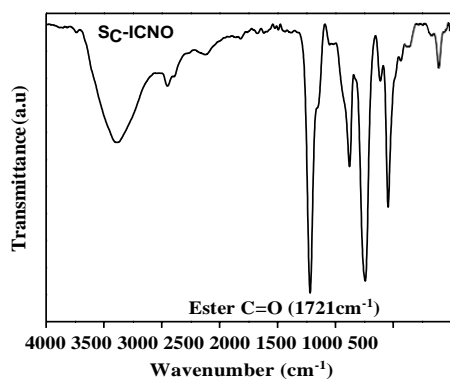
Figure 7: Graph of water obtained on presence of (A) WCNO series (B) WICO series

When using nanocomposite (ICNO, WCNO, WINO, and WICO) as a catalyst in the esterification reaction, the water obtained ranges from 7 - 9 ml for 6-hour reaction. But on using super acid (S_F-ICNO, S_F-WCNO, S_F-WINO, S_F-WICO) or sulphate coated nanocomposites as catalyst (S_C-ICNO, S_C-WCNO, S_C-WINO, S_C-WICO) in the esterification reaction, the water obtained for super acids is 8.5 ml - 10.2 ml and for sulphate coated nanocomposite 9.3ml - 10.8ml for 2hr reaction itself. The water produced by utilising nanocomposites ranges from 7.0 to 9.0 ml, and it is produced after a 2-hour reaction when super acids or sulphate coated nanocomposites are used. When the esterification reaction is observed up to 6 hr, solid super acids

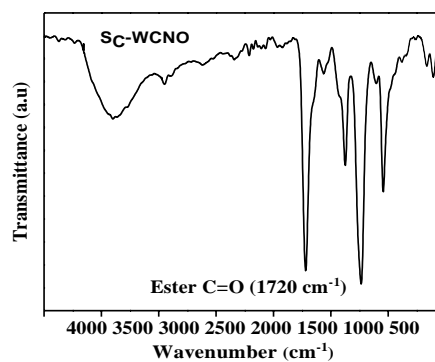
produce 10.4 ml - 11.2 ml of water and sulphate-coated nanocomposites produces 12.0 ml - 12.8 ml of water, respectively. This means that more acetic acid molecules would be converted to ester molecules as a result. As a result, both super acids and sulphate coated nanocomposites have higher catalytic activity than nanocomposites.

In contrast, 10.6 ml of water is produced after a 6-hour esterification process using sulphuric acid as the catalyst but, on using super acids or sulphate coated nanocomposites 10.4 ml - 11.2 ml of water and 12.0 ml - 12.8 ml of water is obtained for 6-hour reaction. In contrast to sulphuric acid solution, more acetic acid molecules are converted as ester molecules simultaneously more water is created in the presence of either solid super acids or sulphate-coated nanocomposite. As a result, super acids and sulphate coated metal oxides have stronger catalytic activity than sulphuric acid solution.

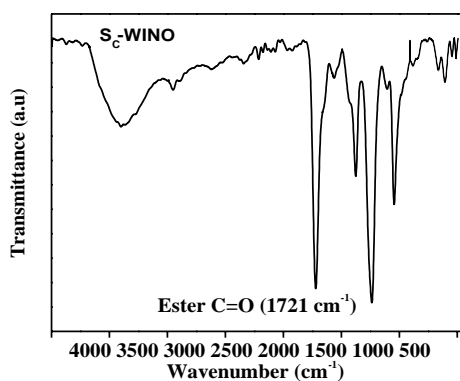
Since, more acetic acid molecules converted as ester molecules simultaneously more water is produced in the esterification reaction on presence of either super acids or sulphate coated nanocomposite than the presence of nanocomposite for 6hrs reaction. Because of, (18) the sulphate ions should be bonded or adsorbed on the surface of nanocomposites in the super acid or sulphate coated nanocomposite and hence the sulphate ion act as to prevent that the adsorption of oxygen from the environment therefore, the monoclinic phase is converted into tetragonal phase but, this is not possible in the case of nanocomposite. The catalytic activity of the nanomaterial would be higher if it were tetragonal, or lower if it were monoclinic. As a result, super acids and sulphate coated nanocomposites has higher catalytic activity than nanocomposites.



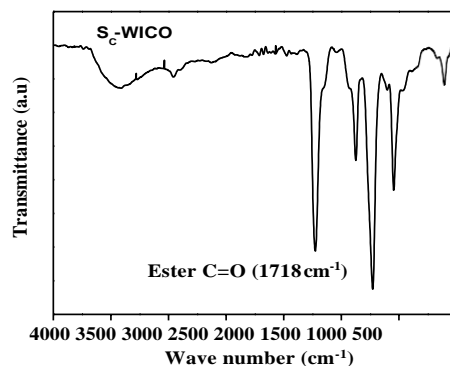
(i)



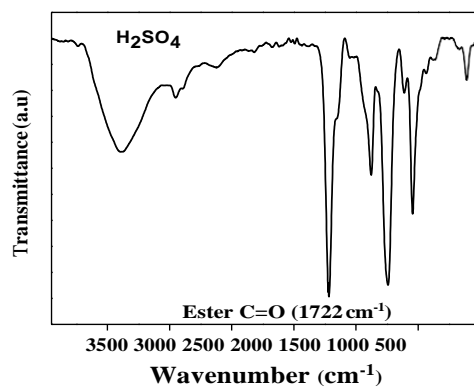
(j)



(k)



(l)



(m)

FT-IR of residue on using H₂SO₄

Figure 8: FT-IR of residue on added (a) Sc-ICNO, (b) Sc-WCNO, (c) Sc-WINO, (d) Sc-WICO, (e) H₂SO₄

When comparing between sulphuric acid (H₂SO₄) and super acid, the water produced during the esterification reaction is virtually closer to each other, meaning that the solid super acid catalytic activity is almost equivalent to the catalytic activity of sulphuric acid solution (H₂SO₄). Similarly, on comparison between sulphate coated nanocomposite and others (nanocomposite, super acids) the catalytic activity of sulphate coated metal oxide is higher than others.

The resulting residue solutions are examined by FT-IR spectroscopy after each catalyst-specific esterification process is completed. The ester peak can be seen in the FT-IR spectra of each residue solution, indicating that the ester molecules are created during the esterification reaction of glycerol and acetic acid in the presence of either nanocomposites or super acids, or sulphate coated nanocomposites. The FT-IR spectra of the obtained residue on presence of nanocomposites ICNO, WCNO, WINO, and WICO are shown in figures S₇ (a) - S₇ (d) and their ester peak is shown at 1715 cm⁻¹, 1721 cm⁻¹, 1721 cm⁻¹, and 1718 cm⁻¹, respectively. Figure S₇ (e) - S₇ (h) shows the FT-IR spectra of obtained residue on presence of super acids S_F-ICNO, S_F-WCNO, S_F-WINO, S_F-WICO and its ester peak is appeared at 1714 cm⁻¹, 1720 cm⁻¹, 1721 cm⁻¹, 1718 cm⁻¹ respectively similarly, Figure 8 (a) - 8 (d) exhibits the FT-IR spectra of obtained residue on presence of sulphate coated nanocomposite Sc-ICNO, Sc-WCNO, Sc-WINO, Sc-WICO and its ester peak is appeared at 1721 cm⁻¹, 1720 cm⁻¹, 1721 cm⁻¹, 1718 cm⁻¹ respectively and the figure 8 (e) exhibits that the FT-IR spectra of obtained residue on added sulphuric acid and its ester peak is appeared at 1722 cm⁻¹.

When comparing the catalytic activity of super acid and sulphuric acid (H₂SO₄) with sulphate coated nanocomposites, the catalytic activity of sulphate coated nanocomposite is

higher. However, when comparing the catalytic activity of super acid and sulphuric acid with the overall results, the catalytic activity of super acid is almost equal to that of sulphuric acid (H₂SO₄). Sulphate coated nanocomposite results in a greater quantity of sulphate ions being adsorbed on the surface of its nanocomposite than super acids or H₂SO₄. As a result, the nanocomposite monoclinic phase highly transforms into a tetragonal phase by coating process than sulphonation process. Therefore, the catalytic activity of the synthesised nanomaterial would be enhanced if it were in the tetragonal phase. This is one of the rewards of the nanocomposite coating technique.

3.5.2. Determination of Residual acid strength by Acid-Base titration

Tables 4, 5, 6 and 7 shows, how strong the acetic acid is in the residue solution when metal oxides, solid super acids, or sulphate coated metal oxides are introduced during the esterification. When analysing each residual solution using an Acid-Base titration, the acetic acid concentrations differ from one another. When added each sulphate coated metal oxide S_C-ICNO, S_C-WCNO, S_C-WINO, S_C-WICO in the esterification reaction separately and analysed its residue solution, the strength of acetic acid is low 1.0675 N, 1.1350 N, 1.2100 N, 0.9625 N respectively

Table 4. The strength of Acetic acid present in the residue of ICNO series

Residue solution	ICNO	S _F -ICNO	S _C -ICNO	Standard H ₂ SO ₄ solution
The strength of Acetic acid value	1.5025N	1.2650N	1.0675N	1.1975N

Table 5. The strength of Acetic acid present in the residue of WCNO series

Residue solution	WCNO	S _F -WCNO	S _C -WCNO	Standard H ₂ SO ₄ solution
The strength of Acetic acid value	1.6125N	1.3625N	1.1350N	1.1975N

Table 6. The strength of Acetic acid present in the residue of WINO series

Residue solution	WINO	S _F -WINO	S _C -WINO	Standard H ₂ SO ₄ solution
The strength of Acetic acid value	1.5575	1.3175N	1.2100N	1.1975N

Table 7. The strength of Acetic acid present in the residue of WINO series

Residue solution	WICO	S _F -WICO	S _C -WICO	Standard H ₂ SO ₄ solution
The strength of Acetic acid value	1.8100N	1.2575N	0.9625N	1.1975N

than the strength of acetic acid being in the residue solution on added each metal oxide (ICNO (1.5875N), WCNO (1.6300N), WINO (1.4975N), WICO (1.5425N)) or in the residue solution on added super acid (S_F-ICNO (1.375N), S_F-WCNO (1.2000N), S_F-WINO (1.2575N), S_F-WICO (1.2325N)) because more acetic acid molecules are converted as ester molecules by sulphate coated metal oxides. Because of, the amount of sulphate ions that should be adsorbed on the

surface of the metal oxide in the sulphate-coated metal oxide form should be greater than that of the metal oxide and super acid. As a result, the strength of acetic acid in the residue solution decreases as more acetic acid molecules are converted into ester molecules. Therefore, the catalytic activity of sulphate coated metal oxide is higher than the others. However, the amount of acetic acid in the residual solution is almost identical to the amounts supplied to super acids and H₂SO₄ separately during the esterification reaction.

4. Conclusion

In the research, the co-precipitation approach is used to synthesis the precursor metal oxide, ICNO, which is then modified with sulphuric acid solution to form super acids and sulphate coated nanocomposite. Similar to this, the contiguous exchange of Fe, Co, and Ni components by W results in the synthesis of nanocomposite (WCNO, WINO, and WICO), super acids (S_F-WCNO, S_F-WINO, and S_F-WICO), and sulphate coated nanocomposite (S_C-WCNO, S_C-WINO, and S_C-WICO). With the aid of FT-IR spectroscopy, the functional groups of such synthesised nanocomposite are confirmed as Fe-O, Co-O, Ni-O, W-O, and in super acid, sulphate coated nanocomposite, there is an excess of one functional group SO₄. Thermal studies of synthesised nanomaterials exhibits that the removal of water is observed in the case of nanocomposites on the other hand, the removal of water and sulphur di-oxide is observed in the case of super acids and sulphate coated nanocomposites. The XRD data used to establish that the synthesised nanomaterials are crystal in nature and also the average particle size values of nanocomposites, super acids and sulphate coated nanocomposites vary from 1-4 nm, 1-5 nm, and 1-4 nm respectively. The majority of synthetic nanocomposites have spherical shape, but those covered in super acids and sulphate coated nanocomposites have cubic structures, as shown by their FESEM. The EDX verifies that the synthesised nanomaterials contain the anticipated

components. As shown by measuring the amount of acetic acid present in the residual solution using an Acid-Base titration, a greater number of acetic acid molecules are converted as ester molecules when conducting the esterification reaction in the presence of either super acid or sulphate coated nanocomposite individually than on metal oxide is present.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

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