Novel green sulfated-PWA supported on MCM-41 coated NiFe$_2$O$_4$ MNPs for xanthene and coumarin synthesis

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Abstract

From an environmental and economic point of view, we focused on the preparation of simple catalysts with many advantages such as simple isolation, easy preparation, high stability, and well catalytic activity. Here, we prepared MCM-41 coated NiFe$_2$O$_4$ magnetic nanoparticles and modified their surface with phosphotungestic acid (PWA) and then sulfate. We tested the catalysts' efficiency and reuse towards the formation of xanthene and coumarin derivatives. They can be easily recovered by a simple magnet from the reaction mixture and reused up to several runs without a high decrease in the catalytic activity. The samples have been characterized by SEM, TEM, FT-IR, XRD, VSM, and XPS. XPS indicated the presence of the inverse-cubic spinel phase of NiFe$_2$O$_4$ and the contribution of Fe(III) − O and Ni(II) − O bonds in tetrahedral (T$_h$) and octahedral (O$_h$) sites. The results indicated the good dispersion of sulfate and PWA nanoparticles on the surface and inside NF-MCM-41 which play an important role in increasing the acidity and activity of the catalyst towards the synthesis of xanthene and coumarin derivatives. The catalyst 20S-W/NF-MCM-41-II reveals the highest acidity ($E_i$=586.3 mV) and yields 93.92% 14-aryl-14H-dibenzo[a, j]xanthene and 78.32% 7-hydroxy-4-methyl coumarin.

1. Introduction

In recent decades recyclable catalysts have become important in chemical technologies and pharmaceutical industries. Recycling or reusing catalysts is one of the main aims of green and sustainable chemistry. The catalyst with a long lifetime and high ability for reusing is extremely desirable for industrial applications. So, the economic and environmental considerations are directed mainly to develop new processes that enable the easy separation and reusing of the catalyst. The high activity, selectivity, stability, and low harmful environmental influence are the main requirements of any catalyst to use [1]. Homogeneous solid acid catalysts are known for their very high activity and selectivity, and so they are used widely in many synthetic organic reactions. But they have low stability due to their difficult separation from the reaction mixtures. So, the chemists converted their interests to heterogeneous solid acid catalysts which are easy to handle and can be easily separated from the reaction mixtures allowing the catalyst reuse.

Supports are very important agents in improving the activity, stability, selectivity, and reusing of the catalyst. They aid in the separation of the catalysts from the reaction mixtures [2]. Many materials are used as supports as metal oxides, activated carbon, graphene, and mesoporous materials. Nowadays, Magnetic nanoparticles (MNPs) have attracted the scientific community's attention to be used as efficient supports for catalysts. This can be attributed to their good dispersion in the reaction mixtures without a magnetic field and their easy separation from the product solution after the completion of the reaction by a simple magnetic separation [3]. Also, they can be reused many times without significant loss in their catalytic activity. MNPs contain two components, a magnetic material, such as Co, Ni, or Fe, and a chemical component that has functionality [4].
One of the magnetic nanoparticles is magnetite, Fe$_3$O$_4$, that widely used as catalyst support, but its stability was found to be decreased over time causing a loss of magnetism due to the oxidation process of Fe$^{2+}$ [5]. In contrast, Nano-metal ferrites perform better than magnetite as supports because they have excellent magnetization, mechanical hardness, and thermal stability [6]. They are used in drug delivery, Ferrofluids, and magnetic storage devices [7]. Nevertheless, they have some drawbacks as, high density, self-aggregation, disparity of permittivity and permeability, and few numbers of functional groups [8, 9]. These drawbacks can be eliminated by using a passive coating on the nano-metal ferrites by using an inorganic material such as silica that can reduce the aggregation of the nanoparticles and increase the number of functional groups [10]. In our work, we used NiFe$_2$O$_4$ as MNPs and coated its surface with MCM-41. MCM-41 is mesoporous material used widely as a heterogeneous solid acid catalyst due to its large surface area, high tunable pore diameter, and high chemical, and thermal stability. The presence of Si-OH groups on the surface of MCM-41 modifies the surface by the chemical bonding of organic ligands.

The excellent stability and super acidity of heteropoly acids attract our attention for loading phosphotungstic acid (PWA) on MCM-41 coated NiFe$_2$O$_4$ (NF-MCM-41) and then modifying the surface by sulfate. Sulfated metal ferrite catalysts have many advantages as good acidity, high stability against moisture, air, and heat, easy isolation, low corrosivity to reactors and containers, and being more friendly to the environment [11]. So, they have been extensively used in many organic catalytic reactions, For example, sulfated zinc ferrite has been used for the preparation of nopol by Prins condensation of pinene and paraformaldehyde and can be used in various reactions like isomerization, aldol condensation, and acetalization [12, 13]. The super acidity of these materials is attributed to the Bronsted acid sites, created or already existing, and increased by the presence of neighboring strong Lewis acid sites that can arise from the inductive effect of the sulfate group.

Here, Sulfated PWA loaded on MCM-41 coated Nickel ferrite (S-W/NF-MCM-41) MNPs are prepared by co-precipitation of nickel ferrite with MCM-41 then adding PWA and SO$_4^{2-}$ by impregnation technique. The catalysts’ activities are tested in the formation reactions of dibenzo xanthene and coumarins. Xanthene derivatives have received great attention due to their antibacterial, anti-inflammatory, and antiviral properties [14]. Coumarins are widely used as anticoagulants, anticarcinogenic, and in a wide range of applications as photodynamic therapy for the treatment of tumor cells, laser technology, visualization of biomolecules, and others [15].

2. Experimental
2.1. Preparation of the catalysts

MCM-41 was prepared through the formation of a homogenous solution of 2 g of Cetyltrimethylammonium bromide (CTAB, 98%) dissolved in 100 mL of distilled water under continuous stirring.11.5 ml NH$_4$OH (25%) was slowly added to this homogeneous solution until pH was between 8-9.5. Then, 10 mL of Tetraethyl orthosilicate (TEOS, 99%) was added drop by drop until obtaining white
precipitate. The precipitate was filtrated, washed well with deionized water, then dried at 80 °C for 24 h, and finally calcined at 550 °C for 4 h [16].

MCM-41 coated Nickel ferrite (NF-MCM-41) catalyst was prepared using the same procedures but 1 mmol of NiCl₂·6H₂O and 2 mmol of FeCl₃ dissolved in 20 mL of distilled water were added to the homogeneous mixture and stirred well for 30 minutes before adding NH₄OH solution [17].

PWA-supported MCM-41 coated Nickel ferrite (W/NF-MCM-41) catalyst was prepared by an impregnation method. 1 g of calcined NF-MCM-41 was dispersed under vigorous stirring into a solution of the desired amount of PWA in 20 mL of water for 2 h to obtain 10 wt.% PWA. After removing water by evaporation, the sample was dried at 80 °C in an oven and then calcined at 450°C for 4 h and designated as 10W/NF-MCM-41.

Sulfated PWA-supported MCM-41 coated Nickel ferrite (S-10W/NF-MCM-41) MNPs were prepared also by an impregnation method. 1 g of 10W/NF-MCM-41-II was dispersed under vigorous stirring into a solution of the desired amount of 3 M H₂SO₄ for 2 h to prepare (5, 10, 15, 20, 25, 30, 35, and 50) wt. % S-10W/NF-MCM-41. The samples were soaked for 24 h, then dried at 80°C and calcined at 450°C. The sample 20S-10W/NF-MCM-41 was calcined at 400 and 550°C to study the effect of calcination temperature on it. The numbers I, II, and III were added to the catalyst symbol to distinguish between the different calcination temperatures; 400, 450, and 500°C, respectively.

For studying the effect of different supports, we prepared three different catalysts, 20 wt. % sulfate supported NF-MCM-41, 20 wt. % sulfate supported MCM-41 and 20 wt. % sulfate supported W-MCM-41 to obtain 20S/NF-MCM-41, 20S/MCM-41, and 20S-10W/MCM-41 catalysts, respectively.

2.2. Characterization techniques

X-ray measurements were used to obtain the crystalline structure of the prepared catalysts using Philips's apparatus PW 150 using Ni filtered Cu Kα radiation (λ = 1.540Å) at 40 kV. FT-IR spectra of the samples between 400 and 4000 cm⁻¹ were measured by Thermo SCIENTIFIC NICOLET iS10 apparatus. SEM is used to give the images of the sample's surface with the JEOL Model JSM 6510LV SEM scanning electron microscope. TEM images were estimated using A JEOL JEM 1200 EXII electron microscope working at 120 kV. X-ray photoelectron spectroscopy, XPS, is a surface-sensitive quantitative spectroscopic technique that is used to measure the elemental composition, empirical formula, chemical state, and electronic state of the elements that exist within a material. The energy of an X-ray with wavelength is known (for Al Kα X-rays, E_{photon} = 1486.7 eV). The magnetic properties of the catalysts were examined by a vibrating sample magnetometer (VSM). The range of the applied field was −20000 to 20000 Oesterd.

2.3. Surface-acidity measurements

The total number of acid sites of the prepared MNPs were measured through the potentiometric-titration method [18]. 0.05 g of the catalyst was activated in an oven for two hours, then suspended in 20 mL
acetonitrile and stirred for about three hours. The suspension was titrated against n-butylamine (0.02 N) with a rate of 0.005 mL/min. The variation of electrode potential is recorded with an Orion 420 digital model.

The type of acid sites of the MNPs whether Brønsted or Lewis was determined through pyridine adsorption at room temperature [19]. The catalysts were heated at 250°C in a high-vacuum oven, then the oven flashed with pyridine. After 30 days the excess pyridine was removed and the acid sites of the catalysts were measured using Thermo SCIENTIFIC NICOLET iS10 FT-IR spectrophotometer.

2.4. Catalytic activity

2.4.1. Synthesis of xanthene derivate

Xanthene derivative was synthesized through the addition of 0.05 g of the catalyst to a mixture of 2 mmol of 2-naphthol, and 1 mmol of benzaldehyde in a round-bottomed flask and heated at 120 °C in the oil bath for 180 minutes. After completion of the reaction, and examination by TLC, the catalyst was separated easily from the product by the magnet and washed well for reuse. The separated product was washed with water, recrystallized, and dried at 80 °C to be calculated according to the equation

\[
\text{Yield\%} = \left( \frac{\text{Obtained Product weight}}{\text{Theoretical Product weight}} \right) \times 100
\]

The FTIR of the obtained product is identical to the one reported in the literature [20, 21].

2.4.2. Synthesis of 7-hydroxy-4-methyl coumarin

7-hydroxy-4-methyl coumarin was synthesized by a reaction of 2 mmol ethyl acetoacetate and 1 mmol resorcinol in presence of 0.1 g of the prepared catalyst in a 50 mL round flask placed in an oil bath and refluxed for 2 h at 120 °C [16]. The resultant mixture was filtered and added to crushed ice for precipitation. The catalyst was separated from the product by the magnet and reused while the product was washed well, recrystallized, and dried well to calculate its percent as mentioned previously. The product is characterized by melting point (185 °C) and FT-IR.

3. Results And Discussion

The fabrication of S-W/NF-MCM-41 MNPs was occurred, as shown in Scheme 1, through a straightforward four-step procedures. Firstly, magnetic NiFe₂O₄ was prepared by a co-precipitation method. Secondly, the surface was coated with a thin layer of MCM-41. Thidly, 10 wt.% PWA was loaded on the surface. Finally, different amounts of sulfate were loaded onto the surface.

3.1. XRD

Figure 1 shows the XRD patterns of NF-MCM-41, 10W/NF-MCM-41, 20S-10W/NF-MCM-41, 20S/NF-MCM-41, 20S-10W/MCM-41 and 20S/MCM-41 catalysts. A broad peak appears in the samples with MCM-41 at
\[ \theta = 15-30^\circ \] reflecting its amorphous nature [16]. The XRD pattern of NF-MCM-41 exhibits (220), (311), (400), (422) and (440) planes characteristic of face-centered cubic spinel structure of nickel ferrite at \( \theta = 30.1, 35.7, 43.1, 57.3 \) and 62.8\(^\circ\), respectively [22, 23]. The intensities of these peaks increase by the addition of 10 wt.% PWA, this may be ascribed to the good dispersion of PWA nanoparticles in the NF-MCM-41 pores due to the smaller pore size of PWA compared with that of MCM-41 [24]. By loading 20 wt.% sulfate, the degree of crystallization is decreased than that of the catalysts without sulfate treatment [20]. Adding of \( \text{SO}_4^{2-} \) inhibited the growth of crystalline grains of 10W/NF-MCM-41 and refers to good dispersion of \( \text{SO}_4^{2-} \) on 10W/NF-MCM-41 surface. The possible mechanism for the prevention of the growth of crystalline grains by sulfate could be observed according to the defect sites on the surface of 10W/NF-MCM-41 that are assumed to play a key role in the crystal growth. The addition of sulfate species can occupy or deactivate the defect sites of 10W/NF-MCM-41. Also, the \( \text{SO}_4^{2-} \) species on the surface of W/NF-MCM-41 inhibit direct contact of particles according to the steric effect [22]. This can be confirmed by the examination of the patterns of 20 wt.% sulfate in different supports.

### 3.2. FTIR Spectroscopy

By investigating the FTIR spectra for the prepared catalysts as shown in Fig. 2A, we find that all the samples maintain the mesoporous structure of MCM-41 by revealing the peaks at 473, 805, 969, and 1000–1330 cm\(^{-1}\) characteristic of Si-O-Si and Si-OH bonds [16, 25]. The samples containing NF reveal a more intense peak at 459 cm\(^{-1}\), characteristic of Fe-O bond and octahedral site Fe\(^{3+}\) vibrations and stretching overlaps with that of Si-O bond, and peak at 589 cm\(^{-1}\), characteristic of Ni-O bond and tetrahedral site Ni\(^{2+}\) vibrations and stretching [26, 27]. The characteristic peaks of O-H stretching vibration appear at 1644 and 3460 cm\(^{-1}\). The spectra containing PWA reveal peaks assigned to Keggin anions of PWA at approximately 1081, 955, and 809 cm\(^{-1}\). These peaks, attributed to \( \nu_{\text{as}}(\text{P-O}_a) \), \( \nu_{\text{as}}(\text{W-O}_a) \), \( \nu_{\text{as}}(\text{W-O}_b-W) \), respectively and overlap with that of MCM-41 causing an increase in the intensity. A new peak appears in the spectra of the sulfated samples at 665 cm\(^{-1}\) due to the bidentate chelating structure of \( \text{SO}_4^{2-} \) [28, 29]. The partially ionic nature of the S-O bond is important for the Brønsted acid sites in sulfated samples [30, 31]. Figure 2B reveals the effect of calcination temperature on the IR spectra of 20S-10W/NF-MCM-41. When the calcination temperature increases to 550\(^\circ\)C, the intensities of the bands decrease, this may be due to the decomposition of sulfate to \( \text{SO}_3 \) gas [32].

### 3.3. Scanning Electron Microscopy (SEM)

SEM images in Fig. 3 reveal irregular hexagonal and spherical shapes of MCM-41 and NF nanoparticles with some few plates of PWA. By loading sulfate, the particles’ size decrease, and all the shapes change into irregular spherical ones with maintaining the morphology of W/NF-MCM-41. In presence of sulfate ions as \( \text{SO}_4^{2-} \) species on the surface of the support, the crystallite size decreases due to the inhibition of the growth of the particles. This type of effect is also noticed in \( \text{PO}_4^{3-} \) and \( \text{WO}_3 \) [33]. Increasing the calcination temperature on the sample 20S-10W/NF-MCM-41 to 550 \(^\circ\)C, results in increasing the particle size may be due to the partial decomposition of sulfate on the surface of the support [34].
3.4. Transmission electron microscopy (TEM)

Figure 4 exhibits TEM images for the prepared catalysts. All the samples maintain the mesoporous nature of MCM-41. The sample 10W/NF-MCM-41 with different magnifications reveals the fine dispersion of PWA particles on the surface of the support. The modification of the NF-MCM-41 surface by sulfate produces a dark region that covers most of the surface of the support. By increasing the calcination temperature for the sample 20S-10W/NF-MCM-41 from 450 to 550°C, partial evaporation of SO$_3$ can occur as illustrated before [35]. TEM image for 20S-10W/MCM-41 confirms the difference between the hexagonal structure of MCM-41 as support and the spherical structure of NF-MCM-41 as support.

3.5. X-ray photoelectron spectroscopy (XPS)

The XPS for 10W/NF-MCM-41, 20S-10W/NF-MCM-41-II, and 20S-10W/NF-MCM-41-III catalysts and their fitting results are shown in Fig. 5. The survey scan of 10W/NF-MCM-41 catalyst indicates including Ni, Fe, Si, W, and O elements. These elements are observed in addition to the S element in 20S-10W/NF-MCM-41-II and 20S-10W/NF-MCM-41-III catalysts. In the figure, we can see the division 2p peak regions of Fe and Ni which infers the presence of two different bonds that may arise from two types of lattice sites for cations. There are three strong peaks of Fe2p; Fe2p$_{3/2}$ at 715.3 and 711.3 eV and Fe2p$_{1/2}$ at 724.3 eV indicating the inverse cubic spinel phase of NF and formation of tetrahedral (T$_h$) and octahedral (O$_h$) bond between Fe$^{3+}$ and oxygen [36]. Also, the spectra of Ni2p confirm the contribution of Ni$^{2+}$–O bonds in tetrahedral and octahedral sites by reflecting Ni2p$_{3/2}$ peaks at 861.1 and 857.1 eV and Ni2p$_{1/2}$ peak at 873.8 eV [37]. The slight differences observed in the intensity and location of the peaks for the examined catalyst may be due to the change in their chemical environment by the loading of sulfate. O1s XPS spectra reveal signals at around 534.1 and 532.9, 530.3 eV matches to O-H, metal-O, and W=O bonds [37]. W4f XPS spectra reflect two strong peaks at 35.9 eV and 38.1 eV due to W4f$_{7/2}$ and W4f$_{5/2}$, respectively [38]. There is only one peak characteristic of Si2p at 103.7 eV and only one peak characteristic of S2p due to sulfur with oxidation number +6.

3.6. Magnetic properties

The magnetic properties of NF, 10W/NF-MCM-41, and 20S-10W/NF-MCM-41-II are examined by a vibrating sample magnetometer (VSM) at room temperature. The range of the applied field was – 20000 to 20000 Oesterd. The magnetic saturation, $M_s$, for 10W/NF-MCM-41 and 20S-10W/NF-MCM-41-II catalysts values as shown in Fig. 6 are 12.6 and 11.2 emu g$^{-1}$, respectively. These results reflect the decrease in $M_s$ values compared with that of Nickel ferrite; 15.8 emu g$^{-1}$. This may be attributed to the non-magnetic nature of MCM-41, PWA, and sulfate. However, all the samples are still isolated easily from the reaction mixture with an external magnet [36].

3.7. Surface acidity determination:

3.7.1. Nonaqueous potentiometric titration:
Nonaqueous potentiometric titration can be used to determine the acidity strength via the determination of the initial electrode potential, $E_i$, and the total number of acid sites/g [16]. The values of acidity measurements and the acidity curves are shown in Table 1 and Fig. 7, respectively. As shown in Table 1, the $E_i$ value and the total number of acid sites of NF-MCM-41 catalyst are relatively high compared with that of MCM-41 due to the strong interaction of Si-OH groups of MCM-41 with NiFe$_2$O$_4$. Loading of pure Brønsted acid as PWA on NF-MCM-41 improves the acidity of the surface reaching the $E_i$ value 227 mV [39]. This acidity, as seen in Fig. 7A and Table 1, still increases gradually by loading sulfate on the surface of 10W/NF-MCM-41 and increasing its amount to 20wt.%. Further increase in the sulfate amount above this percent is followed by a gradual decrease in acidity. Firstly, sulfate particles dispersed finely on the surface of 10W/NF-MCM-41 till the complete saturation of the surface and formation of a monolayer at 20wt.%. which leads to increasing the acidity, then the increase of sulfate amount above 20wt.% causes aggregation of the sulfate particles on the support surface and formation of other layers which leads to decreasing the acidity [18]. Figure 7B and Table 1 reflect the important role of both NiFe$_2$O$_4$ and PWA in enhancing the surface acidity by studying the differences between the acidity values of 20S-10W/NF-MCM-41, 20S/NF-MCM-41, 20S-10W/ MCM-41 and 20S/MCM-41 catalysts. From Fig. 7C and Table 1, we can study the effect of calcination temperatures on the acidity measurements. The acidity of the 20S-10W/NF-MCM-41 catalyst increases firstly by increasing the calcination temperature from 400 to 450 °C, then decreases at 550 °C. This means that the sample 20S-10W/NF-MCM-41-II has the maximum acidity values. The decrease in the surface acidity at 550 °C may be due to the evaporation of some sulfate groups and/or change in the sulfate groups’ structures.
Table 1
Acidity and catalytic activity studies of the prepared MNPs.

<table>
<thead>
<tr>
<th>sample</th>
<th>E_i (mV)</th>
<th>No. of acid sites g(^{-1}) . 10(^{-20})</th>
<th>B/L</th>
<th>Xanthene (%)</th>
<th>Coumarin (%)</th>
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<tbody>
<tr>
<td>MCM-41</td>
<td>88</td>
<td>0.13</td>
<td>......</td>
<td>6.70</td>
<td>.....</td>
</tr>
<tr>
<td>NF-MCM-41</td>
<td>195</td>
<td>0.56</td>
<td>......</td>
<td>40.68</td>
<td>.....</td>
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<tr>
<td>10W/NF-MCM-41</td>
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<td>1.29</td>
<td>0.73</td>
<td>49.87</td>
<td>30.39</td>
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<td>55.53</td>
<td>34.49</td>
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<td>1.73</td>
<td>68.52</td>
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<tr>
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<td>64.67</td>
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</table>

3.7.2. FTIR Spectra of adsorbed Pyridine

To determine the nature and the type of acid sites, the FTIR spectra of adsorbed pyridine on the prepared catalysts are determined and shown in Fig. 8. Also, the ratio of Brønsted to Lewis acid sites (B/L) is calculated from the area of each peak and tabulated in Table 1. As shown in Fig. 8A and Table 1, The sample 10W/NF-MCM-41 reveals three peaks at 1449, 1493, and 1545 cm\(^{-1}\), characteristic of Lewis, Lewis + Brønsted, and Brønsted acid sites, respectively. The heteropoly acids in general are known by their Bronsted acidity, while the enhancement of Lewis acidity may become from the presence of NF which is the source of Ni\(^{2+}\) and Fe\(^{3+}\) transition metal cations which work as electron acceptors [19]. By loading sulfate on 10W/NF-MCM-41, there is one peak characteristic of Lewis acid sites appears at 1451 cm\(^{-1}\), three peaks characteristic of Brønsted acid sites appear at 1543, 1560, and 1578 cm\(^{-1}\), and one common
peak of Brønsted and Lewis acid sites at 1493 cm$^{-1}$. Increasing the amount of sulfate increases the intensities of these peaks gradually and increases the ratio of B/L to 20wt.%sulfate, then any increase in the amount of sulfate above 20wt.% decreases both peak intensities and B/L ratio. The enhancement of Lewis acidity by the presence of sulfate may be ascribed to the presence of the surface sulfur complex which has a covalent S = O bond, that acts as an electron-withdrawing group that increases the Lewis acidity on the adjacent metal cations by the inductive effect [40]. While the enhancement of the Brønsted acidity results from the generation of more Brønsted acid sites by the coordinated surface sulfate groups. It is expected that, at a low amount of sulfate (< 20wt.%), the surface is rich with hydroxyl, bridging hydroxyl groups, and bisulfate groups, and by raising the temperature, the bisulfate undergoes a kind of condensation reaction with the adjacent hydroxyl groups to evolve water and forms bridging bidentate sulfate group on the surface. The water may then react with the adjacent sulfate groups to yield adsorbed bisulfate (HSO$_4^-$) and hydroxyl groups [41]. The decrease of the B/L ratio and surface acidity above 20wt%. sulfate may be due to the agglomeration of sulfate species on 10W/NF-MCM-41 surface and the formation of poly layers [18]. Table 1 and Fig. 8B reveal the effect of calcination temperatures on the Lewis and Brønsted acid sites for the 20S-10W/NF-MCM-41 catalyst. As the calcination temperature increases from 450 to 550 °C, the number of Brønsted and Lewis acid sites and consequently the B/L ratio decrease. This may be resulted from the removal of some sulfate groups by raising the calcination temperature [42]. By examining Fig. 8C and Table 1, we can compare the effect of 20wt.% S on different supports. As seen, the catalysts can be arranged in the order 20S-10W/NF-MCM-41-II  20S-10W/MCM-41-II  20S/NF-MCM-41-II  20S/MCM-41-II according to the acidity and the B/L ratio. This explains the role of PWA and NF in enhancing acidity.

### 3.8. Catalytic activity

#### 3.8.1. Synthesis of 14-aryl-14H-dibenzoanthene

The preparation of 14-aryl-14H-dibenzoanthene occurred via the reaction of 2-napthol and benzaldehyde in presence of 50 mg of the activated catalyst at 120 °C for 90 min.

**Reaction Conditions:** Several effects are studied on the catalyst 20S-10W/NF-MCM-41-II for testing the best reaction conditions. The best molar ratio of 2-naphthol: benzaldehyde is found to be 2:1 as it yields 93.2% of the product. 1:1, 3:1 and 4:1 molar ratios give 60.4, 85.2, and 68.3% of the product, respectively. By changing the time of the reaction from 30, 60, 90 to 120 min, the %yield of the product changes from 60.5, 77.2, 93.2, and 92.9%, respectively. So, 90 min is selected as the best reaction time. Also, by testing the reaction using different weights of 20S-10W/NF-MCM-41-II catalyst as 30, 50, 70, and 100 mg. The best yield (93.2%) is obtained by the weight of 50 mg while 30, 70 and 100 mg give yields of 69.5, 93.0, and 92.9%, respectively.

**Effect of sulfate content**

As investigated in Table 1, By using MCM-41 as a catalyst for the formation of 14-aryl-14H-dibenzoanthene, the yield is only about 6.7%. While by using NF-MCM-41 as a catalyst the yield reaches
40.7% due to the presence of Lewis acid sites. Loading 10wt.% PWA increases the yield to 49.9% due to the enhancement of both Lewis and Brønsted acid sites. By loading sulfate on 10W/NF-MCM-41 and increasing its content from 5 to 20 wt.%, the yield increases to 93.9% then decreases by increasing the sulfate content above 20wt.%. This is in good agreement with the results of B/L ratio, total acidity, and $E_i$ as illustrated in Fig. 9A. The synthesis reaction of 14-Aryl-14H-dibenzoxanthenes is found to be catalyzed by Brønsted and/or Lewis acid sites.

**Effect of calcination temperatures**

The effect of calcination temperature on the synthesis of xanthene for 20S-10W/NF-MCM-41 catalyst is shown in Table 1 and Fig. 9B. By raising the calcination temperatures from 400 to 450 °C, the yield increases from 89.2–93.9%, respectively, then decreases again to 91.6% by raising the temperature to 550 °C in a good relationship with the $E_i$, the total number of acid sites and the B/L ratio.

**Effect of different supports**

By comparing the results in Table 1, we found that 20S/MCM-41-II catalyst yields 69.2% of xanthene. This percentage increases to 81.7, 88.5, and 93.9% in the case of using 20S/NF-MCM-41-II, 20S-10W/MCM-41-II, and 20S-10W/NF-MCM-41-II catalysts, respectively. This reflects the role of the support in enhancing the catalytic activity as well as the acidity.

**The reaction Mechanism**

The mechanism for the formation of 14-aryl-14H-dibenzoxanthenes using 20S-10W/NF-MCM-41 MNP as shown in Scheme 2 can be explained via the activation of the benzaldehyde carbonyl group by the acid sites of the catalyst resulting in a fast nucleophilic attack of 2-naphthol and synthesis of a carbocation. Then the carbocation converts to an intermediate which finally converts to 14-aryl-14H-dibenzoxanthenes via the cyclization and dehydration step [43].

**Comparison studies**

To reveal the good effects of S-W/NF-MCM-41 MNPs, the comparison of the xanthene yields obtained from our results are examined with previously reported using other catalysts and tabled in Table 2. According to the comparison, the prepared catalyst in our work reflects a good percent of the xanthene yield in comparison with other catalysts. Many advantages can distinguish our catalyst from the others as ease of separation from the reaction medium, low reaction time, reusing, and the high purity of the yield.
Table 1
Comparison between different catalysts in the formation of 14-aryl-14H-dibenzoxanthene.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polytungstozincate acid</td>
<td>81</td>
<td>80</td>
<td>60</td>
<td>[44]</td>
</tr>
<tr>
<td>Cellulose sulfuric acid</td>
<td>87</td>
<td>120</td>
<td>110</td>
<td>[45]</td>
</tr>
<tr>
<td>HO$_3$S-SNPs</td>
<td>92</td>
<td>45</td>
<td>110</td>
<td>[46]</td>
</tr>
<tr>
<td>SO$_3$H-functionalized</td>
<td>90</td>
<td>60</td>
<td>80</td>
<td>[47]</td>
</tr>
<tr>
<td>N-sulfonic acid PVP Cl</td>
<td>80</td>
<td>30</td>
<td>100</td>
<td>[48]</td>
</tr>
<tr>
<td>Silica sulfuric acid</td>
<td>89</td>
<td>45</td>
<td>80</td>
<td>[49]</td>
</tr>
<tr>
<td>S-W/NF-MCM-41</td>
<td>94</td>
<td>90</td>
<td>120</td>
<td>Our work</td>
</tr>
</tbody>
</table>

Reusability

After completing the reaction, the 20S-10W/NF-MCM-41-II catalyst was separated easily by a magnet from the reaction medium and washed well with ethyl alcohol, then dried in an oven at 100 °C for 2 h and reused in other reactions. It can be reused at least three runs without a high loss in the catalytic activity as seen in Fig. 10.

3.8.2. Synthesis of 7-hydroxy-4-methyl coumarin:

7-hydroxy-4-methyl coumarin can be formed easily from the reaction between 1 mmol resorcinol and 2 mmol ethyl acetoacetate in presence of 100 mg of the activated catalyst at 120 °C for 2 h.

The reaction conditions: The best reaction conditions are examined by studying the effects of some parameters on the reaction using the 20S-10W/NF-MCM-41-II catalyst. By studying the effect of different molar ratios of resorcinol and ethyl acetoacetate; 1:1, 1:1.5, and 1:2; the % yield is found to increase from 45.6 to 64.3, 78.3%, respectively, then decrease to 75.2% at 1:3 molar ratio due to blocking of the catalyst acid sites as a result of the surface saturation by ethyl acetoacetate [19]. So, we used resorcinol: ethyl acetoacetate with a 1:2 molar ratio in the synthesis of 7-hydroxy-4-methyl coumarin. In addition, the effect of different weights of the catalyst is studied and 100 mg is taken as the best catalyst weight for the reaction as it gives the best yield of 78.3% compared with 30, 50, and 70 mg which yield 46.2, 59.2 and 70.6%, respectively. On another hand by studying the effect of the reaction time on the reaction yield, it is found that the yield increases gradually with increasing the reaction time from 30 min to 120 min every 30 min then becomes constant after 120 min. So, 120 min is taken as the best reaction time for the
coumarin synthesis. Finally, we studied the effect of different temperatures, 80, 100, 120, and 140 °C, on the reaction and 120 °C gives the best results so it is used as the temperature for the reaction.

Effect of sulfate content: By investigating Table 1, we can notice that no coumarin yielded by using MCM-41 or NF-MCM-41 but by using 10W/NF-MCM-41, the yield reaches 30.39%. This reflects the role of Brønsted acid sites of PWA in the coumarin synthesis and indicates that the mechanism of the reaction is dependent on the Brønsted acid sites and explains the absence of the yield in the case of using MCM-41 or NF-MCM-41 as catalysts because they have Lewis acid sites \[ \text{[39, 50]} \]. By loading sulfate on 10W/NF-MCM-41 and increasing its content from 5 to 20 wt.%, the yield increases to 78.32% then decreases by increasing the sulfate content above 20 wt.%. This is in good agreement with the results of the B/L ratio, total acidity, and \( E_i \) as illustrated in Table 1 and Fig. 11A.

Effect of calcination temperatures

The effect of calcination temperature on the coumarin synthesis for 20S-10W/NF-MCM-41 catalyst is illustrated in Fig. 11B and Table 1. By raising the calcination temperatures from 400 to 450 °C, the yield increases from 73.23–78.32%, respectively, then decreases again to 75.94% by raising the temperature to 550 °C in a good relationship with \( E_i \), total number of acid sites and B/L ratio.

Effect of different supports

By comparing the results in Table 1, we found that 20S/MCM-41-II catalyst yields 60.47% of coumarin. This percentage increases to 64.67, 75.19, and 78.32% in the case of using 20S/NF-MCM-41-II, 20S-10W/MCM-41-II, and 20S-10W/NF-MCM-41-II catalysts, respectively. This reflects the role of the support in enhancing the catalytic activity as well as the acidity.

The reaction mechanism: The suggested mechanism of the synthesis of 7-hydroxy-4-methyl coumarin in presence of S-W/NF-MCM-41 MNPs can be summarized in three steps: 1) The protonation of the carbonyl group of EAA is activated by the \( H^+ \) of Brønsted acid sites, 2) This enhances the nucleophilic-attack of the hydroxyl group of resorcinol causes a formation of an intermediate, 3) The intermediate is converted to the 7-hydroxy-4-methyl coumarin through cyclization via intermolecular-condensation as illustrated in Scheme 3.

The comparison studies

We compared our catalyst towards the formation of 7-hydroxy-4-methyl coumarin with that previously reported using other catalysts as revealed in Table 3. The prepared catalyst in our work reflects a good percent of the coumarin yield in comparison with other catalysts. Many advantages can distinguish our catalyst from the others as ease of separation from the reaction medium, low reaction time, reusing, and the high purity of the yield.
Table 3
Comparison between different catalysts in the formation of 7-hydroxy-4-methyl coumarin.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic ionic liquid</td>
<td>2</td>
<td>75</td>
<td>[51]</td>
</tr>
<tr>
<td>SA-MIL-101</td>
<td>2</td>
<td>73</td>
<td>[52]</td>
</tr>
<tr>
<td>PMA/ Cr-Mg-MOF</td>
<td>2</td>
<td>69</td>
<td>[39]</td>
</tr>
<tr>
<td>H-Beta zeolite</td>
<td>4</td>
<td>72</td>
<td>[53]</td>
</tr>
<tr>
<td>S-W/NF-MCM-41</td>
<td>2</td>
<td>78</td>
<td>This work</td>
</tr>
</tbody>
</table>

Reusability of catalyst

Recycling the catalyst is an important test for any industrial process. After completing the reaction, the catalyst was separated from the reaction mixture by a magnet and washed well with ethyl alcohol, then dried in an oven at 100 °C for 2 h and reused in other reactions. There is a slight loss in the activity of the 20S-10W/NF-MCM-41-II catalyst after three times as shown in Fig. 12.

4. Conclusion

In summary, we prepared novel magnetic catalysts, including sulfated-PWA supported on MCM-41 coated nickel ferrite. Although modification of NF-MCM-41 by 10 wt.% PWA enhances the acidity and the catalytic activity towards the formation of xanthene and coumarin, modification of 10W/NF-MCM-41 by $\text{SO}_4^{2-}$ enhances them more. The prepared materials are found to be very good in the synthesis of coumarin and xanthene derivatives. The simple magnetically isolation, high catalytic activity, low reaction time, and reusability give the catalysts an economic and industrial interest.

Declarations

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Authors Contributions: All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by W. S. Abo El-Yazeed, O. R. Hayes and Awad I. Ahmed. The first draft of the manuscript was written by W. S. Abo El-Yazeed and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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**Schemes**

Schemes 1-3 are available in the Supplementary Files section.

**Figures**
Figure 1

XRD of the prepared magnetic nanoparticles.
Figure 2

(A) FTIR spectra of the prepared catalysts calcined at 450 °C, and (B) FTIR spectra of 20S-10W/NF-MCM-41 catalysts calcined at different temperatures.
Figure 3

SEM images of the prepared magnetic nanoparticles.
Figure 4

TEM images of the prepared magnetic nanoparticles.

Figure 5
High-resolution XPS of the prepared magnetic nanoparticles.

Figure 6

The saturation magnetization values for the magnetic nanoparticles.
Figure 7

Nonaqueous potentiometric titration for the prepared magnetic nanoparticles.
Figure 8

FTIR spectra of pyridine adsorbed on the prepared MNPs.
Figure 9

The effect of total number of acid sites, $E_i$, B/L ratio, (A) Sulfate content and (B) calcination temperatures on xanthene synthesis.
Figure 10

Reuse of 20S-10W/NF-MCM-41-II MNP in xanthene synthesis.
Figure 11

The effect of the total number of acid sites, $E_i$, B/L ratio, (A) sulfate content, and (B) calcination temperatures on coumarin synthesis.
Figure 12

Reuse of 20S-10W/NF-MCM-41-II catalyst in coumarin synthesis.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Scheme1.png
- Scheme2.png
- Scheme3.png