Synthesis, Characterization and Application of Phosphotungstic Acid /MCM- 41 Coated Nickel Ferrite

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Abstract: Phosphotungstic acid (PWA) supported on MCM-41 coated nickel ferrite was prepared by impregnation of PWA. The samples have been characterized using X-ray analysis (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Transmission Electron Microscopy (TEM). Acidity has been measured by using non-aqueous potentiometric titration of n-butylamine in acetonitrile and catalytic activity has been examined in synthesis of xanthene. The results indicated that the pore structure of MCM-41 was an ordered hexagonal and changed into spherical in MCM-41 coated nickel ferrite. The results showed also that there was an excellent dispersion of PWA on MCM-41 coated nickel ferrite surface. The acidity measurements indicated that the acidity and catalytic activity sharply increase by adding nickel ferrite and PWA to MCM-41.The sample doped with 55 wt. % PWA/MCM-41 coated nickel ferrite measures the highest surface acidity (592.4mV) with catalytic conversion reached to (94.7%). The catalysts can be separated from the reaction mixture by using a magnet.

keywords: MCM-41, Nickel ferrite, xanthene , Phosphotungstic acid

1.Introduction

Preparation of recyclable catalysts is importance for chemical technologies and pharmaceutical industries [1]. Mesoporous materials have a unique structure, high thermal, stability, good distribution of acid sites, selectivity and can be used in many important catalytic reaction .MCM-41 is one of highly ordered mesoporous materials [2, 3]. MCM-41have the lack of crystallinity of their pore walls. MCM-41 with

silanol groups (single or germinal) and siloxane bridges on its surface can be simply modified chemical bonding of organic ligands with silanol groups. Modification of MCM-41by metal ferrite is an important tool because the magnetic catalysts can be isolated from the reaction by using external magnet and avoided loss catalysts.Metal ferrite are used in many applications such as magnetic devices[4], magnetic resonance imaging, microwave devices [5], magnetic labeling of biological systems [6-9] and environmental remediation [10]. Disadvantage of metal ferrite is aggregation due to the self-interactions. To prevent aggregation, addition of SiO_2 and other inert surface and then modified by

phosphotungstic acid by the same method has been reported [11]. HPAs ($H_3PW_{12}O_{40}$)can be immobilized on silica coated nickel ferrite to obtain a heterogeneous catalyst system that has high surface area for excellent catalytic activity.HPAs are strong Bronsted acids due to the density of the anion over the large sized polyanion [12], leading to a weak interaction with the counter-ions. Herein, the results showed that nickel ferrite and phosphotungstic acid (PWA) content have affected on the structural properties, surface acidity and activity of MCM-41 catalysts. These catalysts are used for the synthesis of 14-aryl 14-H dibenzoxanthene. Xanthenes derivatives have a great important due to their antibacterial [13], anti-inammatory[14],antiviral properties[15]and photodynamic therapy in the treatment of tumor cells. Synthesis of benzoxanthenes were carried out by the reaction of aldehydes with 2-naphthol in the presence of catalysts such as wet cyanuric chloride, molecular iodine and silica/ sulfuric acid. These catalysts had disadvantages such as a small yield, use of special apparatus, long time of reaction and unreusable catalysts. HPA

catalysts can be used as safety alternative catalysts to enter dangerous mineral acids such as H_2SO_4 and HF. The reusability tests of the magnetic catalysts observed that the catalysts can be used several times without losing in its activity [16].

2. Experimental

2.1. Preparation of the catalyst

To prepare MCM-41, 2 g of Cetyltrimethyl ammonium bromide (CTAB, 98 %) was dissolved in 100 mL of distilled water then,an aqueous solution of ammonia (25%) was slowly added until pH was between 8 and 9.5 (~ the amount of ammonia was 11.5 mL) and stirring for 30 minutes. 10 mL of tetraethylorthosilicate (TEOS ,99%) was added drop by drop until a white precipitate was obtained , and then stirring for 2 h. The precipitate was filtrated, washed to remove chlorine and other impurities, dried at (60-80 °C) for 24 h and calcined in muffle at 550 °C for 4h[17].Preparation of MCM-41 coated magnetic nickel ferrite was carried out by using the same procedure but after drying MCM-41 , 20 mL of distilled water containing1 mmol of $NiCl_2.6H_2O$ and 2 mmol of $FeCl_3$ were added and then stirring for 30 min before adding an aqueous solution of ammonia.

By using an impregnation method, PWA was loaded on MCM-41 coated nickel ferrite. Thus 1g of calcined MCM-41 coated nickel ferrite was added to a solution of 20mL distilled water containing the desired amount of PWA to obtain 55 wt % PWA. The mixture was stirring

for 2 h at room temperature and then the water was removed by evaporation and the sample was dried at 80 °C overnight and then calcined at 450 °C in a muffle for 4h.

3. Characterization techniques

3.1. X-ray analysis (XRD)

X-ray diffraction is used as a powerful tool to estimate the crystalline structure of synthesized samples according to Bragg's law.

$$n\lambda = 2d_{100}\sin(\theta)$$

$$a_0 = 2d_{100}/\sqrt{3}$$

X-ray diffraction patterns was recorded using Philips apparatus PW 150 which is used

Ni filtered Cu Kα radiation($\lambda = 1.540$Å) at 40 kV. 2θ angle from 1 to 80°

3.2.Fourier Transform Infrared Spectroscopy (FT-IR)

.The region of IR scanning is between 400-4000 cm^{-1} and with 4 cm^{-1} scans. 0.1 g of KBr with 0.01 g of the sample was pressed into thin wafer which was put inside IR cell and the spectrum was recorded.

3.3. Transmission electron microscopy (TEM)

A Jeol-Jem 1200 EX II electron microscope working at 120 kV was used to obtain image and particle size of the samples. TEM samples were prepared by ultrasonically dispersed an alcohol and drop casting onto strong carbon coated copper grids.

3.4. Surface acidity measurements:

Potentiometric titration method was used to measure, the number and the strenght of acid sites of the solid samples. (0.05 g) of activated solid catalyst (heating the sample at 120 C^o for 2 h) was added in 15 mL acetonitrile and then stirring for 4 h . The suspended catalyst was titrated against 0.02N n-butylamine in acetonitrile in the presence of double junction electrode, the variation of electrode potential with the volume of the titre was recorded with the help of an Orion 420 digital a model.

3.5. Catalytic activity

3.5.1. Synthesis of xanthene derivatives:

The xanthene derivative was synthesized by adding 0.05 g of freshly prepared activated catalyst to a mixture benzaldehyde (1 mmol) and 2-naphthol (2 mmol) in a round bottomed flask and heated at 120°C using an oil bath for 50 min, the used catalyst was recovered from reaction mixture by a simple magnet. After that, the system was cooled to room temperature then the product was isolated and washed with water, followed by recrystallization. The solid product was dried in an oven at 80 $^{°}$C and the % yield was calculated using the following relation :

$$\text{Yield (wt\%)} = \left(\frac{\text{Obtained weight of product}}{\text{Theoretical weight of product}} \right) \times 100$$

4. Results and discussion

4.1. X-Ray analysis

Fig (1) showed the X-ray diffraction patterns of MCM-41, MCM-41coated nickel ferrite and 55wt. % PWA/MCM-41coated nickel ferrite. The figure indicates the amorphous nature of MCM-41 as indicated from the appearance of a broad hump with the range of 2θ from 20^0 to 30^0. MCM-41 coated nickel ferrite, showed XRD diffraction pattern characterized by the presence of different peaks located at $2\theta= 30^0, 35^0, 43^0, 54^0, 65^0$ and 66^0). All the observed peaks confirmed the formation of spinel sturucture. [18-20]. After loading of 55wt% PWA on MCM-41 coated nickel ferrite the intensity of peaks increases.
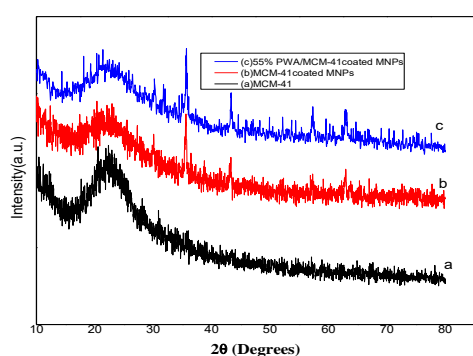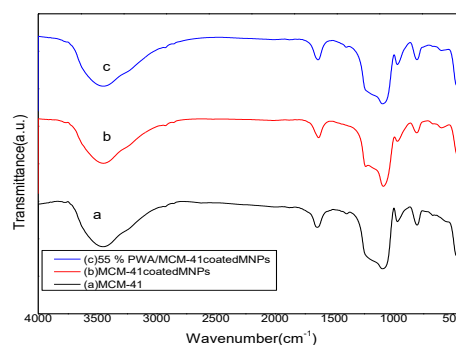

Fig (1): (a) MCM-41, (b) MCM-41coated nickel ferrite and (c) 55% PWA/MCM-41coated nickel ferrite.

4.2. FT- IR spectroscopy

Fig (2) contains the FT-IR spectra of pure MCM-41, MCM-41 coated nickel ferrite and 55wt. % PWA/MCM-41 coated nickel ferrite catalysts calcined at 450 °C. The spectrum of MCM-41 shows a broad band around 1004-1300 cm^{-1} due to the asymmetric vibration of Si-O-Si bond [21]. A broad band at 3460 cm^{-1} was observed in all samples due to the O–H stretching vibration of the adsorbed molecules of water or Si-O-H. The band at 1630 cm^{-1} can be assigned to the bending vibration mode of water. The band at 802 cm^{-1} may be due to symmetric vibration and bending vibration of rocking mode of Si–O–Si. The band at 969cm^{-1} can be observed due to symmetric vibration of Si–OH. The spectrum of MCM-41 coated nickel ferrite shows two bands at 591 and453 cm^{-1} due to octahedraland tetrahedral sites of positive

ions (Fe^{3+} and Ni^{2+}) for spinel type structure.

The intensity of absorptionbands at 967 cm^{-1} decreases after the formation of nickel ferrite and interaction betweenMCM-41 and metal ferrite. The intensity of absorption bands at 594 cm^{-1}increasecompared with MCM-41 which confirms that Si-OH group reactswith Fe-OH due to –OH condensation [22]. The spectra of 55 %PWA onMCM-41 coated nickel ferrite which the intensity of absorption peak at 804, 967, 1080 cm^{-1} increase. According to the fingerprint peaks assigned to keggin anions of PWA at approximately 1080, 967 and 802 cm^{-1}are observed. These peaks were assigned to v(P–O), v(W–O) and v(W–O–W) which can be assigned to the stretching vibrations of P–O, W– O and W–O–W respectively.

Fig (2): FT-IR spectra of (a)MCM-41, (b)MCM-41coated nickel ferrite and (c)55% PWA/MCM-41coated nickel ferrite.

4.3. Morphology characterization (TEM):

TEM technique was performed on MCM-41 sample to confirm the morphology of hexagonal structure Fig (3) [23]. TEM image for MCM-41coated nickel ferrite changes into spherical shape [24].After the addition of PWA,dark spots was observed due to the formation of some nanocrystals of PWA on MCM-41 coated nickel ferrite surface.
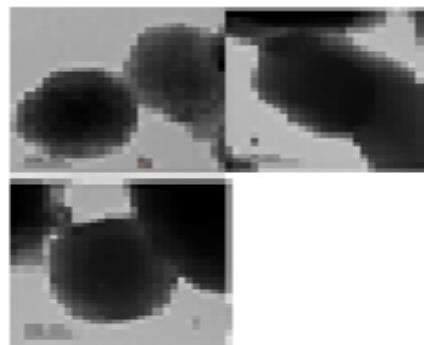
Fig (3): TEM for (a) MCM-41, (b) MCM-41coated nickel ferrite and (c) 55%PWA/MCM41coated nickel ferrite.

4.4. Surface Acidity of the catalysts:

Fig (4) and table (1) indicate that the acidity and the acid strength as indicated from initial electrode potential of MCM-41 is low (E_i=+88mv) due to the presence of weak acid onMCM-41 surface.Coating of MCM-41 with $NiFe_2O_4$ and calcination at $550C^o$ leads to increase the acid strength (E_i =+195.8 mV) due to the appearance of stronger acidic sites of Fe-OH. Addition of PWA to MCM-41 coated nickel ferrite sharply increases the acid strength and the number of acid sites (E_i =+ 592.4mV) [25].
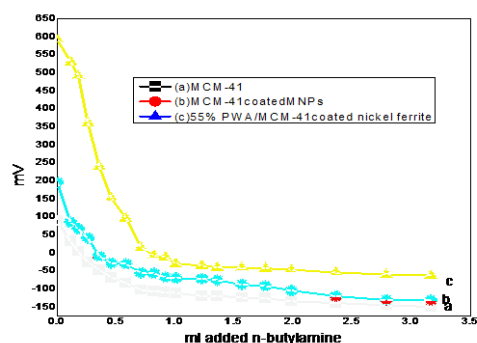
Figure(4): Potentiometric titration curves for MCM-41, MCM-41 coated nickel ferrite and PWA/MCM-41 coated nickel ferrite catalysts calcined at 450 $^°$C.

6. Catalytic activity

6.1. Synthesis of 14-aryl14-H dibenzoxanthene

The product has been obtained from the reaction of 2-naphthol with benzaldehyde in presence of 0.05 g of activated catalyst (by heating the sample at 120 °C in an oven for 1h).The yield of xanthene in the presence of pure MCM-41 is low. The yield increases by using MCM-41coated nickel ferrite due to the presence of strong Lewis acid sites. Loading of MCM-41 coated nickel ferrite sample with 55wt% PWA greatly increasing in catalytic conversion of xanthene(Type of reaction by Bronsted or Lewis reaction) due to the presence of Bronsted and Lewis acid sites, The conversion yield was reached to 94.7% as indicated from Fig(5) and the data presented in Table 1 . According the data of acidity, it seems that the synthesis of xanthenes was related to the surface acidity of the samples.

Table (1): Surface acidity, number of acid sites and yield of xanthene for MCM-41, MCM-41 coated metal ferrite and 55% PWA/MCM-41coated metal ferrite catalysts.

sample	E_i	No of acid sites (g x10^{-20})	Yield% of xanthene
MCM-41	88	0.1	3.9
MCM41coated metal ferrite	195.8	0.5	37.6
55%PWA/MCM-41coated metal ferrite	592.4	6.7	94.7
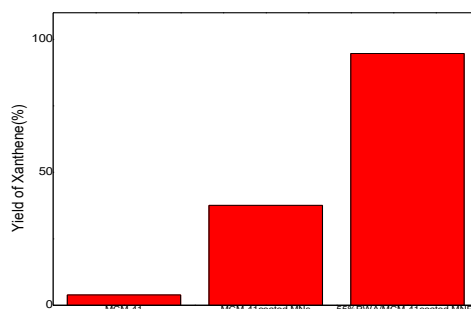
Fig (5): The yield of xanthene for MCM-41, MCM-41 coated nickel ferrite and 55% PWA/MCM-41coated nickel ferrite.

Conclusion

In summary, we have prepared a novel magnetic catalyst of MCM-41 coated metal ferrite supported PWA on silica coated metal ferrite. The magnetic catalysts were characterized by XRD, FT-IR and TEM. Modification of MCM-41 by metal ferrite leads to increase surface acidity and catalytic activity in the synthesis of 14-aryl-14Hdibenzoxanthene.Modification of MCM-41 coated nickel ferrite by loading 55 wt. % PWA improves the surface acidity and catalytic activity which reaches to 94.7%. PWA has Bronsted and Lewis active sites and increases the yield of xanthene. The used catalystscan be isolated from the product by a simple magnet.

6. Reference

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