Synthesis of pyranopyrazoles using $COFe_2O_4$ magnetic nanoparticles functionalized with Melamine Sulfonic acid

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Abstract: In this Research, $CoFe_2O_4$ magnetic nanoparticles functionalized with melamine sulfonic acid, was synthesized and characterized by different techniques such as FT-IR, SEM, EDX, XRD, TGA and VSM. Then, catalytic activities of the synthesized magnetic nanoparticles, was investigated in the synthesis of heterocyclic compounds such as pyranopyrazole derivatives. The $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA magnetic nanoparticles have capability of recovery and reusability for the several times.

Keywords: magnetic nanoparticles, pyranopyrazole, Melamine Sulfonic acid, condensation reaction

INTRODUCTION

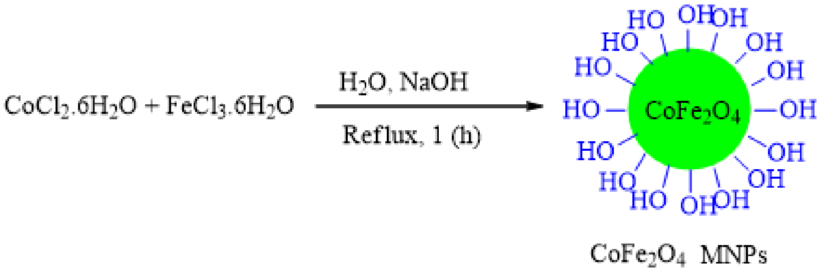
Multicomponent reactions are one of the useful methods for the synthesis of molecules and complex heterocyclic compounds that have a lot of biological activity. Multicomponent-one-pot reactions have a green approach and are actually environmentally friendly. They are very useful in terms of atom saving, efficiency, time, cost and energy. These reactions have caused the development of intermediate compounds and transformation and increase in the formation of carbon-carbon bonds, and it is a cycle compatible with functional groups. Most multicomponent reactions are carried out in mild conditions [1 and 2]. Nanomaterials are of great importance in various fields, from basic research to various applications in electronics, biochemical sensors, catalysts and energy.Nano-sized particles increase the active surface of the catalyst and thus significantly increase the contact between the reactant and the catalyst, the reactions are carried out at a higher speed. Nanocatalysts mimic homogeneous catalysts and are a suitable alternative to other conventional catalysts. One of the advantages of such catalysts is their high activity, selectivity and high stability. Filtering and centrifugation are used to separate nano-catalysts from the reaction solution. But a major problem that nanocatalysts have is that they cannot be easily separated and recycled (due to their small size) from the reaction solution. Many works have been done to overcome this limitation of nanocatalysts. Among these measures, creating a catalytic substrate for the placement of nanoparticles is known as a useful method, and they emphasize the use of nanosubstrates for the development of green chemistry. Magnetic substrates have better capabilities. The magnetic nanocatalysts created by an external magnet can be easily separated from the reaction solution and do not need to be filtered and centrifuged [3-4 and 5]. In this project, derivatives of pyrano [3-c and 2] pyrazoles from condensation Four derivatives of benzaldehyde, ethyl acetoacetate, malononitrile and hydrazine hydrate were synthesized in the presence of catalyst.

MATERIALS AND METHODS

Experimental

Synthesis of $CoFe_2O_4$ Nano Particle

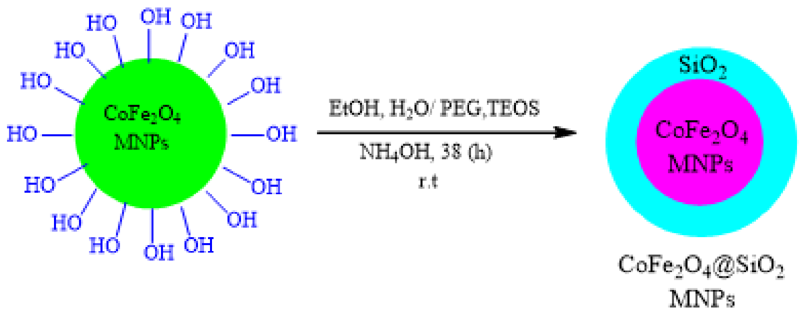
At first, 1.19 grams (0.005 mol) of $CoCl_2.6H_2O$ and 2.705 grams (0.01 mol) of $FeCl_3.6H_2O$ were dissolved in 50 ml of water in a 100 ml round bottom flask. Next, 3 grams of sodium hydroxide was dissolved in 25 ml of water and added to the mixture, and the reaction mixture was refluxed for 1 hour. After completion of the reaction, the mixture was cooled to room temperature. The black sediment was extracted with an external magnet and washed four times with water and ethanol and dried at room temperature [6].



Scheme 1. Synthesis of $CoFe_2O_4$ Nano Particle

Synthesis of $CoFe_2O_4@SiO_2$

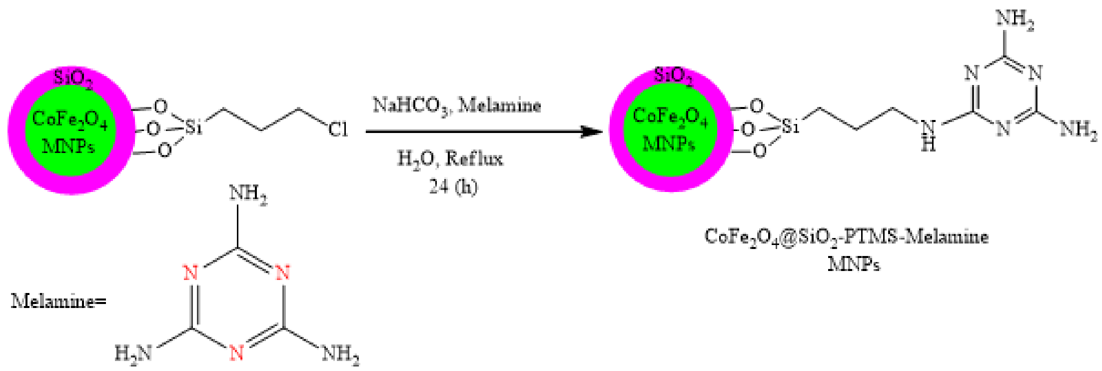
In a 150 ml flask, 1 g of $CoFe_2O_4$ was dispersed in 10 ml of water for 30 minutes in an ultrasonic device, and then 25 ml of ethanol, 2.68 g of polyethylene glycol (PEG), 10 1 ml of water, 5 ml of aqueous ammonia solution and 1 ml of tetraethylorthosilicate (TEOS) were added to it and the reaction mixture was stirred by a magnetic stirrer at room temperature for 38 hours. After this time, an external magnetic field was used to separate the product and the precipitate was washed four times with ethanol and dried at room temperature [6].



Scheme 2. Synthesis of $CoFe_2O_4@SiO_2$

Synthesis of $CoFe_2O_4$@SiO_2-PTMS-Melamine

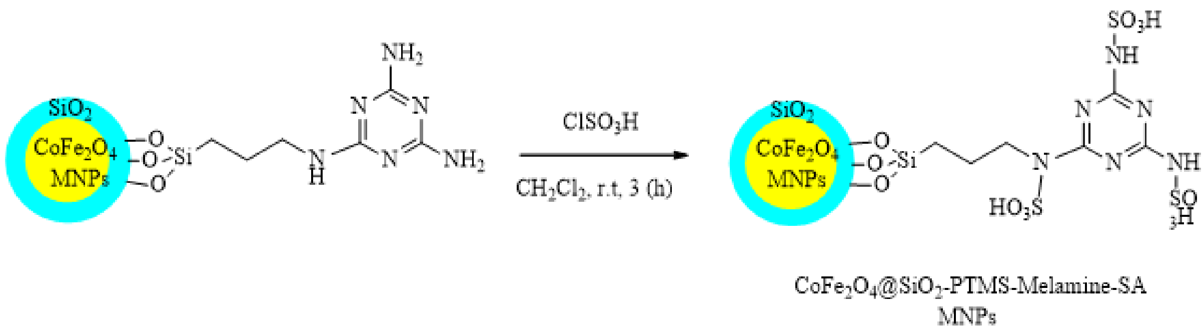
At this stage, 1 gram of $CoFe_2O_4$@SiO_2-CPTMS nanoparticles was dispersed in 8 ml of water in an ultrasonic device for 10 minutes in a 100 ml flask. Then 0.008 mol of sodium bicarbonate and 0.004 mol of melamine were added to it and the mixture was stirred for 24 hours under reflux conditions by a magnetic stirrer. After the completion of the reaction, $CoFe_2O_4$@SiO_2-PTMS-Melamine magnetic nanoparticles were separated using an external magnet and washed four times with water and then ethanol and dried at room temperature [7].



Scheme 3. Synthesis of $CoFe_2O_4$@SiO_2-PTMS-Melamine

Synthesis of $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA

In a 100 ml flask, 0.5 g of synthesized nanoparticles ($CoFe_2O_4$@SiO_2-PTMS-Melamine) in the previous step was dispersed in 10 ml of dichloromethane for 20 minutes in an ultrasonic device. Then 1.5 ml of chlorosulfonic acid was added to the mixture and stirred for 3 hours at room temperature. At the end, the acidic nanocatalyst was separated and washed twice with dichloromethane, twice with ethanol, and then twice with dichloromethane and dried at room temperature [7].



Scheme 4. Synthesis of $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA

RESULTS AND DISCUSSION

FT-IR Analysis of $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA

Infrared spectroscopy (FT-IR) has been used to identify and distinguish functional groups in $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA nanocatalyst. The spectra of five compounds (A) $CoFe_2O_4$, (B) $CoFe_2O_4$@SiO_2, (C) $CoFe_2O_4$@SiO_2-CPTMS, (D) $CoFe_2O_4$@SiO_2-PTMS-Melamine, (E) $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA are shown in Figre 1.

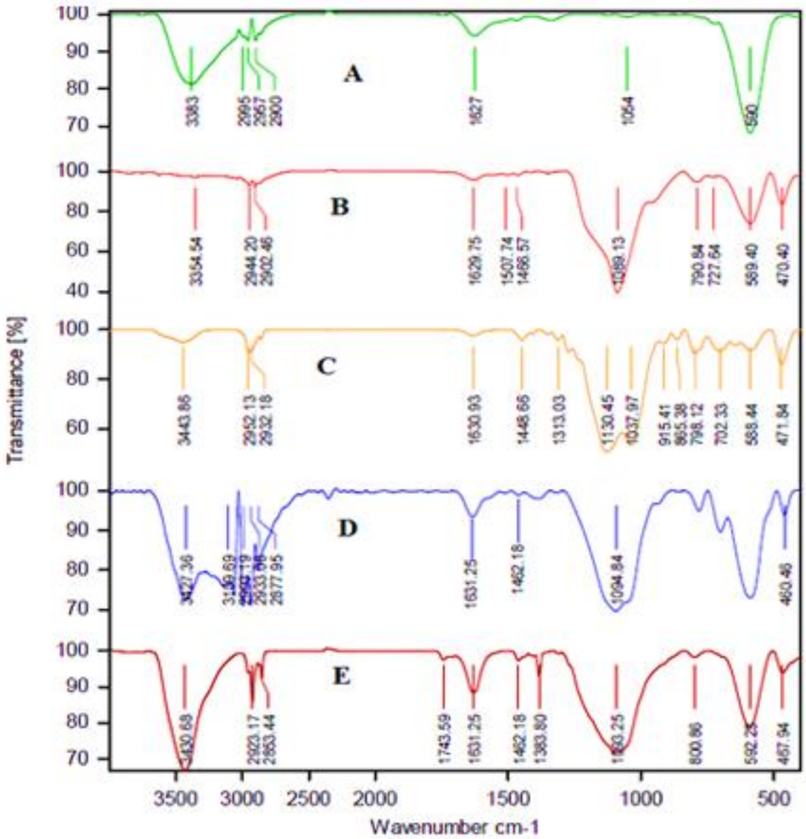


Figure1: FT-IR of $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA

SEM Analysis of $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA

One of the methods of identifying magnetic nanoparticles is the use of the scanning electron microscope (SEM) technique. This method is used to determine the size of nanocatalyst particles. As it is clear from figure (2), the particles are spherical and have been synthesized on a nanoscale and in a size of about 29 nm.

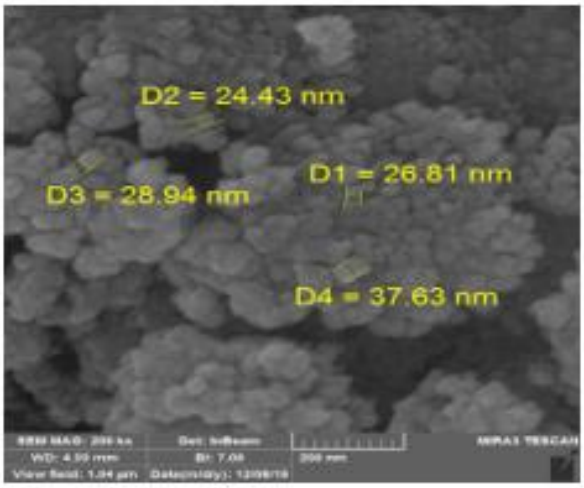


Figure 2: SEM of $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA

EDX Analysis of $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA

X-ray Energy Diffraction Spectroscopy (EDX) is an analytical method used to analyze the structural or chemical properties of a sample. This method is based on examining the interaction between an X-ray excitation source and a sample. By interpreting the data obtained from the analysis (EDX), it is clear that Co, Fe, Si, O and

S elements are present in the structure of the catalyst and this indicates that the synthesis of $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA catalyst is well Figure (3) has been done.

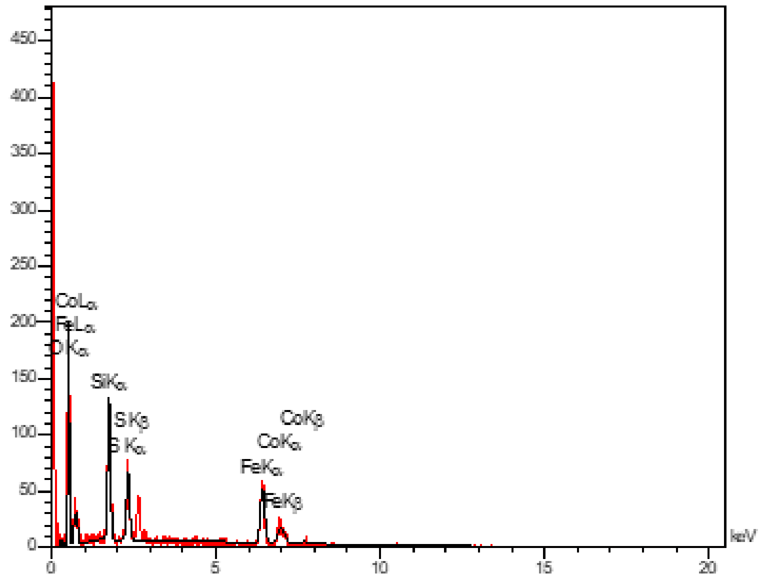


Figure3: EDX of $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA

XRD Analysis of $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA

X-ray diffraction was used to determine the crystal structure and analyze the synthesized nanocatalyst. The spectra of two compounds (a) $CoFe_2O_4$ and (b) $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA are shown in Figure (4-4). According to two graphs a and b, it is confirmed that the structure of magnetite ($CoFe_2O_4$) is preserved despite the functionalization and has peaks at the angles of (30/45°), (35/70°), (50°) 43), (60/53), (25/57), (63/74) = θ2, which is completely consistent with the standard pattern found in the sources [7].

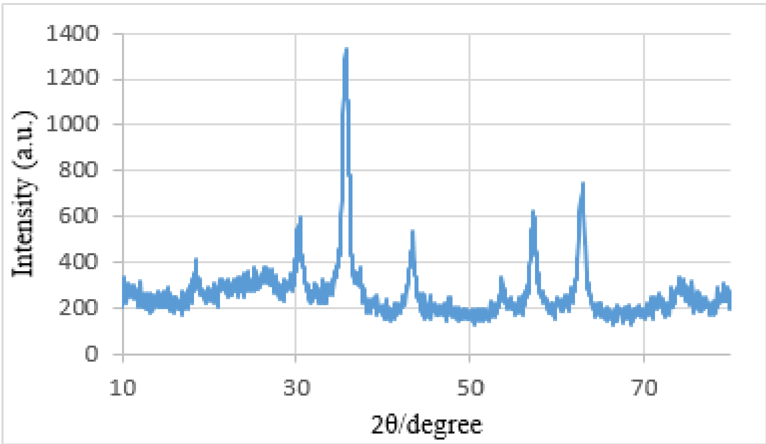


Figure 4: XRD of $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA

TGA analysis of $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA

By changing the temperature, there are changes in the structure and physical properties of the material, the thermal stability of the prepared nanocatalyst can be investigated, therefore, thermal gravimetric analysis (TGA) has been used. According to figure (5), a weight loss of 5% has occurred in the catalyst at a temperature lower than 250 degrees Celsius, which is caused by the removal of water and solvents absorbed on the surface of the catalyst. Also, the weight loss of 15% at a temperature of about 250 to 500 degrees Celsius is related to the destruction of organic groups on the surface of the nanocatalyst.

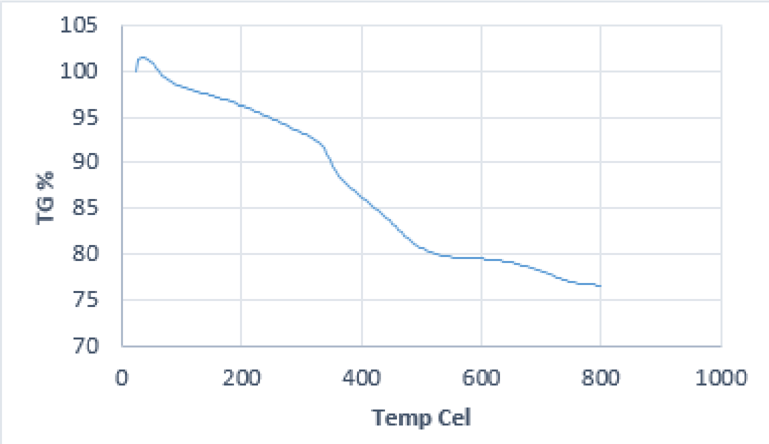


Figure 5: TGA of $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA

VSM analysis of $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA

Since magnetic nanoparticles have magnetic properties, the degree of magnetism of the desired material was investigated in terms of temperature, magnetic field and sample orientation by VSM magnetometric test. According to figure (6), we see that $CoFe_2O_4$ nanocatalyst (diagram a) has a higher magnetic property around 37 emu/g. The $CoFe_2O4@SiO_2$ nanocatalyst (diagram b) has a magnetic property of 29 emu/g. In the third diagram (diagram c) of the $CoFe_2O_4@SiO_2$-PTMS-Melamin-SA nanocatalyst, we see a further decrease in its magnetic property and it is around 27 emu/g, which indicates that the active surface of the catalyst is covered with SiO_2 The comment is fixed on the surface of the nanocatalyst.

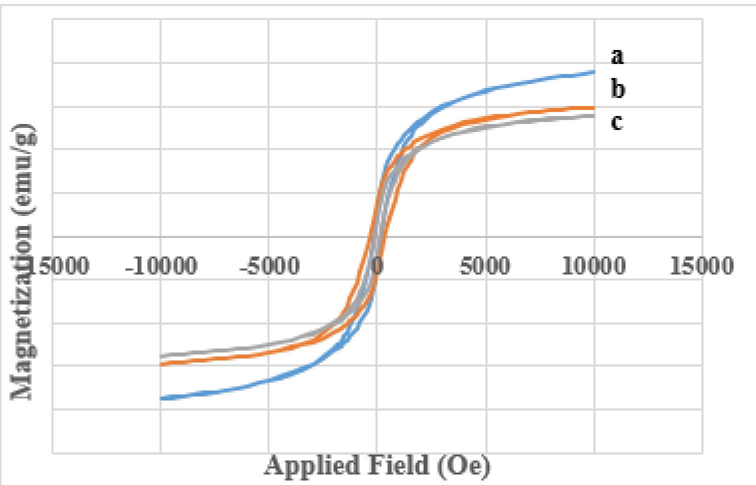


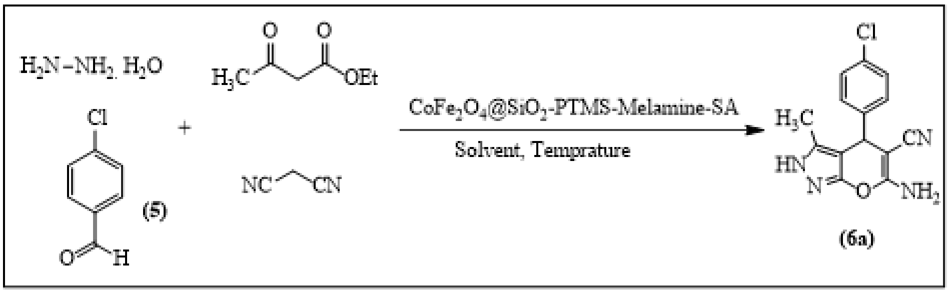
Figure 5: VSM analysis (a) $CoFe_2O_4$, (b) $CoFe_2O_4@SiO_2$, (c) $CoFe_2O_4@SiO_2$ -PTMS-Melamine-SA

Application of $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA catalyst for the synthesis of pyrano[c-3 and 2]pyrazole compounds:

Pyranopyrazoles are heterocyclic compounds containing oxygen and nitrogen atoms. These compounds are of special importance and have medicinal and biological properties. In this section, the application of $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA magnetic nanocatalyst in the synthesis of substituted pyrazole [c-3] and 2[pyrazole] compounds will be investigated.

Optimization of reaction conditions and synthesis of derivatives of pyrazole compounds [c-3 and 2] using $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA catalyst:

In order to obtain optimal reaction conditions, the reaction of ethyl acetoacetate, hydrazine, malononitrile and para-chlorobenzaldehyde compounds was chosen as a model reaction and the effect of temperature parameters, solvent and different amounts of $CoFe_2O_4$@SiO_2-PTMS-Melamine-SA catalyst on it. was examined.

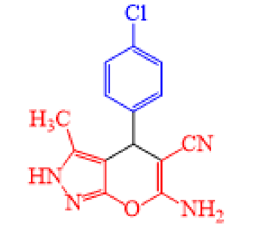
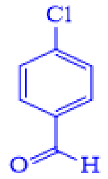
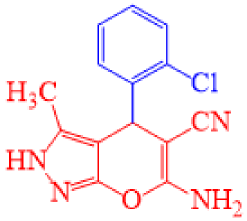
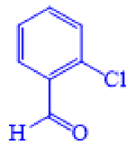
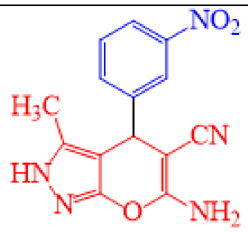
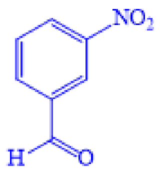


At first, the reaction was investigated in the vicinity of different amounts of catalyst in water solvent and at different temperatures. The highest yield was obtained in the shortest time in the presence of (10 mg) catalyst and at room temperature. In the next step, the effect of different solvents was investigated, as we can see in table (1), water solvent was chosen as the optimal solvent because the product efficiency was higher.

Table (1): Optimum conditions for the synthesis reaction of pyrano[3-c and 2] pyrazole

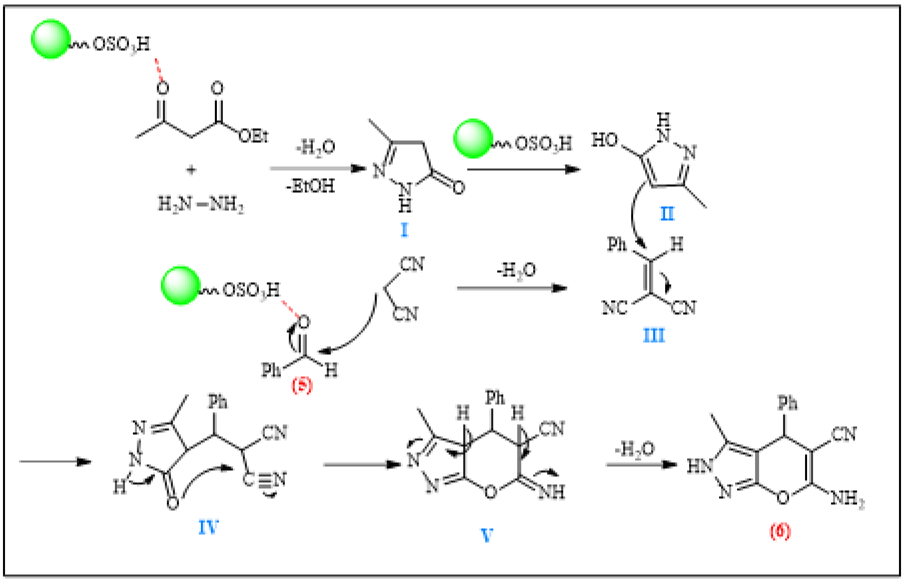
Efficiency (%)	time (minutes)	catalyst (mg)	temperature (oC)	Solvent	Row
90	10	5	Rom.tr	Water	1
90	5	10	Rom.tr	Water	2
90	5	20	Rom.tr	Water	3
90	5	30	Rom.tr	Water	4
90	5	40	Rom.tr	Water	5
40	5	10	Rom.tr	Ethanol	6
50	5	10	Rom.tr	H2O:EtOH	7
30	5	10	Rom.tr	Ethyl acetate	8
trac	5	10	Rom.tr	Aceto nitrile	9
trac	5	10	Rom.tr	n-hexane	10

Table(2): Synthesis of pyrano [C-3 and 2] pyrazole derivatives using $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA catalyst.

M.p (ºC) [Ref]	Efficiency (%)	time (minutes)	Efficiency	aldehyde	Row
-242 240 [34]	90	5			1
-249 247 [34]	85	10			2
-235 233 [34]	85	10			3

Proposed mechanism for synthesis reaction of pyrano[C-3 and 2]pyrazole derivatives using $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA catalyst

According to the reaction conditions, various methods have been proposed for the synthesis of pyrano[c-3 and 2]pyrazoles. The following mechanism has been proposed for the synthesis of pyranopyrazole derivatives using $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA catalyst [15].



Scheme 5. Synthesis mechanism of pyrano[C-3 and 2]pyrazoles

Recycling and reuse of $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA catalyst in the synthesis reaction of pyrano[c-3 and 2]pyrazole derivatives

One of the twelve principles of green chemistry is the use of catalysts that can be recycled and reused, so after the synthesis reaction of the derivative (6a), the $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA catalyst was separated from the reaction product and repeated several times. It was washed with ethyl acetate and finally dried and used for the next steps. The recovery of the catalyst was carried out by maintaining the magnetic properties up to six consecutive stages (Figure 5).

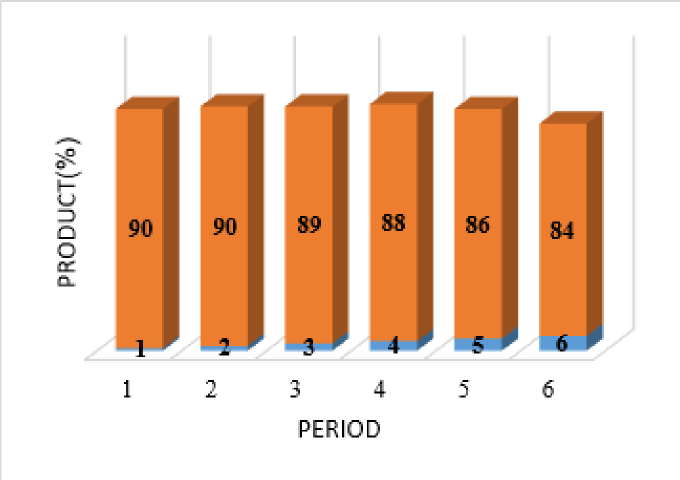


Figure (6): The diagram of recovery of nanocatalyst $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA in the synthesis reaction of pyrano[C-3 and 2]pyrazole.

Conclusion

In this reserch, the magnetic nanocatalyst $CoFe_2O_4@SiO_2$-PTMS-Melamine-SA was designed and synthesized and used in the synthesis of pyrano[c-3 and 2] substituted pyrazole compounds which are structures with medicinal and biological properties. Also, the synthesis of substituted pyranopyrazole compounds was carried out in water solvent, which is a green solvent. The used nanocatalyst has advantages such as high yield of products, ability to separate and reuse, and good stability.

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