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Facial Preparation of Sulfonic Acid-Functionalized Magnetite-Coated Maghemite as a Magnetically Separable **Catalyst for Pyrrole Synthesis**

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Dedicated to Professor Habib Firouzabadi on the occasion of his 70th birthday

The synthesis, characterization, and catalytic performance of the new sulfonic acid supported on the magnetic nanoparticles with maghemite coating were reported. The morphology, particle size, structure, magnetic properties, and the formation of nanoparticles with narrow size distribution were investigated. Chemical analysis was performed by using TEM, wide-angle XRD, FTIR spectroscopy, and X-ray fluorescence, and magnetic measurements were performed by using vibrating sample

magnetometry. The catalyst was found to be active for the synthesis of pyrroles. The nanometer size range of these particles facilitates the catalytic process owing to the increased surface area available for the reaction. The easy separation of the catalyst by an external magnet from liquid-phase reactions and its usability for at least nine consecutive trials without any decrease in activity are additional advantages.

Introduction

The heterogenization of the active catalytic molecules is one of the efficient ways to overcome the problem of isolation and separation of a homogeneous catalyst.^[1-4] Heterogeneous catalysts can be recovered through filtration or centrifugation. However, these methods are time-consuming and may cause catalyst loss. Furthermore, conventional separation methods may become inefficient with particle sizes less than 100 nm. In line with this, magnetic nanoparticles are of great interest to researchers because with a large surface-to-volume ratio relative to bulk materials,^[5,6] these nanoparticles demonstrate high activity and selectivity (like a homogeneous catalyst) and can be easily separated and recovered. Magnetically supported catalysts can be recovered with an external magnet owing to the paramagnetic character of the support, and the catalysts can be reused in another cycle. Considering the iron oxide nanoparticles, the iron atoms on the surface act as Lewis acids and coordinate with molecules that donate lone pair electrons and functionalize the iron oxide surface hydroxyl groups. These hydroxyl groups are amphoteric and may react with acids or bases.^[7] The coatings also provide stability to nanoparticles. Iron oxide nanoparticles can be coated with silica, gold, or gadolinium(III).^[8-13] Magnetically separable catalysts can be used for designing surface functionalities along with catalyst preparation.

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Sulfonic acid catalysts are widely used in various industries; however, it is often difficult to isolate and separate the final product after the reaction is complete. Notably, even if it is possible to separate the catalyst from the reaction mixture, trace amounts of the catalyst are likely to remain in the final product. In recent years, with the aim of switching to increasingly efficient and benign processes, the immobilization of sulfonic acid on the magnetic support as the reusable catalyst that avoids the use of toxic reagents and reduces the timeconsuming wasteful separations^[14-16] is a challenging task. However, there are several factors that limit the use of these catalysts. For instance, the applicable reagents are expensive and have harsh preparation conditions. Hence, one of the main goals of the present work is to overcome these drawbacks through the design of a new one-pot preparation of sulfonic acid supported on the magnetic nanoparticles with magnetic maghemite $(\gamma - Fe_2O_3)$ coating as a powerful recoverable catalytic system.

The pyrrole ring system is a useful structural element in medicinal chemistry^[17] and has found broad application in the development of, for example, antibacterial, antiviral, anti-inflammatory, antitumoral, and antioxidant drugs.^[18] They are a highly versatile class of intermediates in the synthesis of natural products and in heterocyclic chemistry^[19] and are widely used in materials science.^[20] Thus, many synthetic methods have been developed for the preparation of these compounds.^[21] Of the many methods developed, the Paal-Knorr^[22] and Clauson-Kass^[23] reactions are still considered to be the most attractive methods for the synthesis of pyrroles. In these methods, 1,4-dicarbonyl or 2,5-dimethoxytetrahydrofuran compounds are converted to pyrroles through the reaction with primary amines in the presence of various promoting



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agents.^[24] However, some of these methods often suffer from certain drawbacks such as the use of hazardous organic solvents, high-cost reagents, relatively expensive or stoichiometric amounts of catalysts, tedious workup, which leads to the generation of large amounts of toxic metal-containing waste, and low product yields. Therefore, the development of facile and environmentally friendly methods for the synthesis of pyrroles is necessary for organic synthesis.

Results and Discussion

Magnetite (Fe $_3O_4$) nanoparticles with a mean size of 10–15 nm^[25] were prepared by using the coprecipitation technique [Eq. (1)].

In this way, Fe₃O₄ is not very stable and is sensitive to the oxidation. Fe₃O₄ is then transformed into γ -Fe₂O₃ in the presence of oxygen. Notably, oxidation in air is not the only way to transform Fe₃O₄ into γ -Fe₂O₃. According to Equation (2), various electrons or ions transferred are involved, depending on the pH of the suspension. Under acidic and anaerobic conditions, the surface Fe²⁺ ions desorb as hexa-aqua complexes in the solution, whereas under basic conditions, the oxidation of Fe₃O₄ involves the oxidation–reduction of the Fe₃O₄ surface.^[26]



Herein, we design a one-pot method for the preparation of sulfonic acid supported on the magnetic nanoparticles with γ -Fe₂O₃ coating as a powerful recoverable catalytic system [Eq. (3)].



The magnetically separable sulfonic acid nanocatalysts were characterized by using FTIR spectroscopy, XRD, X-ray fluorescence (XRF), SEM, TEM, potentiometric titration, and vibrating sample magnetometry.

The XRD spectra of the Fe_3O_4 and $Fe_3O_4@\gamma$ - Fe_2O_3 - SO_3H materials are shown in Figure 1, which are also used for the deter-



Figure 1. XRD spectra of a) Fe₃O₄ and b) Fe₃O₄@Fe₂O₃-SO₃H.

mination of the structural order. The XRD patterns of Fe₃O₄ shown in Figure 1a are in good agreement with a cubic structure, whereas the XRD patterns shown in Figure 1b confirm the conversion of the Fe₃O₄ core structure to Fe₃O₄@ γ -Fe₂O₃ during the sulfonation process. These observations confirm that the magnetic particles change from Fe₃O₄ to Fe₃O₄@ γ -Fe₂O₃.

The FTIR spectra of the synthesized nanoparticles with and without SO_3H loading are shown in Figure 2. For the bare magnetic nanoparticles (Figure 2), the vibration band at 557 cm⁻¹ is the typical IR absorbance induced by structure of the Fe–O



Figure 2. FTIR spectra of Fe₃O₄ and Fe₃O₄@\gamma-Fe₂O₃-SO₃H.

vibration. The three new bands appeared at 1200–1250, 1010– 1100, and 650 cm⁻¹ corresponding to the O=S=O asymmetric and symmetric stretching vibrations and S–O stretching vibration of the sulfonic groups (–SO₃H), respectively. The increase in the intensities of the band at 3000–3600 cm⁻¹ confirms that the sulfonic groups functionalized the surface of the magnetic nanoparticles.

The analysis of the XRF results (Table 1) of the catalyst confirms the presence of sulfonic acid on the catalyst surface and demonstrates the existence of Fe_2O_3 on the outer layer of the catalyst (Figure 3).

The TEM and SEM images of $Fe_3O_4@\gamma$ - Fe_2O_3 - SO_3H are shown in Figure 4. These images demonstrate the uniformsized particles (mean size range: 10–15 nm) with spherical morphology.

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Table 1. Results of XRF analysis.				
Compound	Concentration [wt%]			
Fe ₂ O ₃	42.65			
SO₃	20.26			
CI	1.66			
V ₂ O ₅	0.073			
Al ₂ O ₃	0.041			
MnO	0.034			
CaO	0.029			
CuO	0.020			
ZnO	0.009			
LOI ^[a]	35.48			
Total	100.26			
[a] Loss on ignition ($T = 1000 ^{\circ}$ C, $t = 2$ h).				



Figure 3. XRF analysis of Fe $_3O_4@\gamma$ -Fe $_2O_3$ -SO $_3H$.



Figure 4. a) TEM and b) SEM images of Fe₃O₄@γ-Fe₂O₃-SO₃H.

The amount of sulfonic acid groups on the magnetic nanoparticles with γ -Fe₂O₃ coating was calculated by using the neutralization titration method and was found to be in the range of 3–3.2 mmolg⁻¹. The surface acidity of Fe₃O₄@ γ -Fe₂O₃–SO₃H was calculated by using the potentiometric titration method with *n*-butyl amine. To interpret the results, the acid strength was assigned according to the following scale: maximum acid strength (MAS) \geq 100 mV, very strong acid sites; 0 < MAS < 100 mV, strong acid sites; -100 mV < MAS < 0 mV, weak acid sites; and MAS \ll M- > 100 mV, very weak acid sites.^[27] A remarkable difference in acid strength between pure Fe₃O₄ and Fe₃O₄@ γ -Fe₂O₃–SO₃H (in the millivolt range) can be seen in Figure 5. A pure magnetic particle is a weakly acidic oxide (*E*= 2 mV); however, it is modified through the –SO₃H addition,



Figure 5. Potentiometric titration curves of a) Fe_3O_4 and b) $Fe_3O_4@\gamma\mathchar`-Fe_2O_3\mathchar`-SO_3H.$

which generates very strong acid sites (E = 600 mV) on the magnetic particle surface. These results indicate that Fe₃O₄@ γ -Fe₂O₃-SO₃H is a very strong solid acid with a high density of acid sites. The acid sites in the samples are approximately six times larger than those in Nafion,^[28] which is a highly active and stable perfluorosulfonate ionomer.

To determine whether the particles demonstrate magnetic properties, the sulfonic acid-loaded magnetic particles were dispersed in water, which resulted in a brown suspension. Within approximately 5 s of the application of an external magnet, the sulfonic acid-functionalized magnetic nanoparticles were completely collected onto the stirrer bar or the side of the cuvette wall and the solution became clear and transparent (Figure 6).



Figure 6. Separation of Fe₃O₄@γ-Fe₂O₃-SO₃H with an external magnet.

The magnetization curves of Fe₃O₄ and Fe₃O₄@ γ -Fe₂O₃-SO₃H were recorded at room temperature (Figure 7). The two measured samples demonstrate a superparamagnetic behavior, as confirmed by zero coercivity and remanence on the magnetization loop. The saturation magnetization value of Fe₃O₄@ γ -Fe₂O₃-SO₃H is 55 emu g⁻¹ (Figure 7 b), which is a slightly lower than that of the uncoated magnetic particles ($\approx 60 \text{ emu g}^{-1}$; Figure 7a) but is nearly twice that of Fe₃O₄@ γ -Fe₂O₃-SO₃H^[16] ($\approx 28 \text{ emu g}^{-1}$; Figure 7c).

To show its catalytic activity, $Fe_3O_4@\gamma$ - Fe_2O_3 — SO_3H was used as a catalyst in the Paal–Knorr and Clauson–Kaas pyrrole synthesis reactions. Aniline and 2,5-heptadione was chosen as model substrates for the optimization of the Paal–Knorr reaction and the identification of the best amount of the catalyst.

By screening loading of the catalyst and considering the effect of the solvent and temperature on the reaction rate, it

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Figure 7. Magnetization loops of a) Fe₃O₄, b) Fe₃O₄@γ-Fe₂O₃-SO₃H, and c) γ -Fe₂O₃-SO₃H.^[16] All the data are recorded at RT.

was found that only 0.05 g of $Fe_3O_4@\gamma$ - Fe_2O_3 -SO₃H was sufficient to condense aniline (1 mmol) with 2,5-heptadione (1.2 mmol) at room temperature under solvent-free conditions (Table 2).

Table 2. Optimization of the reaction conditions.					
$ \bigcirc -NH_2 + \checkmark \bigcirc \bigcirc \bigcirc -N \bigcirc \bigcirc$					
Entry	Catalyst [mol %]	Solvent	7 [°C]	t [h]/Conv. [%]	
1	-	_	25	8/20	
2	Fe ₃ O ₄ (5)	-	25	8/100	
3	$Fe_{3}O_{4}@\gamma-Fe_{2}O_{3}-SO_{3}H$ (3)	-	25	4/100	
4	$Fe_{3}O_{4}@\gamma-Fe_{2}O_{3}-SO_{3}H$ (7)	-	25	1.5/100	
5	$Fe_{3}O_{4}@\gamma-Fe_{2}O_{3}-SO_{3}H$ (10)	-	25	1.15/100	
6	$Fe_{3}O_{4}@\gamma-Fe_{2}O_{3}-SO_{3}H$ (7)	CH₃CN	25	5/100	
7	$Fe_{3}O_{4}@\gamma-Fe_{2}O_{3}-SO_{3}H$ (7)	Et ₂ O	25	3/100	
8	$Fe_{3}O_{4}@\gamma-Fe_{2}O_{3}-SO_{3}H$ (7)	EtOAc	25	6/100	
9	$Fe_{3}O_{4}@\gamma-Fe_{2}O_{3}-SO_{3}H$ (7)	<i>n</i> -hexane	25	24/100	
10	$Fe_{3}O_{4}@\gamma-Fe_{2}O_{3}-SO_{3}H$ (7)	-	50	1/100	
11	$Fe_{3}O_{4}@\gamma-Fe_{2}O_{3}-SO_{3}H$ (7)	-	80	1/100	

After this finding, the general applicability of the method was studied through the reaction of structurally diverse amines with hexane-2,5-dione under similar reaction conditions. With use of this method, aromatic and aliphatic amines easily reacted with hexane-2,5-dione and gave N-substituted pyrroles in good to excellent yields. Aliphatic amines reacted more efficiently than aromatic amines and gave N-alkyl pyrroles in excellent yields. The results are summarized in Table 3.

The possibility of recycling the magnetic catalyst was also examined. For this purpose, the reaction of aniline and 2,5heptadione in the presence of Fe₃O₄@Fe₂O₃-SO₃H was studied. After completion of the reaction, diethyl ether (10 mL) was added to the mixture, the catalyst was collected onto the reaction vessel with an external magnet, and the reaction solution was decanted. The resulting catalyst was washed with diethyl ether to remove the residual product, dried under vacuum,



and reused in a subsequent reaction. Fe₃O₄@y-Fe₂O₃-SO₃H was reused directly without any deactivation even after nine consecutive runs (Figure 8).

Notably, the stability of Fe₃O₄@y-Fe₂O₃-SO₃H nanoparticles makes the storage of this catalyst convenient. The reaction of aniline and 2,5-heptadione in the presence of Fe₃O₄@Fe₂O₃-SO₃H was studied at different times, and it was found that these particles are stable for more than 2 months (Figure 9 and Table 4).

The Clauson-Kaas reaction is another attractive route to produce N-substituted pyrrole. Aniline and 2,5-dimethoxytetrahydrofuran were chosen as the model substrates for the optimi-

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Figure 8. Recovery of the Fe₃O₄@ γ -Fe₂O₃-SO₃H catalyst in 1.5 h.



Figure 9. Stability of the $Fe_3O_4@\gamma$ - Fe_2O_3 - SO_3H catalyst.

Table 4. Optimization of the reaction conditions. \swarrow NH_2 + O O MW \sim O O $Cat.$ N						
Entry	Catalyst [mol %]	t [min]	Conversion [%]			
1	-	5	20			
2	Fe ₃ O ₄ (5)	5	40			
3	$Fe_3O_4@\gamma$ - Fe_2O_3 - SO_3H (5)	15	100			
4	Fe ₃ O ₄ @γ-Fe ₂ O ₃ —SO ₃ H (10)	8	100			
5	$Fe_{3}O_{4}@\gamma$ - $Fe_{2}O_{3}$ - $SO_{3}H$ (15)	5	100			
6	$Fe_{3}O_{4}@\gamma$ - $Fe_{2}O_{3}$ - $SO_{3}H$ (20)	2	100			
[a] MW = microwave radiation.						

zation of the Clauson–Kaas reaction conditions. The best reaction condition was achieved under microwave irradiation in the presence of 0.07 g of the catalyst under solvent-free conditions.

Encouraged by this result, we have performed the reactions of various amines with 2,5-dimethoxytetrahydrofuran to probe the scope and reactivity of the new catalyst and the results are summarized in Table 5. Reactions with most of the examined amines containing strong electron-deficient (*p*-NO₂, *m*-NO₂, and *m*-COCH₃) or strong electron-donating (*p*-MeO) anilines gave the corresponding pyrroles in good to excellent yields



(Table 5). Notably, in the case of strong electron-deficient amine, a longer reaction time was needed.

Conclusions

The Fe₃O₄@ γ -Fe₂O₃—SO₃H nanoparticles prepared by using the simple method are the efficient and magnetically recyclable heterogeneous catalysts for pyrrole synthesis. In contrast to other catalysts, the magnetically separable sulfonic acid catalysts can be easily removed from the reaction mixture and the separation and purification of the products do not require a complicated process. The preparation of magnetically separable sulfonic acid catalysts is easier, faster, and cheaper than that of other catalysts. Moreover, this catalyst is a solid acid catalyst, which is environmentally friendly as well.

Experimental Section

Raw materials for the reaction were purchased from Merck and Fluka and were used without any further purification. The reaction

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progress was followed by using TLC. The reaction product was determined from IR, ¹H NMR, and ¹³C NMR analysis. The whole process was performed with TLC-Card Silica Gel-G/UV 254 nm; analytical balance Mitller/Colleg 150; OVEN/Model: U30/W:800-Shimaz CO; FTIR: Spectrometer-Spectrum RX 1 Perkin–Elmer AVE (4000–400 cm⁻¹); ¹H NMR and ¹³C NMR: Bruker Avance 400 MHz spectrometer; pH meter: Horiba model:f-IIE.

Preparation of the Fe₃O₄ nanoparticles

The Fe₃O₄ nanoparticles were prepared by using the published method with a slight modification.^[24] First, FeCl₃·6H₂O (20 mmol, 5.40 g) and FeCl₂·4H₂O (10 mmol, 2.00 g) were added to deionized water (40 mL) and the resulting mixture was vigorously stirred under nitrogen gas for 30 min. Then, the mixture was heated to 60 °C. Finally, ammonium hydroxide (15 mL, 28 wt%) was added quickly to the solution and the solution immediately turned black. The reaction mixture was kept at 60 °C for 2 h. The black precipitate was separated with an external magnet.

Preparation of the stabilized sulfonic acid on the ${\rm Fe}_3{\rm O}_4$ nanoparticles

A suction flask equipped with a constant-pressure dropping funnel and a gas inlet tube for passing HCl gas through an adsorbing solution (water) was used. Cholorosulfonic acid (1.0 mL) was added dropwise to a mixture of Fe_3O_4 (1.00 g) and dichloromethane (20 mL) at RT. The resulting mixture was stirred vigorously until HCl gas evolution stopped. The resulting magnetic nanoparticles with γ -Fe₂O₃ coating were separated with an external magnet, washed with dichloromethane (3×5 mL), and dried in an oven at 40 °C. A brown solid Fe₃O₄@ γ -Fe₂O₃=SO₃H was obtained.

General method for the Paal-Knorr reaction

Fe₃O₄@Fe₂O₃–SO₃H (0.05 g) was added to a mixture of amine (1 mmol, 0.09 mL) and 2,5-heptadione (1.2 mmol, 0.17 mL). The resulting mixture was stirred for 1.5 h at RT. The reaction progress was monitored by using TLC (*n*-hexane/ethyl acetate eluent 8:2). After completion of the reaction, absolute ethanol (5 mL) was added to the reaction mixture and the resulting mixture stirred for 2 min. Fe₃O₄@ γ -Fe₂O₃–SO₃H was separated by using a permanent magnet, and the reaction solution was decanted. Fe₃O₄@ γ -Fe₂O₃–SO₃H was washed 3 times with absolute ethanol (3×5 mL). After the evaporation of ethanol, pure products were obtained in good to excellent yields.

General method for the Clauson-Kaas reaction

Amine (1 mmol), 2,5-dimethoxytetrahydrofuran (1.2 mmol, 0.15 mL), and the catalyst (0.07 g) were irradiated in a microwave under solvent-free conditions. The reaction progress was monitored by using TLC (*n*-hexane/ethyl acetate eluent 8:2). After completion of the reaction, absolute ethanol (5 mL) was added to the mixture and the resulting mixture was stirred for 2 min. Fe₃O₄@ γ -Fe₂O₃-SO₃H was separated with an external magnet and then washed 3 times with absolute ethanol (3×5 mL), after which pure products were obtained.

Method for the reuse of the catalyst

Fe₃O₄@ γ -Fe₂O₃-SO₃H (0.15 g) was added to the mixture of aniline (3 mmol, 0.27 mL) and 2,5-heptadione (3.3 mmol, 0.47 mL). The resulting mixture was stirred at RT until aniline disappeared (1.5 h). Absolute ethanol (5 mL) was added to the reaction mixture, and the resulting mixture was stirred for 2 min. Fe₃O₄@ γ -Fe₂O₃-SO₃H was separated with an external magnet. Fe₃O₄@ γ -Fe₂O₃-SO₃H was washed 3 times with absolute ethanol (3 × 5 mL) and dried at RT. The same catalyst was used in 9 cycles for pyrrole synthesis.

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Keywords: heterogeneous catalysis • iron • magnetic properties • nanocatalysis • pyrroles

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FULL PAPERS

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Facial Preparation of Sulfonic Acid-Functionalized Magnetite-Coated Maghemite as a Magnetically Separable Catalyst for Pyrrole Synthesis



Magnetic aura: The catalytic application of sulfonic acid-functionalized magnetite-coated maghemite as a powerful magnetically separable catalyst in pyrrole synthesis has been investigated. The catalyst can be recovered and reused several times in Paal–Knorr and Clauson–Kaas reactions.