Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information for the article:

Sulfonic Acid-Functionalized Magnetic Nanoparticles as a Recyclable and Eco-friendly Catalyst for Atom Economical Michael Addition Reaction and Bis Indolyl Methane Synthesis

Hajar Mahmoudi[a], Abbas Ali Jafari*[a], Soroosh Saeedi [a], and H. Firouzabadi*[b]

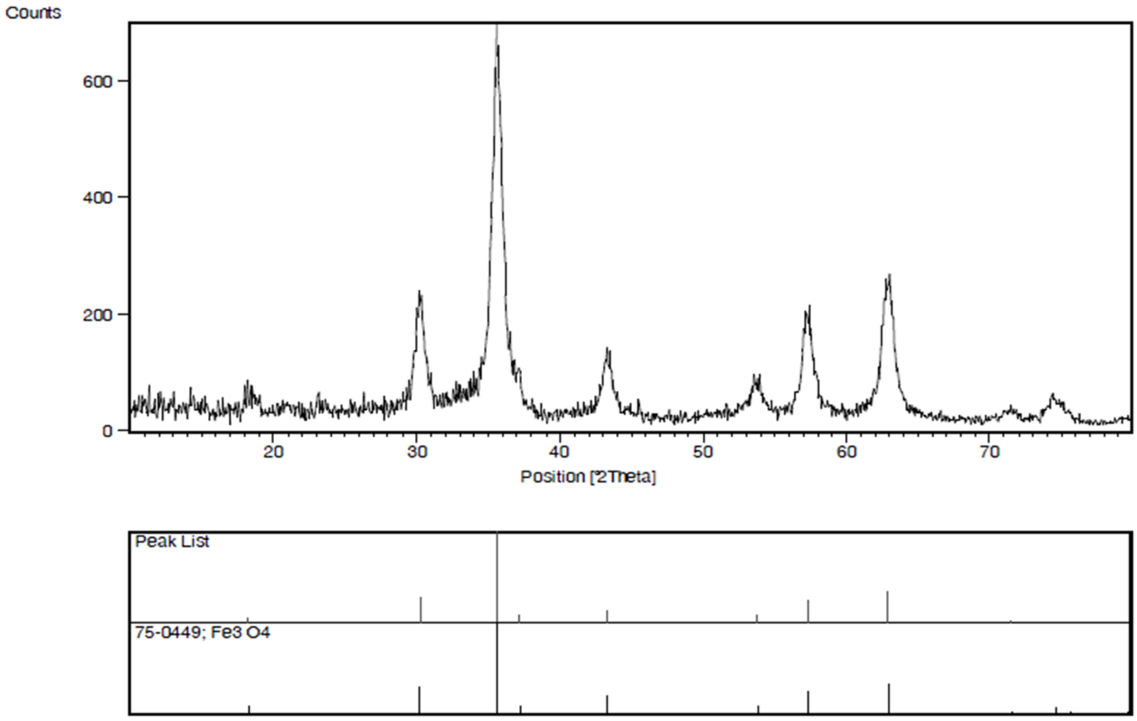
a) Chemistry Department, Yazd University, Yazd, P.O.BOX 89195-741 (Iran) Fax: (+)98 351 8210644.

b) Late Professor Ali Akbar Moshfegh Laboratory, Chemistry Department, Shiraz University, Shiraz 71454, Iran

Contents:

1. Preparation of Fe_3O_4 nano particles:

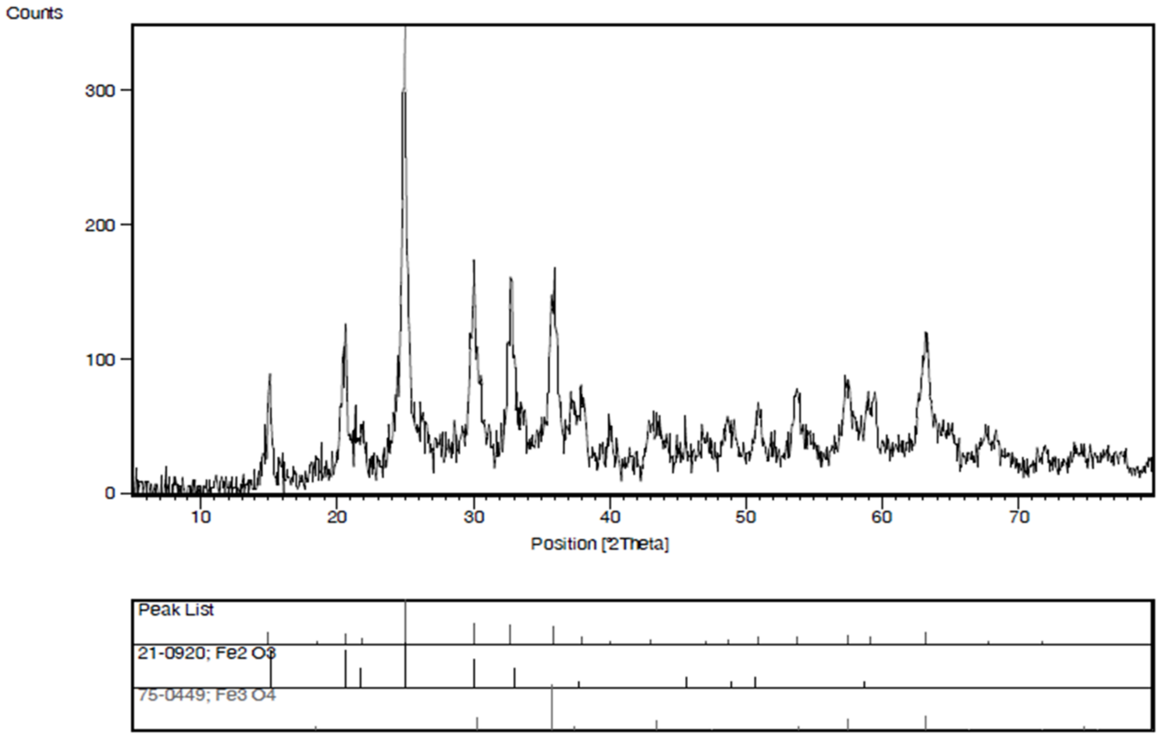
$FeCl_3 \cdot 6H_2O$ (20 mmol) and $FeCl_2 \cdot 4H_2O$ (10 mmol) were added to deionized water (40 mL) under nitrogen atmosphere with ultrasound irradiation for 5 min at 60 °C. Then, ammonium hydroxide (15 mL, 28 wt%) was added rapidly to the resulting solution. The solution was immediately turned black. The reaction was kept at 60 °C for 20 min under ultrasound irradiation. The black precipitates were collected with an external magnet and washed with distilled water. The resulting Fe_3O_4 NPs were dried for 12h at room temperature under vacuum and characterized by XRD, FTIR.



XRD Spectra of Fe_3O_4

2. Preparation of Fe_3O_4@ Fe_2O_3- SO_3H catalyst:

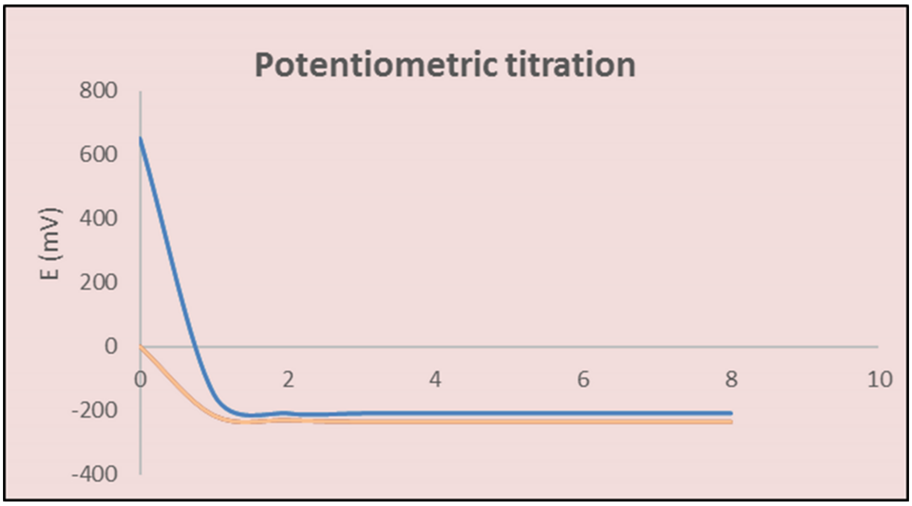
A suction flask was equipped with a constant-pressure dropping funnel and a gas inlet for leading the generated HCl into water. To this flask, which contains Fe_3O_4 (1.00 g) in dichloromethane (20 mL), cholorosulfonic acid (1.0 mL) was added drop wise at room temperature for 15 min under ultrasound irradiation. The resulting mixture was sonicated until HCl gas evolution was stopped. The resulting MNHS material was separated by an external magnet and washed with dichloromethane (3×5 mL) and finally dried in an oven at 40˚C. A brown solid $Fe_3O_4@\gamma Fe_2O_3$-SO_3H was obtained that was characterized by XRD and Potentiometric titration.



XRD Spectra of Fe_3O_4@ Fe_2O_3- SO_3H

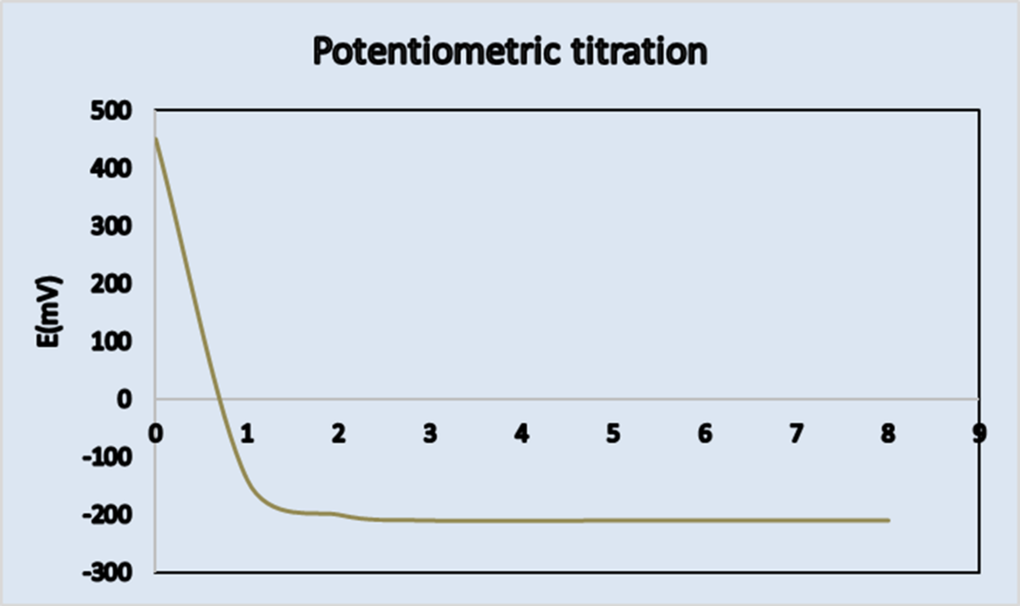
3. Potentiometric titration curves a) Fe_3O_4 and b) Fe_3O_4@ Fe_2O_3- SO_3H:

To evaluate the surface acidity of the $Fe_3O_4@Fe_2O_3$-SO_3H, we use the potentiometric titration method with n-butyl amine. As a criterion for interpreting the obtained results, the acid strength can be assigned according to the following scale: M.A.S. > 100 mV, very strong acid sites; 0 < M.A.S. < 100 mV, strong acid sites; -100 mV < M.A.S. < 0 mV, weak acid sites and M.A.S. < -100 mV, very weak acid sites. In figoure a) the remarkable difference in acid strength between pure Fe_3O_4 and Fe_3O_4@ Fe_2O_3-SO_3H can be observed from the millivolts range. Pure magnetic particle is a weakly acidic oxide (E = 2 mV) but it is modified by the -SO_3H addition, which generates very strong acidic sites (E = 650 mV) on the magnetic particle surface. These results indicate that $Fe_3O_4@Fe_2O_3$-SO_3H is a very strong solid acid with a high density of acid sites.



a) Potentiometric titration curves a) Fe_3O_4 and b) $Fe_3O_4@Fe_2O_3$-SO_3H under ultrasonic irradiation with 1.0 mL cholorosulfonic acid

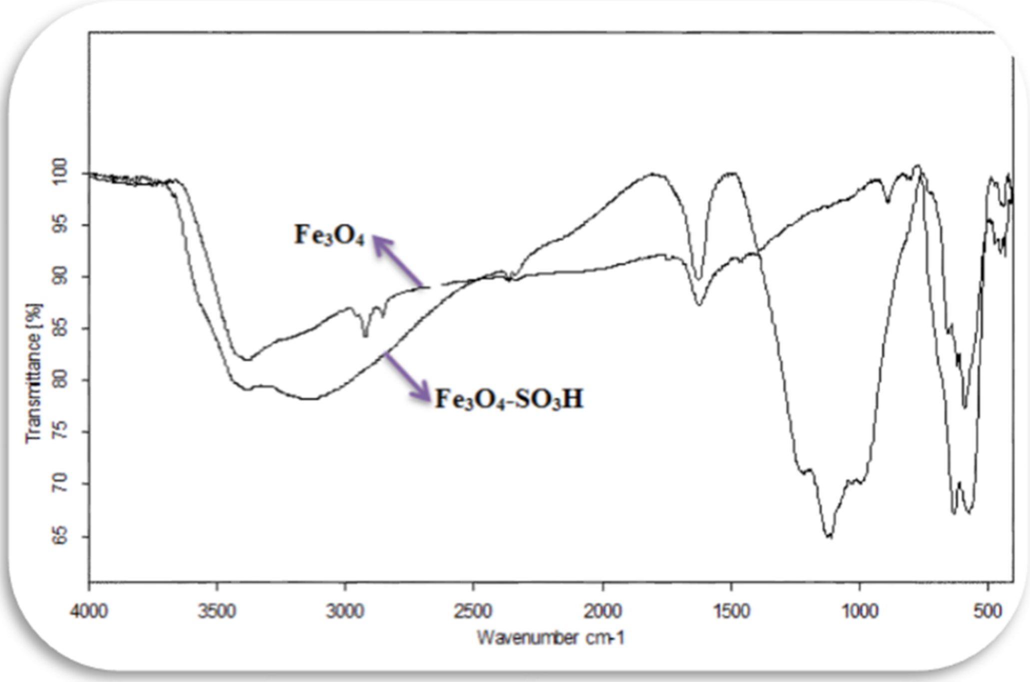
In figoure b), the difference of acid strength between Fe_3O_4@Fe_2O_3-SO_3H with 2 mL cholorosulfonic acid and Fe_3O_4@Fe_2O_3-SO_3H with 1 mL cholorosulfonic acid can be observed from the millivolts range. It is found that, the peresence of larger amount of cholorosulfonic acid increases the conversion of Fe_3O_4 to γFe_2O_3 and reduces amount of Fe^{2+} on the magnetic particle surface.



b) Potentiometric titration curves Fe_3O_4@Fe_2O_3-SO_3H under ultrasonic irradiation with 2.0 mL cholorosulfonic acid

4. FTIR of Fe_3O_4 and Fe_3O_4@ Fe_2O_3- SO_3H:

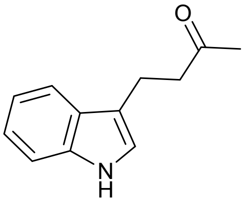
Figure c shows the FT-IR spectra of the magnetic nanoparticles with and without SO_3H loading. The three new bands appeared at 1200–1250, 1010–1100 and 650 cm^{-1} are corresponding to the O=S=O asymmetric and symmetric stretching vibration and S-O stretching vibration of the sulfonic groups (-SO_3H).



c) FT-IR Spectra of Fe_3O_4 and SAMN.

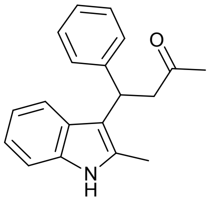
5- The FT-IR, ^{1}H- and ^{13}C-NMR spectrums of some products:

4-(1-H-3-indolyl)-2-butanone (entry 1, Table 3)



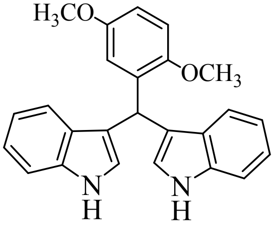
Pinkish solid, m.p: 91-93 ˚C; FT-IR: υmax (neat)= 3321, 1701, 1401cm^{-1};□ ^{1}HNMR (500 MHz, $CDCl_3$): δ= 8.37 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.22 (m, 3H), 6.94 (s, 1H), 3.10 (t, *J* = 7.1 Hz, 2H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.18 (s, 3H) ppm; ^{13}CNMR (125 MHz, $CDCl_3$): δ= 209.6, 136.4, 127.2, 122.0, 21.8, 119.2, 118.7, 114.7, 111.5, 44.1, 30.1, 19.5 ppm.

4-(2-methyl-1H-3-indolyl)-4-phenylbutan-2-one (entry 3, Table 3)



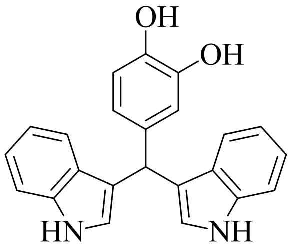
Oil, FT-IR: υmax (neat)= 3311, 1707, 1460, 1220 cm^{-1};□ ^{1}HNMR (500 MHz, $CDCl_3$): δ= 7.77 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.21 (m, 8H), 4.74 (dd, J_1= 8.3 Hz, J_2= 6.5 Hz, 1H), 3.32 (dd, J_1= 16.2 Hz, J_2= 8.3 Hz, 1H), 3.20 (dd, J_1= 16.2 Hz, J_2= 6.5 Hz, 1H), 2.21 (s, 3H), 1.93 (s, 3H) ppm; ^{13}CNMR (125 MHz, $CDCl_3$): δ= 208.3, 144.2, 135.5, 131.9, 128.4, 127.6, 126.0, 120.8, 119.2, 113.0, 110.6, 48.4, 36.9, 30.8, 12.1 ppm.

3-((2,5-dimethoxyphenyl)(1H-indole-3-yl)methyl)-1H-indole (entry 2, Table 5)



pinkish solid, m.p: 161-162 ˚C; FT-IR: υmax (neat)= 3422, 3350, 2949, 1494, 1454cm^{-1};□ ^{1}HNMR (500 MHz, $CDCl_3$): δ= 7.77 (s, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.73 (d, *J* = 3.1 Hz, 1H), 6.68 (dd, J_1 = 8.7 Hz, J_2= 5.6 Hz, 1H), 6.56 (s, 2H), 6.29 (s, 1H), 3.74 (s, 3H), 3.60 (s, 3H) ppm; ^{13}CNMR (125 MHz, $CDCl_3$): δ= 153.8, 151.7, 137.2, 134.7, 127.6, 124.1, 121.9, 120.2, 119.4, 119.2, 117.1, 112.2, 111.5, 111.0, 57.0, 55.8, 32.5 ppm.

4-(di(1H-indole-3-yl)methyl)benzene-1, 2-diol (entry 3, Table 5):



Yield: 94%, brown solid; m.p.: 145-146 ˚C; FT-IR: υ_{max}(KBr)= 3412, 1610, 1519, 1218, 743 cm^1; ^{1}HNMR (500 MHz, $CDCl_3$): δ= 8.45 (s, 2H), 7.38 (d, *J* = 8.0Hz, 2H), 7.31 (d, *J* =8.1 Hz, 2H), 7.11 (t, *J* = 7.9 Hz, 2H), 6.95 (t, *J* =7.7 Hz, 2H), 6.75-6.80 (m, 3H), 6.62 (s, 2H), 5.73 (s, 1H), 2.15 (s, 2H) ppm; ^{13}CNMR (125 MHz, $CDCl_3$): δ= 144.4, 143.2, 137.1, 137.0, 127.5, 124.2, 121.8, 120.9, 120.2, 120.0, 119.1, 116.2, 115.5, 111.6, 40.1 ppm.