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Research Article

Synthesis and characterization of molybdenum chelate-bonded supported on magnetic nanoparticle as an efficient and recyclable catalyst system for C–N cross coupling of amides

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ABSTRACT

Immobilization of molybdenum (VI) ions onto magnetic nanoparticles have been successfully prepared and applied for C–X cross-coupling reactions with aryl halides in green deep eutectic solvents. The results prove that the $Fe_3O_4@SiO_2$−HNPABA−Mo(VI) magnetic nanoparticles show high catalyst activity and good stability. It was also revealed that this complex can be recycled up to five times without any significant loss in catalytic activity

Keywords: Cross-coupling; Magnetic; Nanocatalyst; Immobilization

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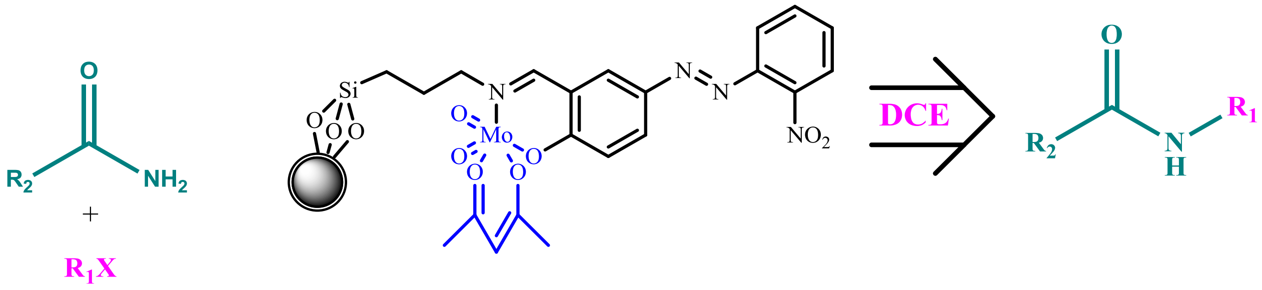
1. Introduction

Amides as valuable compounds are used widely in the synthesis of several biologically, medicinally, and materially potent molecules. In this regard, using the transition metal as catalyst for cross coupling of amides has attracted increasing attention in recent years. Many transition metals such as palladium, CuI and $Co(C_2O_4)$ have been used to synthesize N–

arylbenzamides. However, these metals require strict reaction conditions including various ligands and toxic solvents. As a result, achieving successful C–N cross coupling poses a great challenge from a green chemistry point of view. [1–5].

The use of magnetic nanoparticles (MNPs) as efficient supports for homogeneous catalysts has recently undergone intensive research. Magnetic nanoparticles often contain two components, a magnetic material and a chemical component that has functionality. These particles can be well dispersed in various solvents and easily separated magnetically from the medium after adsorption, eliminating the need for catalyst filtration and centrifugation. In addition, they can be reused up to several cycles almost without significant degradation of catalytic activity [6-12].

In this work, we used potassium carbonate and glycerol in different molar ratios to prepare a DES solvent and applied 2-Hydroxy-5-(2-nitrophenyl-diazenyl)benzaldehyde modified in magnetic nanoparticles ($Fe_3O_4@SiO_2$−HNPABA−Mo(VI)) as a green catalyst for *N*-arylations of amides with various types of aryl halides. This method has been described in a one-pot manner and under green (both solvent and catalyst) conditions (Scheme 1).



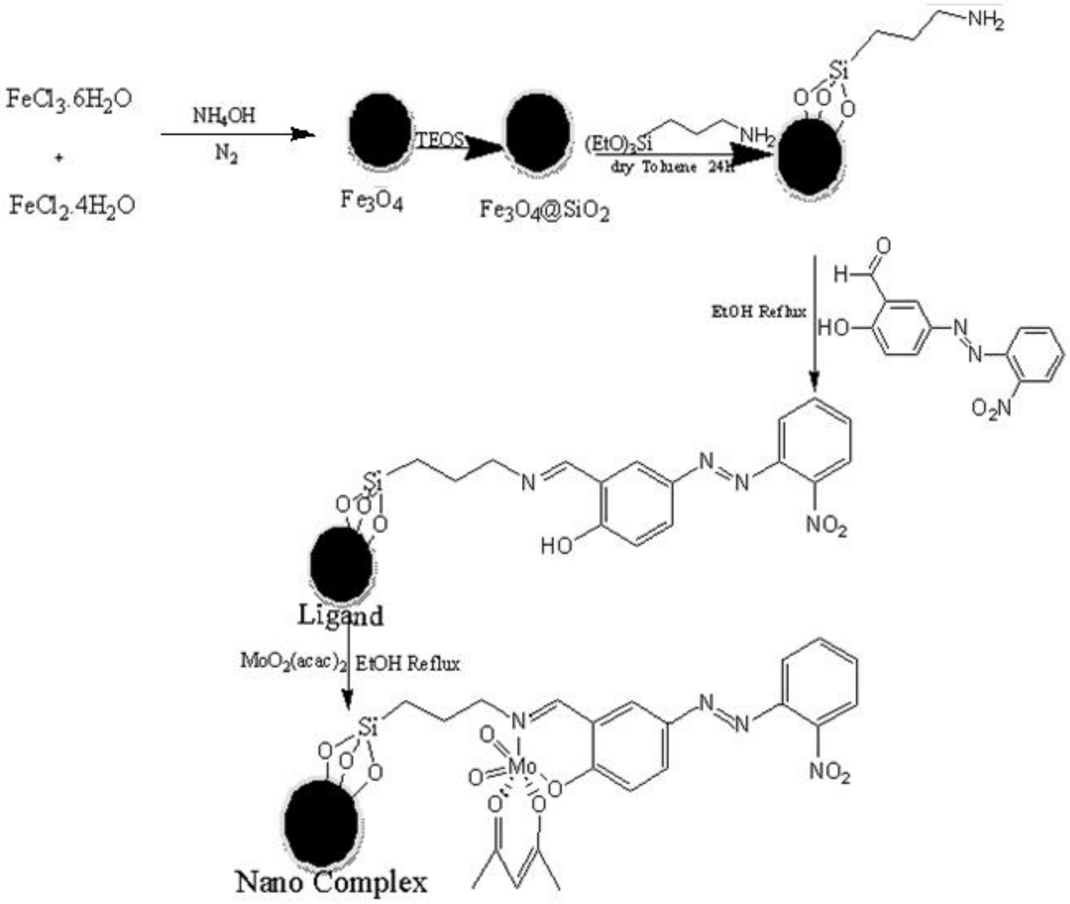
Scheme 1: Synthesis of Diversity of amides from aryl halides, catalyzed by $Fe_3O_4@SiO_2$−HNPABA−Mo(VI)

2. Experimental

All chemical materials were purchased from Sigma-Aldrich or Merck Chemical Companies. Purity of the synthesized compounds was monitored by TLC, visualizing with ultraviolet light and all yields refer to isolated products. Scanning electron microscopy (SEM) analysis was performed using a Zeiss-Vp-500 instrument equipped with an EDS analytical system. IR spectra of synthesized compounds were recorded on KBr pellets on a Bomem MB-1998 spectrophotometer. Magnetic saturation was carried out using a vibrating sample magnetometer (4 in., Daghigh Meghnatis Kashan Company, Kashan, Iran) at room temperature.

2.1. Preparation of Fe_3O_4@SiO_2−HNPABA−Mo(VI)

SiO_2@Fe_3O_4 (2.0 g) was dispersed in dry toluene (10 mL) and sonicated for 15 min in an ultrasonic bath prior to addition of (3-aminopropyl) triethoxysilane (2 mL). The mixture was stirred and refluxed for 72 h under the atmosphere of nitrogen. The solid materials were filtered off, washed with ethanol and diethyl ether, and dried under reduced pressure. In the second step, HNPABA (0.27 g, 1.0 mmol) was dissolved in ethanol (20 mL). Then, Fe_3O_4@SiO_2–NH_2 (1.0 g) was added to the above solution and allowed to react with HNPABA. The mixture was refluxed upon stirring for 12 h under the atmosphere of nitrogen to yield Fe_3O_4@SiO_2–HNPABA. Finally, the mixture of Fe_3O_4@SiO_2–HNPABA dispersed in ethanol (50 mL) and $MoO_2(acac)_2$ (0.327 g, 1.0 mmol) was refluxed for 24 h. The resulting black material was separated by magnetic decantation, washed with hot ethanol and dried at 50°C for 8 h.



Scheme 2: Preparation of $Fe_3O_4@SiO_2$−HNPABA−Mo(VI)

2.2. General Experimental Procedure for preparation of N-phenyl benzamides

To a stirred solution of amide (1.2 mmol), aryl halide (1.0 mmol), and DES, 0.040 g of the catalyst was added at 80 °C for 24 h. The catalyst was then separated using an external magnet and remnants of the reaction were extracted using ethyl acetate. Finally, the solvent was evaporated under reduced pressure and the pure product was obtained with silica-gel-plate chromatography.

3. Result and discussion

3.1. Characterization of $Fe_3O_4@SiO_2$−HNPABA−Mo(VI)

3.1.1. FTIR spectra

The Fourier-transform infrared spectroscopy (FTIR) spectra of Fe_3O_4 is shown in Figure 1. The typical peak at 572 cm^{-1} could be related to the Fe–O stretching vibration of Fe_3O_4. The peaks at 3209–3258 cm^{-1} and 1097 cm^{-1} are assigned to the hydroxyl O–H, Si-O-Si groups. Spectra of HNPABA show the peak at 1667, 1612, 1579, 1519, 1348, cm^{-1}, which could be attributed to the C=O, C=C, N=N and N=O stretching vibration. The peaks at 1646 and 929 cm^{-1} could be related to the C=N and MoO_2 groups, stretching vibration, respectively, which confirms the formation of the complex.

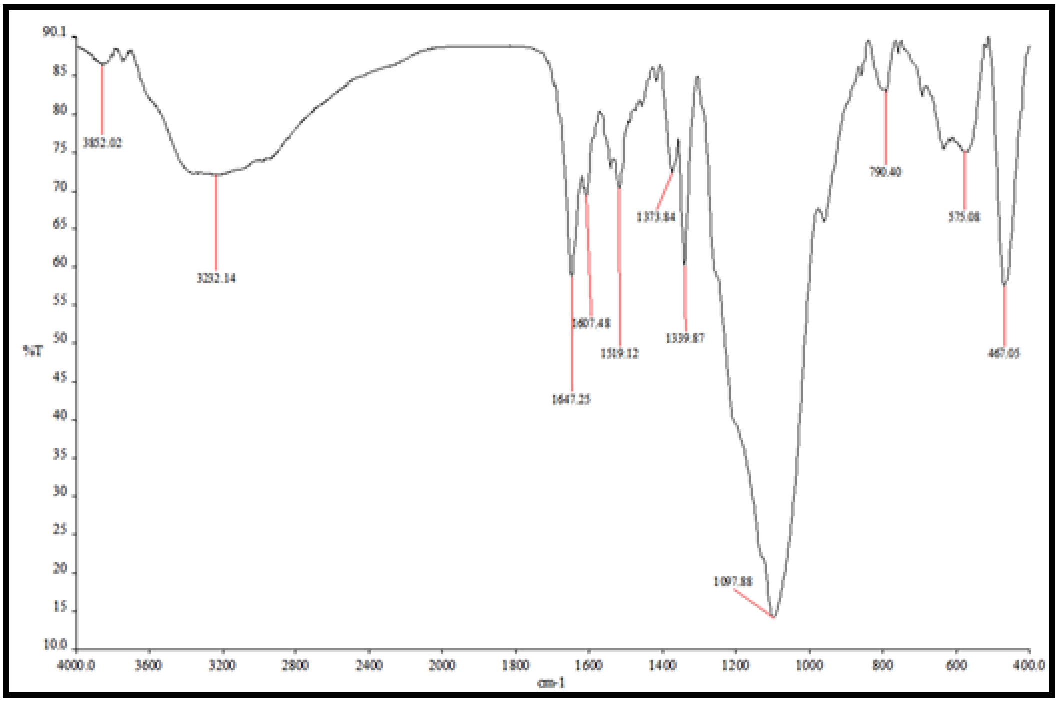


Fig. 1. The FT-IR spectra of $Fe_3O_4@SiO_2$−HNPABA−Mo(VI)

3.1.2. SEM

Scanning electron microscopy (SEM) images of the $Fe_3O_4@SiO_2$−HNPABA−Mo(VI) catalyst were obtained to investigate the morphology of the catalyst (Figure 2). The SEM images show that the nanoparticles are spherical and possess particle diameters less than 70 nm.

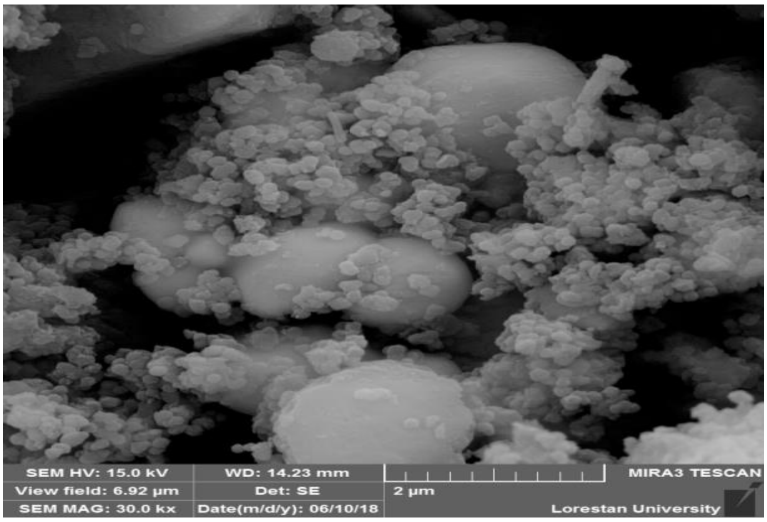


Fig. 2. SEM images of Fe_3O_4@SiO_2−HNPABA−Mo(VI),

3.1.3. EDX analysis

To study the elemental composition of Fe_3O_4@SiO_2−HNPABA−Mo(VI), EDX was performed (Figures 3). The EDX pattern confirms the good dispersion of Fe_3O_4@SiO_2−HNPABA−Mo(VI). Chemical characterization of the nanoparticles showed that they were composed of N, Fe, O, C, Mo and Si elements and this analysis indicated the presence of 1.41% Mo in Fe_3O_4@SiO_2−HNPABA−Mo(VI) (Figures 4).

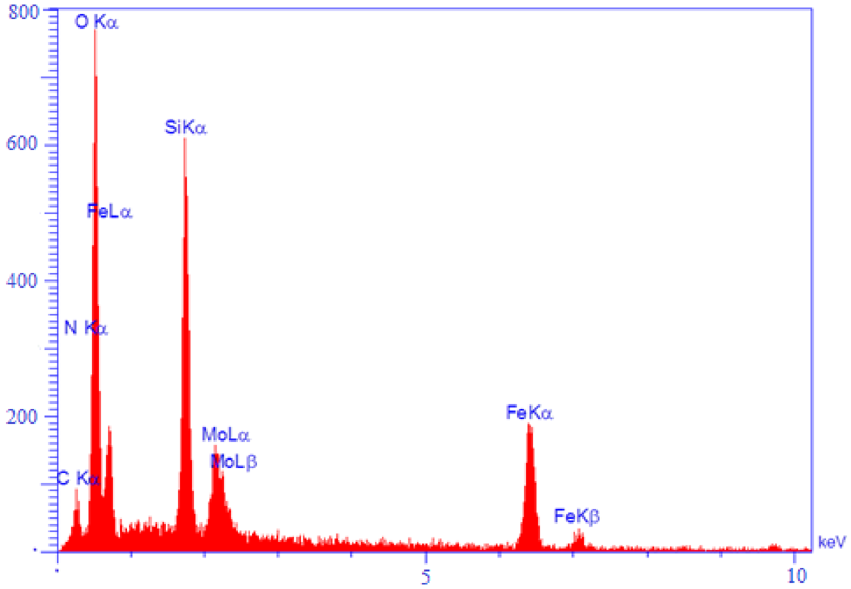
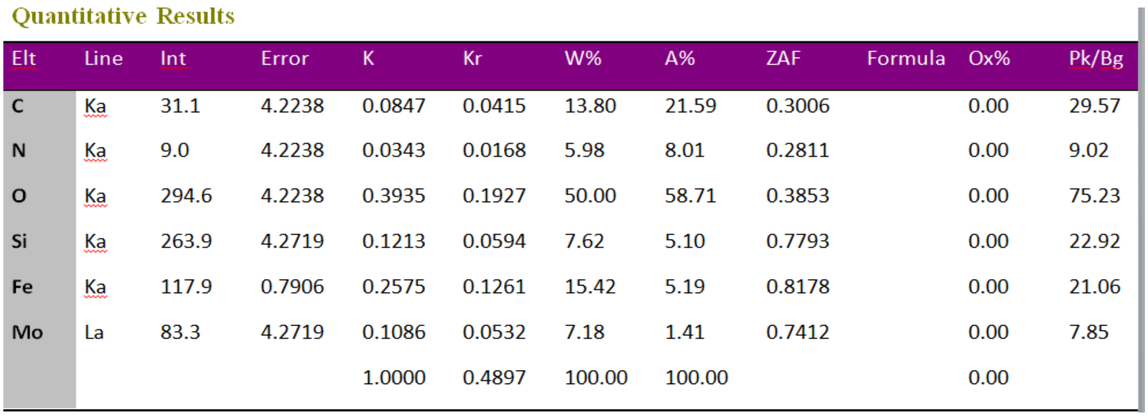


Fig. 3. EDX pattern of surface elements of functionalized nanoparticles



Quantitative Results

Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Pk/Bg
C	Ka	31.1	4.2238	0.0847	0.0415	13.80	21.59	0.3006		0.00	29.57
N	Ka	9.0	4.2238	0.0343	0.0168	5.98	8.01	0.2811		0.00	9.02
O	Ka	294.6	4.2238	0.3935	0.1927	50.00	58.71	0.3853		0.00	75.23
Si	Ka	263.9	4.2719	0.1213	0.0594	7.62	5.10	0.7793		0.00	22.92
Fe	Ka	117.9	0.7906	0.2575	0.1261	15.42	5.19	0.8178		0.00	21.06
Mo	La	83.3	4.2719	0.1086	0.0532	7.18	1.41	0.7412		0.00	7.85
				1.0000	0.4897	100.00	100.00			0.00	

Fig. 4. Weight percent of various elements on the surface of catalyst from EDX analysis

3.1.4. VSM analysis

The magnetic property of nanoparticles was evaluated by vibrating a sample magnetometer at ambient temperature with field sweeping from − 20,000 to + 20,000 Oe. As shown in Figure 5, the saturation magnetization of Fe_3O_4@SiO_2−HNPABA−Mo(VI) is around 20 emu g−1, lower than that of Fe_3O_4 (60 emu g−1). The magnetization curve indicates that these Fe_3O_4@SiO_2−HNPABA−Mo(VI) nanoparticles have paramagnetic properties, which means the nanoparticles can be easily separated from the solution by applying an external magnetic force.

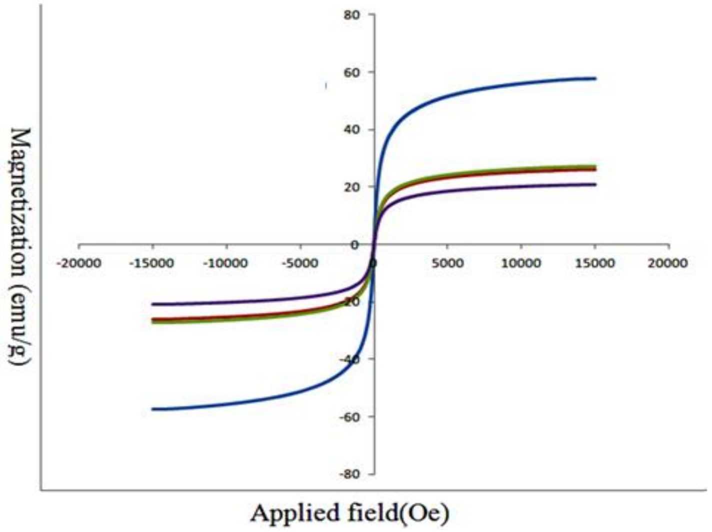


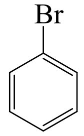
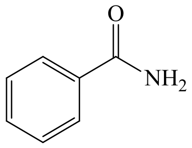
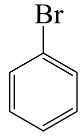
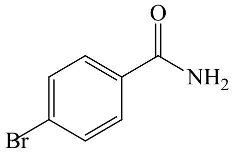
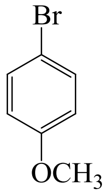
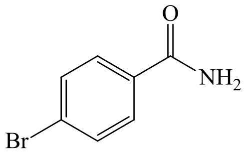
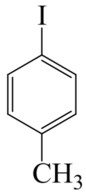
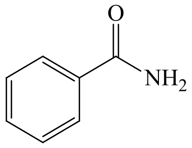
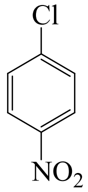
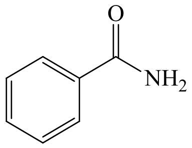
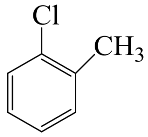
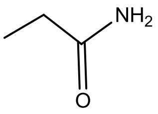
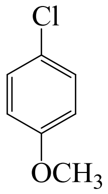
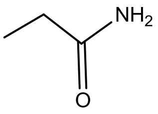
Fig. 5. Magnetization curves of Fe_3O_4 (blue), Fe_3O_4@SiO_2 (green), Fe_3O_4@SiO_2−HNPABA (red), Fe_3O_4@SiO_2−HNPABA−Mo(VI) (purple)

3.2. Catalytic performance

We evaluated the coupling reaction of amides with various aryl halides. We also investigated the effects of temperature, base, and solvent on this reaction. Our results show that in the absence of catalyst and base, no product was obtained. This implies that the catalyst and base play an important role in the transformation. Different bases such as pyridine, K_2CO_3, Et_3N, NaOH, and KOH have applied in this reaction. Among these, K_2CO_3 presented the best yield. Various solvents were evaluated, among which glycerol with K_2CO_3 as eutectic solvent offered excellent results. The best activity for the catalyst was seen in the eutectic solvent at 80 °C. Concerning the amount of catalyst, 0.04 g of $Fe_3O_4@SiO_2$−HNPABA−Mo(VI) was sufficient, as any amount over 0.04 g was worthless.

Under the optimized conditions, a series of reactions were carried out using amides and various types of aryl halides to produce the corresponding amides. The results are summarized in Table 1. It is quite evident that, besides iodobenzene, bromobenzene also gives a high yield. These results indicate that amides could successfully react with aryl halides without any difficulty in the cross-coupling reaction to yield corresponding amides in high to excellent yields (Table 3). Both electron-withdrawing and electron-donating groups were reacted to the phenyl ring of the aryl halide and generated product in high to excellent yields.

Table 1: Diversity of amides

Entry	Halide	Amide	Yield (%)[a]
1			88
2			95
3			92
4			92
5			91
6			85
7			88

[a] Isolated yield.

Reusability is one of the significant properties of a heterogeneous catalyst. Hence, recyclability and reusability of $Fe_3O_4@SiO_2$−HNPABA−Mo(VI) were investigated in model reactions (1-chloro-4-methoxybenzene and propionamide), which revealed the practical reusability and stability of $Fe_3O_4@SiO_2$−HNPABA−Mo(VI) nanoparticles. This nanomagnetic catalyst can be recycled efficiently for up to five times without significant loss in its catalytic activity.

4. Conclusion

In summary, DES was used as a safe, green, and effective solvent for *N*-arylation of amides with different aryl halides in the presence of (Fe_3O_4@SiO_2−HNPABA−Mo(VI)) as catalyst. This nanocatalyst could be recovered and reused for up to five times with no loss in its activity. More importantly, the use of non-toxic and commercially available stating materials, mild reaction conditions, easy recovery and potential recyclability, very high stability of the catalyst, the operational simplicity, high yields in short reaction times, have made this protocol suitable for industrial and pharmaceutical applications.

Acknowledgment

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