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Core–shell structured Fe $_3O_4@SiO_2$ -supported IL/[Mo $_6O_{19}$]: A novel and magnetically recoverable nanocatalyst for the preparation of biologically active dihydropyrimidinones

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Author statement

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Graphical abstract

A novel core–shell structured magnetic silica-supported ionic liquid/hexamolybdate complex $(Fe_3O_4@SiO_2-IL/[Mo_6O_{19}])$ has been prepared and characterized, and its catalytic performance in the Biginelli reaction has been investigated.



Core–shell structured $Fe_3O_4@SiO_2$ -supported IL/[Mo₆O₁₉]: A novel and magnetically recoverable nanocatalyst for the preparation of biologically active dihydropyrimidinones

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Abstract: The synthesis and catalytic application of a novel magnetic silica-nanomaterialsupported ionic liquid/hexamolybdate ($Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$) are reported. The $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ nanocatalyst was prepared through modification of magnetic $Fe_3O_4@SiO_2$ nanoparticles with alkyl-imidazolium ionic liquids followed by treatment with hexamolybdate anions. The $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ was characterized using FTIR, EDX, TGA, SEM, TEM, PXRD, and VSM techniques. This nanocatalyst exhibited excellent activity in the one-pot synthesis of biologically active dihydropyrimidinones through the Biginelli reaction. Furthermore, this magnetically recoverable nanocatalyst could be reused at least seven times without a significant loss of efficiency.

Keywords: Core-shell structure; Nanocatalyst; Polyoxometalate; Biginelli reaction

1. Introduction

Magnetic NPs are a very important group of nanomaterials incorporating Fe, Ni, and/or Co in their cores. Among them, applications of magnetic Ni and Co NPs are limited by their toxicity and high susceptibility to oxidation. Meanwhile, magnetite nanoparticles (MNPs) have attracted much attention from researchers due to their ease of preparation, nontoxicity, and eco-friendly nature [1-10]. However, the stability of Fe₃O₄ NPs has remained a challenge since they are sensitive to acidic and basic conditions and also tend to aggregate due to their magnetic nature. The aggregation and conversion of small MNPs into larger clusters limits their use in various processes [11-15]. To overcome these problems, many methods have been proposed for the protection of MNPs, which has led to the creation of core-shell nanostructures. These structures are defined as composites of nanomaterials with an inner core and one or more outer layer(s) as a shell [16-31]. Such core-shell structured MNPs have found numerous applications in diverse areas, such as biosensors [32-34], bioimaging [32, 35], drug delivery [36-40], optoelectronics [41-43], environmental extraction [44, 45], and especially in the field of catalysis [44, 46-49]. Different types of shell materials, such as polymers [50], silica [51, 52], carbon [48], and noble metals can be used for coating of magnetic NPs [53-55]. Among them, silica is often most attractive due to its facile modification with different organic or inorganic catalytic functional groups. In core-shell structures of this type, iron oxide nanoparticles form the cores and the silica layer acts as a protective shell. Therefore, silica-coated magnetic nanoparticles provide a clear perspective on the design and synthesis of recyclable and efficient magnetic nanocatalysts [56, 57]. Some recently reported magnetic catalytic systems with protective silica shells include Fe₃O₄/SiO₂-PIL [58], Fe₃O₄@SiO₂@mSiO₂-

Fe [59], Fe₃O₄@SiO₂@Ag@COOH [60], Fe₃O₄@SiO₂@ZnO [61], Fe₃O₄@SiO₂@PPy [62], Fe₃O₄@SiO₂/Bi₂WO₆/Bi₂S₃ [63], Fe₃O₄@SiO₂@C-Ni [64], Fe₃O₄@SiO₂-EDTA [65], Fe₃O₄/SiO₂/ZnO/ZnSe [66], and ionic-liquid-functionalized magnetic silica composites [67].

On the other hand, polyoxometalates (POMs) are inorganic complexes with significant physical and chemical properties that are based on transition metals (TM=V, W, Nb, Mo, Ta) in their highest oxidation states and oxygen bridges [68-70]. These are diverse in shape, size, and composition, varying from small species such as $[Mo_6O_{19}]^{2-}$ to nanoparticles such as $([H_xMo_{368}O_{10329}(H_2O)_{240}(SO_4)_{48}])[Mo_{368}]$. The properties of polyoxometalates, such as high thermal stability, solubility in polar solvents, good electron capture and electron capability, and high stability during oxidation reactions, endow them with strong potential for applications in different areas of chemical processing [71-75]. Moreover, variation of the structures of polyoxometalates has facilitated their applications in pharmaceuticals [76], coatings [77], separation [78], sensors [79], membranes [80], dyes [81], electrochemistry [82], capacitors [83], and catalysis [84-90]. However, the high solubility of POMs in polar solvents is a drawback, hampering separation and recovery of these complexes [91]. Therefore, the immobilization of POMs on solid supports such as silica and MNPs is a way to overcome this problem. Some recently developed systems of this type include AILs/HPW/UiO-66-2COOH [92], Fe₃O₄@SiO₂@NH-NH₂-PW [93], Fe₃O₄@SiO₂@ADMPT/H₆P₂W₁₈O₆₂ [94], and Fe₃O₄@D-NH₂-HPA [95].

Meanwhile, multicomponent reactions (MCRs) have a special place in organic and pharmaceutical chemistry, playing a key role in the production of different fine chemicals and drug intermediates [96]. The Biginelli reaction [97] is a type of MCR used for the preparation of dihydropyrimidinones with good biological profiles, such as anti-viral [98], anti-hypertensive [99], and anti-bacterial properties [100]. To date, many homogeneous and heterogeneous catalysts have been used for the Biginelli reaction. These include Fe₃O₄@CM [101], Fe₃O₄-MWCNT [102], IL-HSO₄@MCM-41@Cu [103], ompg-C₃N₄/SO₃H [104], ZnO/AlSBA-15 [105], AgNdSiW₁₁ [106], ZnO@SBA-15 [107], Ca₇Mg₃Hap [108], BPMO–IL–SO₃H [109], Mn@PMO-IL [110], Cu@PMO-IL [111], Cu/SB-Fe₃O₄ [112], PEt@Fe/IL [113], and Fe₃O₄@MCM-41-OB(OH)₂ [114]. However, some of the reported catalytic systems suffer from problems of long reaction times, harsh conditions, the use of a toxic organic solvent, low efficiency, and safety concerns. Therefore, the design and preparation of novel heterogeneous catalysts with high efficiency and recoverability to overcome the aforementioned restrictions is an important challenge in this context.

In view of the above, and due to the importance of polyoxometalates in catalytic processes, we report herein the synthesis and characterization of a novel magnetite core-shell silica-supported ionic liquid/polyoxometalate complex, $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$. This system has been employed as an effective, highly stable, and reusable nanocatalyst in the Biginelli reaction.

2. Experimental

2.1. Materials

All chemicals and reagents, namely iron(II) chloride tetrahydrate (99%), iron(III) chloride hexahydrate (99%), concentrated HCl, tetramethoxysilane (TMOS, 99%), ammonia (28%), 1-methylimidazole (99%), (3-chloropropyl)trimethoxysilane (97%), toluene, dimethyl sulfoxide, and the respective aldehyde derivatives, were purchased from Merck, Fluka, or Sigma-Aldrich.

2.2. Preparation of Fe₃O₄@SiO₂-IL

Firstly, $Fe_3O_4@SiO_2$ NPs were synthesized by a chemical co-precipitation method [115]. To prepare $Fe_3O_4@SiO_2$ -IL, $Fe_3O_4@SiO_2$ NPs (0.5 g) were completely dispersed in toluene (15 mL) under ultrasonication. 1-Methyl-3-(3-trimethoxysilylpropyl)imidazolium chloride (30 mg) was then added and the resulting mixture was heated under reflux for 24 h. The precipitate produced was collected with the aid of an external magnet, washed with EtOH, and dried at 70 °C for 5 h. The product was designated as $Fe_3O_4@SiO_2$ -IL.

2.3. Preparation of Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] nanocatalyst

For this, tetrabutylammonium hexamolybdate $((n-Bu_4N)_2[Mo_6O_{19}])$ was first prepared according to a previously reported procedure [113]. In order to immobilize $[Mo_6O_{19}]^{2-}$ on the Fe₃O₄@SiO₂-IL nanomaterial, Fe₃O₄@SiO₂/IL (0.5 g) was completely dispersed in dimethyl sulfoxide (15 mL) under ultrasonication. $(n-Bu_4N)_2[Mo_6O_{19}]$ (0.2 g) was then added and the resulting mixture was stirred at 25 °C for 24 h. The obtained product was separated magnetically, washed with EtOH, and dried at 60 °C for 5 h. It was designated as Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] nanocatalyst.

2.4. Synthesis of 3,4-dihydropyrimidinones using Fe₃O₄@SiO₂-IL/[Mo₆O₁₉]

For this, $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ nanocatalyst (0.01 g, 0.25 mol%) was added to a mixture of urea (1.5 mmol), aldehyde (1 mmol), and alkyl-acetoacetate (1 mmol). This mixture was sonicated at 65 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, warm EtOH (10 mL) was added and the mixture was filtered while hot. The 3,4-dihydropyrimidinone products were obtained after adding some ice followed by recrystallization from EtOH.

2.5. Characterization

Fourier-transform infrared (FTIR) spectra were recorded on a Bruker Vector 22 spectrometer. Energy-dispersive X-ray spectra (EDX) were obtained on a TESCAN Vega spectrometer. Scanning electron microscopy (SEM) images were acquired with a Philips XL30 emission scanning electron microscope. The magnetic properties of the particles were studied by vibrating sample magnetometry (VSM) on an instrument from Meghnatis Daghigh Kavir Co. Powder X-ray diffraction (PXRD) patterns were acquired with a PANalytical X-Pert diffractometer. TGA was performed using a Netzsch STA 409 PC/PG apparatus. Transmission electron microscopy (TEM) was performed with an FEI TECNAI 12 BioTWIN microscope. Melting points were determined using a Krüss KSB1N apparatus with samples in open capillary tubes. A KMM1-120WE301 ultrasonicator was used to disperse the particles and to promote the organic reactions.

3. Results and discussion

The preparation of $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ nanocomposite is illustrated in Scheme 1. As shown, a silica shell was first coated on the Fe_3O_4 surface through a sol–gel process to give $Fe_3O_4@SiO_2$ nanoparticles. The $Fe_3O_4@SiO_2$ NPs were then reacted with an alkylimidazolium IL to give $Fe_3O_4@SiO_2$ -IL. Finally, $Fe_3O_4@SiO_2$ -IL/[Mo₆O₁₉] nanocatalyst was obtained by treatment of $Fe_3O_4@SiO_2$ -IL with $(n-Bu_4N)_2[Mo_6O_{19}]$ (Scheme 1).



Scheme 1. Preparation of Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] nanocatalyst.

Figure 1 shows the FTIR spectra of the prepared nanomaterials. In the IR spectrum of Fe_3O_4 , the peak at 579 cm⁻¹ is due to the vibration mode of Fe–O bonds and the band at 3478 cm⁻¹ can be assigned to O-H bonds on the surface of the Fe_3O_4 NPs. For the $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ -IL/[Mo₆O₁₉] nanomaterials (Figures 1b, 1c), the peaks at 1091 and 800 cm⁻¹ are related to Si-O-Si bonds [116]. Moreover, the peaks at 3200–

3500 cm⁻¹ are assigned to OH bonds on the silica surface. For the latter sample, Fe-O bands were observed at 550–590 cm⁻¹. In the spectrum of Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] (Figure 1c), weak peaks discernible at 2900–3000 cm⁻¹ are related to aliphatic C-H bonds of methyl and propyl groups, and a peak at 3030 cm⁻¹ can be attributed to aromatic C-H bonds of imidazolium rings. Moreover, peaks at 1640 and 1417 cm⁻¹ can be ascribed to C=N and C=C bonds of IL rings, respectively. In addition, for Fe₃O₄@SiO₂-IL/[Mo₆O₁₉], the peaks at 958 and 796 cm⁻¹, corresponding to stretching vibrations of Mo=O and Mo-O-Mo bonds, respectively, of the [Mo₆O₁₉] complex anion, are overlapped with the Si-O-Si bands [117]. These results fully confirm the incorporation/immobilization and high stability of silica, ionic liquid, and polyoxometalate moieties into/onto the material framework.



Figure 1. FTIR spectra of Fe_3O_4 (a), $Fe_3O_4@SiO_2$ (b), and $Fe_3O_4@SiO_2$ -IL/[Mo₆O₁₉] (c).

The EDX analysis of the $Fe_3O_4@SiO_2$ -IL/[Mo₆O₁₉] catalyst is shown in Figure 2. The pattern demonstrated the presence of C, N, O, Si, Mo, Cl, and Fe in the sample. This result is in good agreement with the FTIR data, indicating immobilization of the ionic liquid and [Mo₆O₁₉] moieties on Fe₃O₄@SiO₂.



Figure 2. EDX analysis of the Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] nanocatalyst.

The thermal stability of the Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] nanocatalyst was studied from 25 to 900 °C by means of thermal gravimetric analysis (Figure 3). The first weight loss observed below 130 °C (about 2%) is related to the removal of H₂O and residual EtOH/MeOH solvents from the extraction process. The second weight loss between 220 and 310 °C (about 2%) corresponds to the removal of organic moieties located on the catalyst surface. The main weight loss at 350–650 °C (about 8%) can be attributed to the decomposition and removal of ionic liquid groups that make up the material network. The final weight loss above 650 °C (about 2%) corresponds to the removal of residual organic groups appended to the material framework.



Figure 3. TG analysis of the Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] nanocatalyst.

The surface morphology of the $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ nanocatalyst was investigated by SEM (Figure 4). This analysis showed the catalyst to be composed of spherical particles. Particles of this type have potential applications in catalytic and adsorption processes.



Figure 4. SEM image of $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$.

A TEM image (Figure 5) of the $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ nanocatalyst clearly showed a core-shell structure, with black cores (magnetite particles) and gray shells (silica layers).



Figure 5. TEM image of Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] nanocatalyst.

Figure 6 shows the PXRD pattern of the nanocatalyst. It features seven reflection peaks at 2θ =30.29°, 35.61°, 43.26°, 53.65°, 57.22°, 62.86°, and 74.48°, corresponding to Miller indices (*hkl*) of 220, 311, 400, 422, 511, 440, and 533, respectively. These are related to the crystalline structure of Fe₃O₄, confirming high stability of magnetite NPs after modification with different functional groups. A weak reflection peak at 2θ =18.14° corresponds to the amorphous silica shell.



Figure 6. PXRD pattern of Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] nanocatalyst.

VSM was carried out to verify the magnetic properties of the designed catalyst (Figure 7). The magnetic saturation value of the catalyst was evaluated as 40 emu/g, confirming its high degree of paramagnetism. This is a very good characteristic, especially in the fields of catalysis and adsorption.



Figure 7. VSM analysis of $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ nanocatalyst.

After characterization of the $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ nanocatalyst, its performance in the Biginelli reaction was studied (Table 1). The condensation of benzaldehyde with ethyl acetoacetate and urea was chosen as a test reaction, and was conducted under ultrasonication.

Table 1. Screening different parameters in a Biginelli reaction catalyzed by Fe ₃ O ₄ @SiO ₂ -								
$IL/[Mo_6O_{19}].$								
$\begin{array}{c} O \\ H \\ H \\ H_{3}C \\ H \\ H_{2}C \\ H \\ H_{2}N \\ H_{2} \\ H \\ H_{2}N \\ H_{2} \\ H \\ H_{2}N \\ H_{2} \\ H \\ H_{2}N \\ H \\ H \\ H_{2}N \\ H \\ $								
Entry	Solvent	Catalyst (mol % of Mo)	T (°C)	Time (min)	Yield (%) ^a			
1	ethanol	0.25	65	40	84			
2	toluene	0.25	65	40	21			
3	H ₂ O	0.25	65	40	73			
4	-	0.25	65	40	92			
5	-	0.2	65	40	81			
6	-	0.3	65	40	93			
7	-	0.25	75	40	93			
8		0.25	45	40	54			
9	- 5	0.25	25	40	<7			
10 ^b	H ₂ O	Fe ₃ O ₄ @SiO ₂ ^b	65	40	5			
11 °	H ₂ O	Fe ₃ O ₄ @SiO ₂ /IL ^c	65	40	10			
12	-	$(n-Bu_4N)_2[Mo_6O_{19}]^d$	65	40	67			
^a Isolated yield. ^b 0.01 g of Fe ₃ O ₄ @SiO ₂ was used. ^c 0.01 g of Fe ₃ O ₄ @SiO ₂ /IL was used. ^d (<i>n</i> -Bu ₄ N) ₂ [Mo ₆ O ₁₉] was used as catalyst.								

Performing the reaction in different solvents, yields of 73% and 84% were obtained in H₂O and ethanol, respectively. In toluene, however, the yield was only 21%. Pleasingly, under solvent-free conditions, the best conversion and yield were obtained (Table 1, entries 1-4). Therefore, in subsequent experiments, the reactions were performed without a solvent. Next, the effect of catalyst amount was studied (Table 1, entries 4-6). The results showed that the reaction gave satisfactory conversions using 0.2 to 0.25 mol% of catalyst. Increasing the catalyst loading to 0.3 mol% did not result in a significant change in the reaction yield. The study also showed the reaction to be affected by temperature, and the best result was observed at 65 °C. Accordingly, 0.25 mol% of Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] under solvent-free conditions, 65 °C, and ultrasonic irradiation were identified as the optimal conditions. In order to demonstrate the effect of the hexamolybdate centers on the catalytic process, the catalytic activities of Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂/IL were also investigated, and the results were compared with those for $Fe_3O_4@SiO_2/IL-Mo_6O_{19}$. These experiments showed that both hexamolybdate-free nanomaterials gave only low yields of the desired product, verifying that the reaction is actually catalyzed by the supported hexamolybdate species (Table 1, entry 4 vs entries 10, 11). Interestingly, the unsupported hexamolybdate also showed significantly lower catalytic activity compared with Fe₃O₄@SiO₂/IL-Mo₆O₁₉, which may be attributed to the tendency of POMs to form agglomerates or inactive dimers in homogeneous solution. Importantly, ionic liquids as stabilizing agents can reduce these drawbacks through electrostatic interaction between the imidazolium cation and the hexamolybdate anions (Scheme 1) [118].

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We then proceeded to apply various aldehyde derivatives as substrates to deliver the corresponding dihydropyrimidinones under the optimal conditions (Table 2).

Table 2. Synthesis of 3,4-dihydropyrimidone derivatives in the presence of Fe ₃ O ₄ @SiO ₂ -									
IL/[Mo ₆ O ₁₉] nanocatalyst.									
ArCHO + H_3C R + H_2N NH ₂ $Fe_3O_4@SiO_2/IL-Mo_6O_{19}$ R NH Solvent free, 65 °C,)))									
Entry	Aldehyde	R	Time (min)	Yield ^a (%)	TON ^b	TOF ^c	m. p. (found)	m. p. (reported)	
1	O H	OEt	40	92	368	557.5	201–203	201–203 [119]	
2	O H	OMe	40	90	360	545.4	210–212	208–211 [120]	
3	Cl O H	OEt	50	88	352	424.0	213–215	213– 215 ^[120]	
4	Cl O H	OMe	50	87	348	419.2	250–252	251–253 [121]	
5	MeO	OEt	50	86	344	414.4	198–200	199–201 [119]	

6	MeO	OMe	50	85	340	409.6	193–195	191–193 [119]
7	O ₂ N H	OEt	30	94	376	752	209–211	210–211 [120]
8	O Br	OEt	55	87	348	382.4	194–196	193–195 [110]
9	НО	OEt	60	83	332	332	233–235	231–233 [120]
^a Isolated yield. ^b Turnover number [defined as yield (%)/ cat. (mol%)]. ^c Turnover frequency [defined as TON/reaction time (h)].								

As can be seen, aldehydes bearing both electron-donating and electron-accepting substituents were employed as substrates, all of which delivered the corresponding Biginelli products in high to excellent yields. It was also found that $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ offers high turnover number (TON) and turnover frequency (TOF) for all products, indicating high performance of the designed catalyst in the preparation of different dihydropyrimidinone derivatives.

The recoverability and reusability of the catalyst were also investigated. These experiments showed that the $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ nanocatalyst could be reused at

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least seven times in the Biginelli process with no significant reduction in efficiency (Figure 8), indicating high stability and durability of this nanocatalyst under the applied conditions.



Figure 8. Reusability of the Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] nanocatalyst.

In the next experiment, a leaching test was performed. For this, after the condensation was about 45% complete, the catalyst was separated magnetically and the reaction of the residue was allowed to continue under the optimum conditions. Interestingly, after 60 min, no further progress of the reaction was observed, confirming the heterogeneous nature of the catalyst as well as the high efficiency of the $Fe_3O_4@SiO_2-IL$ support in the immobilization of active polyoxometalate species.

A mechanism for the Biginelli reaction using $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ catalyst is proposed in Scheme 2. As shown, the aldehyde (1) is first activated by Lewis acidic Mo sites of the

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hexamolybdate species. In the next step, nucleophilic attack of urea (2) on the activated carbonyl group followed by elimination of water produces an *N*-acyliminium cation (3). Subsequently, nucleophilic attack of the enolate form of β -ketoester 4 followed by deprotonation by Lewis basic oxygen groups of the catalyst produces intermediate 5. Finally, the desired Biginelli product is obtained by ring-closure and the elimination of water.



Scheme 2. Proposed mechanism for Biginelli reaction using $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ nanocatalyst.

Finally, the performances of $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ and previously reported catalysts in the Biginelli reaction were compared (Table 3). The results showed that although the previous catalytic systems have advantages of good recoverability and separation, the present catalyst is better, especially in terms of the mild conditions applied, reaction rate, and recovery times. Moreover, the TON and TOF of the present catalytic system exceed those quoted in previous reports. These findings may be attributed to the magnetic nature of this catalyst, the chemically immobilized ionic liquid moieties, as well as the bifunctional properties (both Lewis acidic and Lewis basic sites) of the supported polyoxometalate.

with previously reported catalytic systems in the Biginelli reaction.									
Entry	Catalyst	Conditions	Time	TON	TOF	Recovery	Ref.		
			(min)			times			
1	PEt@Fe/IL	Cat.	90	126.7	84.4	7	[113]		
		(0.75 mol%),							
		solvent-free,							
		80 °C							
2	GO-ZrPPh	Cat.	50	121.3	146.1	4	[122]		

Table 3. Comparative study of the efficiency of the $Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]$ nanocatalyst with previously reported catalytic systems in the Biginelli reaction.

		(0.28 mol%),						
		solvent-free,						
		70 °C						
3	n-ZrSA	Cat. (10 mol%),	30	9.8	19.6	5	[123]	
		solvent-free,						
		90 °C			X			
4	SnCl ₂ /nano SiO ₂	Cat.	40	208.8	316.3	4	[124]	
		(0.45 mol%),						
		EtOH, reflux		R				
5	Fe ₃ O ₄ @SiO ₂ -	Cat.	40	367	557.5	7	This	
	IL/[Mo ₆ O ₁₉]	(0.25 mol%),					work	
		solvent-free,						
		65 °C						
Abbreviations: PEt@Fe/IL: polyethylene-supported Fe/ionic liquid complex; GO-ZrPPh:								
zirconium(IV) porphyrin graphene oxide; n-ZrSA: nano-ZrO ₂ sulfuric acid; SnCl ₂ /nano SiO ₂ :								
nanosilica-supported tin(II) chloride.								

4. Conclusion

A novel core–shell magnetite silica-supported ionic liquid/hexamolybdate complex $(Fe_3O_4@SiO_2-IL/[Mo_6O_{19}])$ has been prepared for the first time, and its properties have been investigated. FTIR, EDX, TGA, SEM, TEM, PXRD, and VSM analyses of the $Fe_3O_4@SiO_2$ -

IL/[Mo_6O_{19}] proved successful coating and immobilization of silica, ILs, and hexamolybdate ions on the surface of the Fe₃O₄ NPs. The Fe₃O₄@SiO₂-IL/[Mo_6O_{19}] catalyst has been heterogeneously and powerfully employed in the Biginelli reaction to give dihydropyrimidinones in high yields. Other advantages of this catalytic system are easy separation of the products and catalyst, short reaction times, solvent-free conditions, low catalyst loading, and high efficiency of the catalyst. Further application of Fe₃O₄@SiO₂-IL/[Mo_6O_{19}] is underway in our laboratory.

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References

[1] K. El-Boubbou, Magnetic iron oxide nanoparticles as drug carriers: preparation, conjugation and delivery, Nanomed., 13 (2018) 929-952.

[2] A.H. Lu, E.e.L. Salabas, F. Schüth, Magnetic nanoparticles: synthesis, protection, functionalization, and application, Angew Chem. Int. Ed. Engl., 46 (2007) 1222-1244.

[3] D. Lisjak, A. Mertelj, Anisotropic magnetic nanoparticles: A review of their properties, syntheses and potential applications, Prog. Mater Sci., 95 (2018) 286-328.

[4] G. Simonsen, M. Strand, G. Øye, Potential applications of magnetic nanoparticles within separation in the petroleum industry, J. Petrol. Sci. Eng., 165 (2018) 488-495.

[5] M.B. Gawande, P.S. Branco, R.S. Varma, Nano-magnetite (Fe_3O_4) as a support for recyclable catalysts in the development of sustainable methodologies, Chem. Soc. Rev., 42 (2013) 3371-3393.

[6] W. Xie, Y. Han, H. Wang, Magnetic Fe_3O_4/MCM -41 composite-supported sodium silicate as heterogeneous catalysts for biodiesel production, Renew. Energy, 125 (2018) 675-681.

[7] S. Ezzah-Mahmudah, I.M. Lokman, M.I. Saiman, Y.H. Taufiq-Yap, Synthesis and characterization of Fe₂O₃/CaO derived from Anadara Granosa for methyl ester production, Energy Convers. Manag., 126 (2016) 124-131.

[8] H. Yang, G. Li, Z. Ma, Magnetic core–shell-structured nanoporous organosilica microspheres for the Suzuki–Miyaura coupling of aryl chlorides: improved catalytic activity and facile catalyst recovery, J. Mater. Chem., 22 (2012) 6639-6648.

[9] M.A. Ashraf, Z. Liu, W.-X. Peng, C. Gao, New copper complex on Fe_3O_4 nanoparticles as a highly efficient reusable nanocatalyst for synthesis of polyhydroquinolines in water, Catal. Lett., (2019) 1-19.

[10] W. Xie, F. Wan, Basic ionic liquid functionalized magnetically responsive $Fe_3O_4@HKUST-1$ composites used for biodiesel production, Fuel, 220 (2018) 248-256.

[11] J. Sun, G. Yu, L. Liu, Z. Li, Q. Kan, Q. Huo, J. Guan, Core–shell structured $Fe_3O_4@SiO_2$ supported cobalt(II) or copper(II) acetylacetonate complexes:

magnetically recoverable nanocatalysts for aerobic epoxidation of styrene, Catal. Sci. Technol., 4 (2014) 1246-1252.

[12] R.-Y. Hong, J.-H. Li, S.-Z. Zhang, H.-Z. Li, Y. Zheng, J.-m. Ding, D.-G. Wei, Preparation and characterization of silica-coated Fe_3O_4 nanoparticles used as precursor of ferrofluids, Appl. Surf. Sci., 255 (2009) 3485-3492.

[13] T. Yao, T. Cui, X. Fang, J. Yu, F. Cui, J. Wu, Preparation of yolk/shell Fe_3O_4 @polypyrrole composites and their applications as catalyst supports, Chem. Eng. J., 225 (2013) 230-236.

[14] G.S. An, J.S. Han, J.R. Shin, D.H. Chae, J.U. Hur, H.-Y. Park, Y.-G. Jung, S.-C. Choi, In situ synthesis of $Fe_3O_4@SiO_2$ core–shell nanoparticles via surface treatment, Ceram. Int., 44 (2018) 12233-12237.

[15] W. Dong, Y. Li, D. Niu, Z. Ma, J. Gu, Y. Chen, W. Zhao, X. Liu, C. Liu, J. Shi, Facile synthesis of monodisperse superparamagnetic Fe_3O_4 core@hybrid@Au shell nanocomposite for bimodal imaging and photothermal therapy, Adv. Mater., 23 (2011) 5392-5397.

[16] A.M. El-Toni, M.A. Habila, J.P. Labis, Z.A. ALOthman, M. Alhoshan, A.A. Elzatahry, F. Zhang, Design, synthesis and applications of core–shell, hollow core, and nanorattle multifunctional nanostructures, Nanoscale, 8 (2016) 2510-2531.

[17] P. Reiss, M. Protiere, L. Li, Core/shell semiconductor nanocrystals, Small, 5 (2009) 154-168.

[18] K. Kamata, Y. Lu, Y. Xia, Synthesis and characterization of monodispersed core-shell spherical colloids with movable cores, J. Am. Chem. Soc., 125 (2003) 2384-2385.

[19] R. Haag, Supramolecular drug-delivery systems based on polymeric core–shell architectures, Angew Chem. Int. Ed. Engl., 43 (2004) 278-282.

[20] K. Aslan, M. Wu, J.R. Lakowicz, C.D. Geddes, Fluorescent core–shell Ag@SiO₂ nanocomposites for metal-enhanced fluorescence and single nanoparticle sensing platforms, J. Am. Chem. Soc., 129 (2007) 1524-1525.

[21] H. Zeng, J. Li, Z. Wang, J. Liu, S. Sun, Bimagnetic core/shell FePt/Fe₃O₄ nanoparticles, Nano Lett., 4 (2004) 187-190.

[22] K. Sasaki, H. Naohara, Y. Cai, Y.M. Choi, P. Liu, M.B. Vukmirovic, J.X. Wang, R.R. Adzic, Core-protected platinum monolayer shell high-stability electrocatalysts for fuel-cell cathodes, Angew Chem. Int. Ed. Engl., 49 (2010) 8602-8607.

[23] C.D. Jones, L.A. Lyon, Synthesis and characterization of multiresponsive core– shell microgels, Macromolecules, 33 (2000) 8301-8306.

[24] Y. Mei, Y. Lu, F. Polzer, M. Ballauff, M. Drechsler, Catalytic activity of palladium nanoparticles encapsulated in spherical polyelectrolyte brushes and core–shell microgels, Chem. Mater., 19 (2007) 1062-1069.

[25] J. Zhang, Y. Tang, K. Lee, M. Ouyang, Nonepitaxial growth of hybrid coreshell nanostructures with large lattice mismatches, Science, 327 (2010) 1634-1638. [26] H.-L. Jiang, T. Akita, T. Ishida, M. Haruta, Q. Xu, Synergistic catalysis of Au@Ag core- shell nanoparticles stabilized on metal-organic framework, J. Am. Chem. Soc., 133 (2011) 1304-1306.

[27] Y. Tak, S.J. Hong, J.S. Lee, K. Yong, Fabrication of ZnO/CdS core/shell nanowire arrays for efficient solar energy conversion, J. Mater. Chem., 19 (2009) 5945-5951.

[28] L. Wang, L. Wang, J. Luo, Q. Fan, M. Suzuki, I.S. Suzuki, M.H. Engelhard, Y. Lin, N. Kim, J.Q. Wang, Monodispersed core–shell Fe₃O₄@Au nanoparticles, J. Phys. Chem. B, 109 (2005) 21593-21601.

[29] Z. Chen, Y.-J. Xu, Ultrathin TiO_2 layer coated-CdS spheres core–shell nanocomposite with enhanced visible-light photoactivity, ACS Appl. Mater. Interfaces, 5 (2013) 13353-13363.

[30] N. Zhang, S. Liu, Y.-J. Xu, Recent progress on metal core@semiconductor shell nanocomposites as a promising type of photocatalyst, Nanoscale, 4 (2012) 2227-2238.

[31] N. Zhang, Y.-J. Xu, Aggregation- and leaching-resistant, reusable, and multifunctional $Pd@CeO_2$ as a robust nanocatalyst achieved by a hollow core–shell strategy, Chem. Mater., 25 (2013) 1979-1988.

[32] K. Chatterjee, S. Sarkar, K.J. Rao, S. Paria, Core/shell nanoparticles in biomedical applications, Adv. Colloid Interface Sci., 209 (2014) 8-39.

[33] C. Ozdemir, O. Akca, E.I. Medine, D.O. Demirkol, P. Unak, S. Timur, Biosensing applications of modified core–shell magnetic nanoparticles, Food Anal. Methods, 5 (2012) 731-736.

[34] P. Scodeller, V. Flexer, R. Szamocki, E. Calvo, N. Tognalli, H. Troiani, A. Fainstein, Wired-enzyme core–shell Au nanoparticle biosensor, J. Am. Chem. Soc., 130 (2008) 12690-12697.

[35] S. Ye, M. Zhao, J. Song, J. Qu, Core-shell structured NaMnF₃: Yb, Er nanoparticles for bioimaging applications, RSC Adv., 7 (2017) 52588-52594.

[36] S.I.U. Madrid, U. Pal, Y.S. Kang, J. Kim, H. Kwon, J. Kim, Fabrication of $Fe_3O_4@mSiO_2$ core-shell composite nanoparticles for drug delivery applications, Nanoscale Res. Lett., 10 (2015) 217.

[37] Q.L. Wang, X.P. Zhang, B.Z. Chen, X.D. Guo, Dissolvable layered microneedles with core-shell structures for transdermal drug delivery, Mater. Sci. Eng. C, 83 (2018) 143-147.

[38] J.T. Peters, S.S. Hutchinson, N. Lizana, I. Verma, N.A. Peppas, Synthesis and characterization of poly(*N*-isopropyl methacrylamide) core/shell nanogels for controlled release of chemotherapeutics, Chem. Eng. J., 340 (2018) 58-65.

[39] M.-C. Liu, B. Liu, X.-L. Chen, H.-C. Lin, X.-Y. Sun, J.-Z. Lu, Y.-Y. Li, S.-Q. Yan, L.-Y. Zhang, P. Zhao, Calcium carbonate end-capped, folate-mediated $Fe_3O_4@mSiO_2$ core-shell nanocarriers as targeted controlled-release drug delivery system, J. Biomater. Appl., 32 (2018) 1090-1104.

[40] S. Sanchez-Salcedo, M. Vallet-Regí, S.A. Shahin, C.A. Glackin, J.I. Zink, Mesoporous core-shell silica nanoparticles with anti-fouling properties for ovarian cancer therapy, Chem. Eng. J., 340 (2018) 114-124.

[41] X. Tong, X.T. Kong, C. Wang, Y. Zhou, F. Navarro-Pardo, D. Barba, D. Ma, S. Sun, A.O. Govorov, H. Zhao, Optoelectronic properties in near-infrared colloidal heterostructured pyramidal "giant" core/shell quantum dots, Adv. Sci., 5 (2018) 1800656.

[42] M.A. Khan, Y. Wahab, R. Muhammad, M. Tahir, S. Sakrani, Catalyst-free fabrication of novel ZnO/CuO core-shell nanowires heterojunction: Controlled growth, structural and optoelectronic properties, Appl. Surf. Sci., 435 (2018) 718-732.

[43] Z.J. Li, E. Hofman, J. Li, A.H. Davis, C.H. Tung, L.Z. Wu, W. Zheng, Photoelectrochemically active and environmentally stable CsPbBr₃/TiO₂ core/shell nanocrystals, Adv. Funct. Mater., 28 (2018) 1704288.

[44] J. Pu, K. Nishikado, N. Wang, T.T. Nguyen, T. Maki, E.W. Qian, Core-shell nickel catalysts for the steam reforming of acetic acid, Appl. Catal. B-Environ., 224 (2018) 69-79.

[45] L. Ling, X.Y. Huang, W.X. Zhang, Enrichment of precious metals from wastewater with core–shell nanoparticles of iron, Adv. Mater., 30 (2018) 1705703.

[46] Y. Guo, J. Tang, Z. Wang, Y.-M. Kang, Y. Bando, Y. Yamauchi, Elaborately assembled core-shell structured metal sulfides as a bifunctional catalyst for highly efficient electrochemical overall water splitting, Nano Eng., 47 (2018) 494-502.

[47] N. Senthilkumar, G. Gnana Kumar, A. Manthiram, 3D hierarchical core–shell nanostructured arrays on carbon fibers as catalysts for direct urea fuel cells, Adv. Energy Mater., 8 (2018) 1702207.

[48] J. Zhao, C. Li, R. Liu, Enhanced oxygen reduction of multi-Fe $_3O_4$ @carbon core-shell electrocatalysts through a nanoparticle/polymer co-assembly strategy, Nanoscale, 10 (2018) 5882-5887.

[49] S. Das, J. Ashok, Z. Bian, N. Dewangan, M. Wai, Y. Du, A. Borgna, K. Hidajat, S. Kawi, Silica–ceria sandwiched Ni core–shell catalyst for low temperature dry reforming of biogas: Coke resistance and mechanistic insights, Appl. Catal. B-Environ., 230 (2018) 220-236.

[50] M.A. Cruz, S. Ye, M.J. Kim, C. Reyes, F. Yang, P.F. Flowers, B.J. Wiley, Multigram synthesis of Cu-Ag core–shell nanowires enables the production of a highly conductive polymer filament for 3D printing electronics, Part Part Syst. Char., 35 (2018) 1700385.

[51] Y. Li, C. Zeng, C. Wang, L. Zhang, Preparation of C@silica core/shell nanoparticles from ZIF-8 for efficient ciprofloxacin adsorption, Chem. Eng. J., 343 (2018) 645-653.

[52] S. Meaney, B. Follink, R.F. Tabor, Synthesis, characterisation and applications of polymer–silica core–shell microparticle capsules, ACS Applied Materials & Interfaces, 10 (2018) 43068–43079.

[53] J.N. Schwämmlein, B.M. Stühmeier, K. Wagenbauer, H. Dietz, V. Tileli, H.A. Gasteiger, H.A. El-Sayed, Origin of superior HOR/HER activity of bimetallic Pt-Ru catalysts in alkaline media identified via Ru@Pt core-shell nanoparticles, J. Electrochem. Soc., 165 (2018) H229-H239.

[54] Y. Lu, J. Zhong, G. Yao, Q. Huang, A label-free SERS approach to quantitative and selective detection of mercury(II) based on DNA aptamer-modified SiO₂@Au core/shell nanoparticles, Sensor Actuat. B-Chem., 258 (2018) 365-372.

[55] H. Xu, P. Song, J. Wang, Y. Shiraishi, Y. Du, Q. Liu, Visible-light-driven 3D dendritic PtAu@ Pt core-shell photocatalyst toward liquid fuel electrooxidation, ACS Sustain. Chem. Eng., 6 (2018) 7159-7167.

[56] R. Fan, H. Min, X. Hong, Q. Yi, W. Liu, Q. Zhang, Z. Luo, Plant tannin immobilized $Fe_3O_4@SiO_2$ microspheres: A novel and green magnetic bio-sorbent with superior adsorption capacities for gold and palladium, J. Hazard. Mater., 364 (2019) 780-790.

[57] M. Gao, W. Li, J. Dong, Z. Zhang, B. Yang, Synthesis and characterization of superparamagnetic $Fe_3O_4@SiO_2$ core-shell composite nanoparticles, World J. Condens. Matter. Phys., 1 (2011) 49.

[58] W. Xie, H. Wang, Immobilized polymeric sulfonated ionic liquid on core-shell structured Fe_3O_4/SiO_2 composites: A magnetically recyclable catalyst for simultaneous transesterification and esterifications of low-cost oils to biodiesel, Renew. Energy, 145 (2020) 1709-1719.

[59] Y. Yang, B. Xu, J. He, J. Shi, L. Yu, Y. Fan, Design and synthesis of $Fe_3O_4@SiO_2@mSiO_2$ -Fe: A magnetically separable catalyst for selective oxidative cracking reaction of styrene using air as partial oxidant, Appl. Catal., A, 590 (2020) 117353.

[60] X. Hu, X. Bian, S. Yu, K. Dan, Magnetic $Fe_3O_4@SiO_2@Ag@COOH$ NPs/Au film with hybrid localized surface plasmon/surface plasmon polariton modes for surface-enhanced Raman scattering detection of thiabendazole, J. Nanosci. Nanotechnol., 20 (2020) 2079-2086.

[61] M. Banihashemi, N. Dalali, N. Sehati, B. Farajmand, Decoration of $Fe_3O_4@SiO_2@ZnO$ as a high performance nanosorbent on a stir bar microextraction device for preconcentration and determination of cadmium in real water samples, Microchem. J., (2020) 104599.

[62] T. Liu, N. Liu, S. Zhai, S. Gao, Z. Xiao, Q. An, D. Yang, Tailor-made core/shell/shell-like $Fe_3O_4@SiO_2@PPy$ composites with prominent microwave absorption performance, J. Alloys Compd., 779 (2019) 831-843.

[63] L. Guo, Q. Zhao, C. Wang, H. Shen, X. an Han, K. Zhang, D. Wang, F. Fu, Magnetically recyclable $Fe_3O_4@SiO_2/Bi_2WO_6/Bi_2S_3$ with visible-light-driven photocatalytic oxidative desulfurization, Mater. Res. Bull., 118 (2019) 110520.

[64] J. Zhang, L. Huang, J. Zheng, J. Xu, A.M. Asiri, H.M. Marwani, M. Zhang, SiO₂-assisted synthesis of $Fe_3O_4@SiO_2@C-Ni$ nanochains for effective catalysis and protein adsorption, J. Magn. Magn. Mater., 497 (2020) 166011.

[65] Y. Liu, R. Fu, Y. Sun, X. Zhou, S.A. Baig, X. Xu, Multifunctional nanocomposites $Fe_3O_4@SiO_2$ -EDTA for Pb(II) and Cu(II) removal from aqueous solutions, Appl. Surf. Sci., 369 (2016) 267-276.

[66] D. Wang, D. Han, Z. Shi, J. Wang, J. Yang, X. Li, H. Song, Optimized design of three-dimensional multi-shell $Fe_3O_4/SiO_2/ZnO/ZnSe$ microspheres with type II heterostructure for photocatalytic applications, Appl. Catal., B, 227 (2018) 61-69.

[67] W. Xie, X. Zang, Lipase immobilized on ionic liquid-functionalized magnetic silica composites as a magnetic biocatalyst for production of *trans*-free plastic fats, Food Chem., 257 (2018) 15-22.

[68] L.S. Van Rompuy, T.N. Parac-Vogt, Interactions between polyoxometalates and biological systems: from drug design to artificial enzymes, Curr. Opin. Biotechnol., 58 (2019) 92-99.

[69] U. Kortz, A. Mueller, J. van Slageren, J. Schnack, N.S. Dalal, M. Dressel, Polyoxometalates: Fascinating structures, unique magnetic properties, Coord. Chem. Rev., 253 (2009) 2315-2327.

[70] B. Hasenknopf, Polyoxometalates: introduction to a class of inorganic compounds and their biomedical applications, Front. Biosci., 10 (2005) 275.

[71] S. Xue, C. Xiang, Y. Wei, Z. Tao, A. Chai, W. Bian, Z. Xu, Synthesis, crystal structure, spectroscopic, and herbicidal activity studies of a series of designed fluoro-functionalized phenylimido derivatives of hexametalate cluster, Cryst. Growth Des., 8 (2008) 2437-2443.

[72] Y. Xia, P. Wu, Y. Wei, Y. Wang, H. Guo, Synthesis, crystal structure, and optical properties of a polyoxometalate-based inorganic–organic hybrid solid, (n-Bu₄N)₂[Mo₆O₁₇(\approx NAr)₂](Ar=*o*-CH₃OC₆H₄), Cryst. Growth Des., 6 (2006) 253-257. [73] Y. Wei, M. Lu, C.F.-c. Cheung, C.L. Barnes, Z. Peng, Functionalization of [MoW₅O₁₉]²⁻ with aromatic amines: Synthesis of the first arylimido derivatives of mixed-metal polyoxometalates, Inorg. Chem., 40 (2001) 5489-5490.

[74] L. Vila-Nadal, E.F. Wilson, H.N. Miras, A. Rodrìguez-Fortea, L. Cronin, J.M. Poblet, Combined theoretical and mass spectrometry study of the formation-fragmentation of small polyoxomolybdates, Inorg. Chem., 50 (2011) 7811-7819.

[75] J. Li, Electronic structures, (dp) π conjugation effects, and spectroscopic properties of polyoxometalates: $M_6O_{19}^{2-}$ (M=Cr, Mo, W), J. Clust. Sci., 13 (2002) 137-163.

[76] J.T. Rhule, C.L. Hill, D.A. Judd, R.F. Schinazi, Polyoxometalates in medicine, Chem. Rev., 98 (1998) 327-358.

[77] B. Ding, C. Li, S. Fujita, S. Shiratori, Layer-by-layer self-assembled tubular films containing polyoxometalate on electrospun nanofibers, Colloids Surf. A, 284 (2006) 257-262.

[78] F.-Y. Yi, W. Zhu, S. Dang, J.-P. Li, D. Wu, Y.-h. Li, Z.-M. Sun, Polyoxometalates-based heterometallic organic–inorganic hybrid materials for rapid adsorption and selective separation of methylene blue from aqueous solutions, Chem. Commun., 51 (2015) 3336-3339.

[79] M. Ammam, Polyoxometalates: formation, structures, principal properties, main deposition methods and application in sensing, J. Mater. Chem. A, 1 (2013) 6291-6312.

[80] Y. Kim, K. Ketpang, S. Jaritphun, J.S. Park, S. Shanmugam, A polyoxometalate coupled graphene oxide–Nafion composite membrane for fuel cells operating at low relative humidity, J. Mater. Chem. A, 3 (2015) 8148-8155.

[81] C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li, C.-D. Wu, A multifunctional organic– inorganic hybrid structure based on Mn^{III}–porphyrin and polyoxometalate as a highly effective dye scavenger and heterogenous catalyst, J. Am. Chem. Soc., 134 (2011) 87-90.

[82] Z. Han, Y. Zhao, J. Peng, Y. Feng, J. Yin, Q. Liu, The electrochemical behavior of Keggin polyoxometalate modified by tricyclic, aromatic entity, Electroanal., 17 (2005) 1097-1102.

[83] Y. Nishimoto, D. Yokogawa, H. Yoshikawa, K. Awaga, S. Irle, Super-reduced polyoxometalates: excellent molecular cluster battery components and semipermeable molecular capacitors, J. Am. Chem. Soc., 136 (2014) 9042-9052.

[84] R. Neumann, M. Gara, Highly active manganese-containing polyoxometalate as catalyst for epoxidation of alkenes with hydrogen peroxide, J. Am. Chem. Soc., 116 (1994) 5509-5510.

[85] O.V. Branytska, R. Neumann, An efficient, catalytic, aerobic, oxidative iodination of arenes using the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate as catalyst, J. Org. Chem., 68 (2003) 9510-9512.

[86] Z. Zhang, W. Zhao, B. Ma, Y. Ding, The epoxidation of olefins catalyzed by a new heterogeneous polyoxometalate-based catalyst with hydrogen peroxide, Catal Commun., 12 (2010) 318-322.

[87] R. Neumann, M. Gara, The manganese-containing polyoxometalate, $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12}$, as a remarkably effective catalyst for hydrogen peroxide mediated oxidations, J. Am. Chem. Soc., 117 (1995) 5066-5074.

[88] M.V. Vasylyev, R. Neumann, New heterogeneous polyoxometalate based mesoporous catalysts for hydrogen peroxide mediated oxidation reactions, J. Am. Chem. Soc., 126 (2004) 884-890.

[89] C.L. Hill, D.A. Bouchard, Catalytic photochemical dehydrogenation of organic substrates by polyoxometalates, J. Am. Chem. Soc., 107 (1985) 5148-5157.

[90] S.O. Ribeiro, C.M. Granadeiro, P.L. Almeida, J. Pires, M.C. Capel-Sanchez, J.M. Campos-Martin, S. Gago, B. de Castro, S.S. Balula, Oxidative desulfurization strategies using Keggin-type polyoxometalate catalysts: biphasic versus solvent-free systems, Catal. Today, 333 (2018) 226-236.

[91] S. Roy, M.C. Mourad, M.T. Rijneveld-Ockers, Synthesis and characterization of large surface hexagonal polyoxometalate platelets, Langmuir, 23 (2007) 399-401.
[92] W. Xie, F. Wan, Immobilization of polyoxometalate-based sulfonated ionic liquids on UiO-66-2COOH metal-organic frameworks for biodiesel production via one-pot transesterification-esterification of acidic vegetable oils, Chem. Eng. Sci, 365 (2019) 40-50.

[93] F. Shahbazi, K. Amani, Synthesis, characterization and heterogeneous catalytic activity of diamine-modified silica-coated magnetite-polyoxometalate nanoparticles as a novel magnetically-recoverable nanocatalyst, Catal. Commun., 55 (2014) 57-64.

[94] M. Ghanbari, S. Moradi, M. Setoodehkhah, $Fe_3O_4@SiO_2@ADMPT/H_6P_2W_{18}O_{62}$: a novel Wells–Dawson heteropolyacid-based magnetic inorganic–organic nanohybrid material as potent Lewis acid catalyst for the efficient synthesis of 1,4-dihydopyridines, Green Chem. Lett. Rev., 11 (2018) 111-124.

[95] A. Jamshidi, B. Maleki, F.M. Zonoz, R. Tayebee, HPA-dendrimer functionalized magnetic nanoparticles ($Fe_3O_4@D-NH_2-HPA$) as a novel inorganic-organic hybrid and recyclable catalyst for the one-pot synthesis of highly substituted pyran derivatives, Mater. Chem. Phys., 209 (2018) 46-59.

[96] R.C. Cioc, E. Ruijter, R.V. Orru, Multicomponent reactions: advanced tools for sustainable organic synthesis, Green Chem., 16 (2014) 2958-2975.

[97] J. Lu, Y. Bai, Catalysis of the Biginelli reaction by ferric and nickel chloride hexahydrates. One-pot synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones, Synthesis, 2002 (2002) 0466-0470.

[98] V. Singh, V. Sapehiyia, V. Srivastava, S. Kaur, ZrO₂-pillared clay: An efficient catalyst for solventless synthesis of biologically active multifunctional dihydropyrimidinones, Catal Commun., 7 (2006) 571-578.

[99] M. Bhat, M. Al-Omar, H. Ghabbour, A. Naglah, A one-pot Biginelli synthesis and characterization of novel dihydropyrimidinone derivatives containing piperazine/morpholine moiety, Molecules, 23 (2018) 1559.

[100] S. Viveka, G.K. Nagaraja, P. Shama, G. Basavarajaswamy, K.P. Rao, M.Y. Sreenivasa, One pot synthesis of thiazolo[2, 3-*b*]dihydropyrimidinone possessing pyrazole moiety and evaluation of their anti-inflammatory and antimicrobial activities, Med. Chem. Res., 27 (2018) 171-185.

[101] H.M. Zaheri, S. Javanshir, B. Hemmati, Z. Dolatkhah, M. Fardpour, Magnetic core–shell Carrageenan moss/Fe₃O₄: a polysaccharide-based metallic nanoparticles for synthesis of pyrimidinone derivatives via Biginelli reaction, Chem. Cent. J., 12 (2018) 108.

[102] J. Safari, Z. Zarnegar, Biginelli reaction on Fe_3O_4 –MWCNT nanocomposite: excellent reactivity and facile recyclability of the catalyst combined with ultrasound irradiation, RSC Adv., 3 (2013) 17962-17967.

[103] N. Yao, M. Lu, X.B. Liu, J. Tan, Y.L. Hu, Copper-doped mesoporous silica supported dual acidic ionic liquid as an efficient and cooperative reusability catalyst for Biginelli reaction, J. Mol. Liq., 262 (2018) 328-335.

[104] M.A.D. Fard, H. Ghafuri, A. Rashidizadeh, Sulfonated highly ordered mesoporous graphitic carbon nitride as a super active heterogeneous solid acid catalyst for Biginelli reaction, Micropor. Mesopor. Mat., 274 (2019) 83-93.

[105] B.N. Mahato, T. Krithiga, Mesoporous ZnO/AlSBA-15 (7) nanocomposite as an efficient catalyst for synthesis of 3,4-dihydropyrimidin-2(1*H*)-one via Biginelli

reaction and their biological activity study, Bull. Chem. React. Eng. Catal., 14 (2019) 634-645.

[106] M. Ghanbarian, S.Y.S. Beheshtiha, M.M. Heravi, M. Mirzaei, V. Zadsirjan, N. Lotfian, A nano-sized Nd–Ag@polyoxometalate catalyst for catalyzing the multicomponent Hantzsch and Biginelli reactions, J. Clust. Sci., (2019) 1-12.

[107] D. Bhuyan, M. Saikia, L. Saikia, ZnO nanoparticles embedded in SBA-15 as an efficient heterogeneous catalyst for the synthesis of dihydropyrimidinones via Biginelli condensation reaction, Micropor. Mesopor. Mat., 256 (2018) 39-48.

[108] S. ben Moussa, A. Mehri, B. Badraoui, Magnesium modified calcium hydroxyapatite: An efficient and recyclable catalyst for the one-pot Biginelli condensation, J. Mol. Struct., 1200 (2020) 127111.

[109] D. Elhamifar, M. Nasr-Esfahani, B. Karimi, R. Moshkelgosha, A. Shábani, Ionic liquid and sulfonic acid based bifunctional periodic mesoporous organosilica (BPMO–IL–SO₃H) as a highly efficient and reusable nanocatalyst for the Biginelli reaction, ChemCatChem, 6 (2014) 2593-2599.

[110] D. Elhamifar, A. Shabani, Manganese-containing periodic mesoporous organosilica with ionic-liquid framework (Mn@PMO-IL): a powerful, durable, and reusable nanocatalyst for the Biginelli reaction, Chem. Eur. J., 20 (2014) 3212-3217.

[111] D. Elhamifar, F. Hosseinpoor, B. Karimi, S. Hajati, Ionic liquid-based ordered mesoporous organosilica-supported copper as a novel and efficient nanocatalyst for the one-pot synthesis of Biginelli products, Micropor. Mesopor. Mat., 204 (2015) 269-275.

[112] D. Elhamifar, P. Mofatehnia, M. Faal, Magnetic nanoparticles supported Schiff-base/copper complex: An efficient nanocatalyst for preparation of biologically active 3,4-dihydropyrimidinones, J. Colloid Interface Sci., 504 (2017) 268-275.

[113] D. Elhamifar, D. Elhamifar, F. Shojaeipoor, Synthesis, characterization and catalytic application of a novel polyethylene-supported Fe/ionic liquid complex, J. Mol. Catal. Chem, 426 (2017) 198-204.

[114] Z. Ramazani, D. Elhamifar, M. Norouzi, R. Mirbagheri, Magnetic mesoporous MCM-41 supported boric acid: A novel, efficient and ecofriendly nanocomposite, Compos. B. Eng., 164 (2019) 10-17.

[115] D. Elhamifar, Z. Ramazani, M. Norouzi, R. Mirbagheri, Magnetic iron oxide/phenylsulfonic acid: A novel, efficient and recoverable nanocatalyst for green synthesis of tetrahydrobenzo[*b*]pyrans under ultrasonic conditions, J. Colloid Interface Sci., 511 (2018) 392-401.

[116] M. Khosroshahi, L. Ghazanfari, Preparation and characterization of silicacoated iron-oxide bionanoparticles under N_2 gas, Physica E, 42 (2010) 1824-1829.

[117] G. Sima, Q. Li, Y. Zhu, C. Lv, R.N.N. Khan, J. Hao, J. Zhang, Y. Wei, Organoimido-derivatized hexamolybdates with a remote carboxyl group: Syntheses and structural characterizations, Inorg. Chem., 52 (2013) 6551-6558.

[118] M. García, J. Honores, F. Celis, F. Fuenzalida, R. Arce, M.J. Aguirre, A. Aracena, Imidazolium-based ionic liquids as stabilizers for electrode modification with water-soluble porphyrin, New J. Chem., 43 (2019) 2338-2346.

[119] Y. Ma, C. Qian, L. Wang, M. Yang, Lanthanide triflate catalyzed Biginelli reaction. One-pot synthesis of dihydropyrimidinones under solvent-free conditions, J. Org. Chem., 65 (2000) 3864-3868.

[120] E.H. Hu, D.R. Sidler, U.-H. Dolling, Unprecedented catalytic threecomponent one-pot condensation reaction: an efficient synthesis of 5alkoxycarbonyl-4-aryl-3,4-dihydropyrimidin-2(1*H*)-ones, J. Org. Chem., 63 (1998) 3454-3457.

[121] N.-Y. Fu, Y.-F. Yuan, Z. Cao, S.-W. Wang, J.-T. Wang, C. Peppe, Indium(III) bromide-catalyzed preparation of dihydropyrimidinones: improved protocol conditions for the Biginelli reaction, Tetrahedron, 58 (2002) 4801-4807.

[122] Z. Ghadamyari, A. Shiri, A. Khojastehnezhad, S.M. Seyedi, Zirconium(IV) porphyrin graphene oxide: a new and efficient catalyst for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones, Appl. Organomet. Chem., 33 (2019) e5091.

[123] E. Kolvari, N. Koukabi, M.M. Hosseini, M. Vahidian, E. Ghobadi, Nano- ZrO_2 sulfuric acid: a heterogeneous solid acid nano catalyst for Biginelli reaction under solvent-free conditions, RSC Adv., 6 (2016) 7419-7425.

[124] J.S. Ghomi, R. Teymuri, A. Ziarati, A green synthesis of 3,4-dihydropyrimidine-2(1H)-one/thione derivatives using nanosilica-supported tin(II) chloride as a heterogeneous nanocatalyst, Monatsh. Chem., 144 (2013) 1865-1870.

Highlights

- A novel magnetic silica-supported IL/hexamolybdate (Fe₃O₄@SiO₂-IL/[Mo₆O₁₉]) has been prepared.
- The Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] has been characterized by means of FTIR, PXRD, TGA, SEM, VSM, and EDX.
- The Fe₃O₄@SiO₂-IL/[Mo₆O₁₉] has been effectively applied as a nanocatalyst in the Biginelli reaction.
- The nanocatalyst could be recovered and reused at least seven times without incurring a significant loss of efficiency.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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