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An efficient clean methodology for the C-S coupling to aryl thioethers and S-S homocoupling to aromatic disulfides catalyzed over Ce(IV)-Leucine complex immobilized mesoporous MCM-41

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Abstract

A novel Ce(IV) anchored L-Leucine covalently bonded over mesoporous MCM-41 has been synthesized by non-hydrothermal post-functionalization approach. It has been characterized thoroughly by sophisticated physicochemical techniques. The material was applied in the efficient green synthesis of aromatic sulfides by C-S coupling using molecular sulfur and haloarenes. Another catalytic application was performed in the synthesis of symmetric disulfides by homocoupling of aromatic thiols in presence of H_2O_2 as oxidant. The ligand-free protocol is simple and clean, free from hazardous chemicals and the catalyst is reusable for several times thus making the methodology sustainably viable.

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1 Introduction

Organosulfur motifs containing one or more C-S bonds are significant class of compounds that have broad spectrum of applications in pharmacological terrain. Many of the sulfur compounds construct the backbone of different natural products. Organo thioethers finds importance as intermediates in organic synthesis,^{1,3} in material science^{4,6} and as potential drug candidates in the treatment of cancer, Parkinson's and Alzheimer's disease.^{7,9} One of the most practicable pathways in constructing aryl-sulfur bonds is the cross-coupling reactions between the organic halides with thiols catalyzed over transition metals.¹⁰⁻¹¹ However, the methodology encompasses drawbacks like slow aerial oxidative homocoupling of thiols resulting disulfides as well as catalyst deactivation by S poisoning.¹²⁻¹³ Still, considering its importance, researchers are incessantly searching for alternative protocols in order to avoid such difficulties.¹⁴⁻²⁰ In accordance with the trend we pursued an approach using molecular sulfur in place of thiols reacting with haloarenes thus averting the chance of disulfide formation.

The aryl disulfides are another important group of organosulfur derivatives. They have drawn significant attentions due to their large number of implications. They are the building blocks of several S containing synthetic compounds as well as natural products.²¹⁻²⁵ The disulfides are used in the metabolism of several marine alkaloids.²⁶⁻²⁸ They possess a wide range of crucial functions in Biochemistry, food chemistry and pharmaceuticals.²⁹⁻³⁶ These disulfanes have also been used for the preparation of self-assembled monolayers (SAMs) and monolayer-protected clusters (MPCs) with a number of versatile properties.³⁷⁻³⁸ Several groups have worked on the synthesis of disulphides following oxidative homocoupling method. ³⁹⁻⁴⁰ Instead of using H₂O₂, a widely used oxidant in this protocol, we brought novelty by carrying out the same using molecular

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oxygen. The use of molecular oxygen in different reactions has already made a benchmark in sustainable chemistry.

In catalytic arena, heterogeneous catalysis has become an automatic choice in lieu of homogeneous catalysis during the last few decades on the ground of their easy recovery and reusability.⁴¹⁻⁴² The irksome work up to isolate the desired product and non recyclability of catalyst has been the prime drawback. Different approaches have been proposed for the immobilization of homogeneous transition metal complexes on heterogeneous supports like silica, alumina, clay, grapheme oxide, zeolites and other metal oxides to circumvent the drawbacks.⁴³⁻⁴⁶ Following that pathway nanocatalysts have come into prominence as an excellent heterogeneous support having appreciable high surface to volume ratio and outstanding recyclability. The nanomaterials, being a quasi-phasic system, construct an efficient bridge between homogeneous and heterogeneous catalysis.⁴⁷⁻⁴⁹

Since the discovery of Mobil scientists (M41S), ordered mesoporous silica have been quite distinctive as heterogeneous support and catalyst due to specific advantages like ease of preparation, uniform pore structure, excellent chemical and thermal stability, large internal surface area, good accessibility, low cost and high concentration of surface hydroxyl groups in order of post functionalization.⁵⁰⁻⁵³ As part of our endeavor for the catalytic sustainable green synthesis, we opted for MCM-41 mesoporous matrix as heterogeneous support. We used L-Leucine amino acid as the chelating ligand for covalent bonding on the silica surface and efficiently anchored Ce (IV) to the system as the active site. Thereafter, the composite catalytic system was used for the synthesis of aryl thioethers by C-S coupling involving molecular S and aryl halides and the synthesis of organic disulfanes by oxidative homocoupling of thiols using molecular O_2 (Scheme 1).⁵⁴⁻⁵⁵ Both the reactions were highly facile in our protocol affording

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high yields in short reaction time. The high surface area material, easy recovery and reusability of catalyst with nominal change in activity in several runs, simple procedure, cheap and stable reagents, easy work up has made the methodology sustainably and economically viable.



Scheme 1 Ce(IV)-Leucine@MCM-41catalyzed synthesis of thiothers and disulfanes





Scheme 2 Synthetic protocol for the synthesis of Ce(IV)-Leucine@MCM-41 catalyst

2 Experimental

2.1 Materials and physical measurements

All solvents and chemicals were purchased from Merck and Sigma-Aldrich and used without further purification. The elemental analysis and Ce content was determined by Energy Dispersive X-ray spectroscopy (EDAX) and inductively coupled plasma-optical emission spectrometry (ICP-OES) respectively. The surface morphology of the catalyst was determined by SEM using FESEM (TESCAN MIRA3) and Powder X-ray diffraction (XRD) measurements using Co radiation with a wave length of 1.78897 Å, operating at 40 kV, respectively. Thermal stability of the material was determined by TGA

measurement in a Shimadzu DTG-60 instrument. Fourier transformed Infrared (FT-IR) spectra of the catalysts were recorded in a Bruker VERTEX 80v instrument. Melting points of thioethers and disulfides were determined with an electrothermal 9100 apparatus.

2.2 Preparation of Ce(IV)-Leucine@MCM-41 nanocatalyst

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The mesoporous MCM-41 was synthesized following a previous reported method by Hajjami et al.⁵⁶ 1.0 gm CTAB, the structure-directing template, was dissolved in a solution containing 3.5 mL 2 (M) NaOH solution and 480 mL deionized water at 80 °C under stirring. 5 mL TEOS, the silica source, was then added slowly to the mixture and stirred for 2 h under same condition. The solid products were filtered, washed several times with deionized water and dried at 60 °C overnight. Finally it was calcined at 550 °C for 5 h at ramping rate of 2 °C / min to afford MCM-41 as a white powder. Subsequently, Leucine@MCM-41 was synthesized by adding 1.5 g of L-Leucine to 1.0 g suspension of MCM-41 in 30 mL distilled water and refluxing at 100 °C for 48 h. The resulting mixture was filtered, washed with ethanol/water and dried in vacuum at 80 °C. Subsequently, 1.08 g Ce(NO₃)₂.6H₂O was added into 1.0 g Leucine@MCM-41 suspension in 30 mL ethanol under reflux conditions for 16 h. The resulting mixture was filtered, washed thoroughly with ethanol and dried under vacuum to afford the final composite material Ce(IV)-Leucine@MCM-41.

2.3 General procedure for the thioetherification reactions

A mixture of molecular sulfur (1.0 mmol), aryl halide (1.0 mmol) and KOH (0.7 g) was stirred in DMSO (2 ml) at 130 °C in presence of 0.05 g MCM-41@Leucine-Ce (IV) catalyst for requisite time. After completion (by TLC), the catalyst was separated by filtration and washed with ethyl acetate. The reaction mixture was added to water and extracted with ethyl acetate. The whole

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organic layer was dried over anhydrous Na₂SO₄, concentrated and purified on preparatory TLC plate to afford the corresponding aryl thioether.

2.4 General procedure for the thiol oxidation reactions

To a stirred suspension of 0.05 g MCM-41@Leucine-Ce (IV) in 5 mL ethanol, 1.0 mmol thiol and H_2O_2 (0.4 mL) was added at room temperature fitted. Also, the reaction was tested in the presence of O_2 as oxidant. After the completion of reaction (monitored by TLC), the catalyst was separated simply by filtration and the reaction mixture was concentrated to get pure disulfide derivatives.

3. Results and Discussion

3.1 Catalytic Characterizations and Data analysis

Upon post-functionalization approached synthesis of the catalyst (Scheme 2), it was thoroughly characterized by advanced analytical techniques like Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX), Powder X-ray diffraction, Thermal Gravimetric Analysis (TGA), N₂ adsorption-desorption isotherm, surface area analysis by BET method, Fourier Transformed Infrared spectroscopy (FT-IR) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

The structural morphology of MCM-41 and Ce(IV)-Leucine@MCM-41 was ascertained using scanning electron microscopy. Fig. 1 depicts the SEM images of the bare MCM-41 (1a) and Ce(IV)-Leucine@MCM-41 at different magnifications (1b-1d). Both the bare and functionalized mesoporous materials are made up of quite homogeneous and uniform spherical particles. A close look of the material represents its floppy nature and that is obviously due to its high porosity. No significant changes were observed in surface engineering over MCM-41.

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Fig. 1 SEM images of calcined MCM-41at 2 μ m (a) and Ce(IV)-Leucine@MCM-41 at 1 μ m (b), 500 nm (c) and 200 nm (d).

The elemental identity was analyzed from EDX spectra of the Ce(IV)-Leucine@MCM-41 catalyst (Fig. 2). The evolved peaks represented the Si, C, N, O and Ce atoms. Presence of C, N and O confirmed the amino acid attachment to Si surface. The exact Ce content in the catalyst was found to be 0.46 mmol/g as determined by ICP-AES analysis.

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Fig. 2 EDX pattern of Ce(IV)-Leucine@MCM-41

The crystalline morphology of MCM-41 and Ce(IV)-Leucine@MCM-41 was determined by powder X-ray diffraction (XRD) study. Fig. 3 depicts the well-resolved peaks of bare MCM-41 with high diffraction intensity corresponding to the (100), (110), and (200) reflections attributed to the P6mm hexagonal space group symmetry. The sharp low angle peaks clarifies high mesoporosity of the material. However, surface immobilization of the Ce (IV) complexes on MCM-41 results in the decrease in the diffraction intensity of the peak triad owing to the difference in scattering contrast of the pores and the walls of the nanochannels of MCM-41. Still, the presence of (100) peak in Ce(IV)-Leucine@MCM-41, although weak, confirms the structural indifference upon post-functionalization.

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Fig. 3 Small angle XRD patterns of MCM-41 and Ce(IV)-Leucine@MCM-41

Fig. 4 assumes the FT-IR analysis of the catalysts. The outcome of bare MCM-41 (blue), Leucine complexed silica (red) and Ce loaded final version of the catalyst (green) has been superposed in the figure. The absorption bands appeared at around 1100-1200 cm⁻¹ and 3000-3600 cm⁻¹ are due to Si–O–Si asymmetric stretching and the Si-OH stretching. The similarity in FT-IR pattern of the post-functionalized materials with MCM-41 conveyed that the basic structural morphology remained intact. However Ce connectivity with the basic matrix could not be proved from FT-IR analysis.



Fig. 4 FT-IR spectrum for bare of MCM-41 (a), Leucine@MCM-41 (b) and Ce(IV)-Leucine@MCM-41 (c)

Thermal stability of the catalyst and quantitative evaluation of the organic groups supported on MCM-41 was determined by TGA analysis and the pattern has been shown in Fig. 5. The TGA curve showed a minute weight loss below 200 °C due to removal of the adsorbed water as well as of the surface OH groups. A steep fall in the curve was observed in the temperature range 200-250 °C indicating the major weight loss occurred in that region. This was mainly due to the decomposition of organic layers on the surface of functionalized MCM-41. The further decrease in mass was due to chemisorbed water.



Fig. 5 The TGA diagram of Ce(IV)-Leucine@MCM-41

The textural property of the catalyst was examined by N₂ adsorption and desorption isotherm experiment. Prior to that, the Ce(IV)-Leucine@MCM-41was degassed at 100 °C under an Ar flow. Fig. 6 represents the isotherm and it clearly indicates to be a Type-IV nature along with a hysteresis loop. These characterize a typical mesoporous material. The isotherm nature at lower pressure region indicates the presence of micropores as well. Surface area of the bare MCM-41 and the functionalized one were determined by BET method and the results are documented in Table 1. As expected, the functionalized MCM-41 has smaller surface area, narrower pore diameter and lower absorption volume than bare MCM-41.



Fig. 6 Nitrogen adsorption/desorption isotherms of Ce(IV)-Leucine@MCM-41.

Table 1						
Texture parameters obtained from N ₂ adsorption/desorption studies.						
Sample	S_{BET} (m ² g ⁻¹)	Pore diameter by	Pore volume			
		BJH method (nm)	$(cm^3 g^{-1})$			
MCM-41	1113.7	2.39	1.39			
Ce(IV)-Leucine@MCM-41	379.68	1.02	0.803			

3.2 Reaction Data analysis

After the synthesis and rigorous characterization of the catalysts, their application appeared important. The endeavor was started with the optimization of reaction conditions in both the schemes. At the outset we chose the thioetherification reaction of haloarenes using molecular sulfur and a base as additive using Ce(IV)-Leucine@MCM-41 as catalyst. We went through the investigations regarding standardization of reaction conditions by variation of different factors like solvent, bases, temperature and catalyst load upon a model reaction of iodobenzene and S₈. The consequences are represented in Table 2. A screening of solvents was carried out with a series of solvents in presence of KOH as base and 70 mg catalyst. There was no reaction output in PEG, CH₃CN, H₂O and toluene. The reaction responded most excellently in DMSO and KOH combination. However, the best result was achieved at 130 °C and 70 mg of catalyst. There is a definite role of base in the reaction mechanism. We varied different bases like NaOH, Na₂CO₃ and Et₃N with the standardized conditions so far but there were no better results further than that with KOH.

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Entry	Solvent	Base	Temp	Cat	Time	Yield	
			(°C)	(mg)	(min)	(%)	
1	DMF	КОН	130	70	200	24	
2	PEG	КОН	130	70	200	N.R	

Table 2.	Optimiz	ation o	f reaction	conditions	for C	-S cou	pling	using	Ce (IV)-	Leucine(a)MC	M-41
									· ·				

3	CH ₃ CN	КОН	130	70	200	N.R
4	EtOH	КОН	130	70	200	17
5	H ₂ O	КОН	130	70	200	N.R
6	Toluene	КОН	130	70	200	N.R
7	DMSO	КОН	80	70	200	15
8	DMSO	КОН	100	70	200	22
9	DMSO	КОН	130	70	200	80
10	DMSO	КОН	130	50	200	48
11	DMSO	КОН	130	90	200	85
12	DMSO	NaOH	130	70	200	N.R
13	DMSO	Na ₂ CO ₃	130	70	200	25
14	DMSO	Et ₃ N	130	70	200	30
^a Isolated yields.						

Upon optimization of conditions, we concentrated on the linearity of those over different substrates. A wide variety of substituted halobenzenes were reacted with molecular S_8 under standard conditions. They were well compatible with the protocol. The results have been depicted in table 3 and moderate to high yields were obtained in each case (1a-1j).

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Table 3 C–S coupling in the presence of Ce(IV)-Leucine@MCM-41								
Entry	Aryl Halide	Product	Time (min)	Yield (%) ^a	M.p (°C)			
1	CH ₃	1a	140	85	47			
2		1b	200	80	65			
3	CI	1c	225	76	67			
4	Br	1d	210	82	65			
5	Br CH ₃	1e	155	79	46			
6	Br OH	1f	130	88	158			
7	OH	1g	100	88	155			
8	OCH ₃	1h	135	85	Oil			

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Based on our reaction study and literature analysis a plausible mechanstic pathway has been drawn in Fig. 7. Initially, the S_8 molecule breaks down in presence of KOH, forming a dipotassium disulfide salt, which acts as the S source. This binds with the catalyst forming a bicyclic ring. Aryl halide further adds to it forming complex bridged intermediates. Subsequently, a second molecule of aryl halide adds to this intermediate and finally liberates the diaryl thioether product retaining the catalytic site free for reuse.



Fig. 7 Mechanistic pathway for the thioetherization reaction over Ce(IV)-Leucine@MCM-41 catalyst.

The endeavor was started with the optimization of reaction conditions in both the schemes. At the outset we chose the oxidative homocoupling of 4-methylthiophenol using our catalyst and H_2O_2 as the oxidant at room temperature. Different factors like solvent, amount of H_2O_2 and amount of catalyst were examined on the outcome of reaction. The results are summarized in table 2. The reaction was not very fruitful in solvents like ethyl acetate or acetonitrile. It was

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quite convincing in EtOH resulting 86% yield. However, the best result was achieved at solventfree conditions. Similarly, after a tedious experimentation, 0.4 mL H_2O_2 and 0.5 g of catalyst was optimized to produce the best conditions (entry 3, table 2).

Table 4. Optimization of the reaction conditions for S-S homocoupling of 4-methylthiophenol using MCM-41@Leucine-Ce (IV).

	Me								
Me-	SH — Cat =	Cat EtOH, R.T		S S	Me				
	a-Jj			4a-4j					
Entry	Solvent	$H_2O_2(mL)$	Cat(mg)	Time (min)	Yield (%) ^a				
1	Solvent-Free	0.4	7	40	97				
2	Solvent-Free	0.4	3	95	66				
3	Solvent-Free	0.4	5	50	94				
4	Solvent-Free	0.5	5	45	95				
5	EtOH	0.4	7	60	85				
6	Ethyl acetate	0.4	7	95	46				
7	Acetonitrile	0.4	7	80	21				
^a Isolated yield.									

After having the optimized conditions in hand we were on to the generality of conditions. A wide variety of aromatic and aliphatic thiophenols were reacted in presence of H_2O_2 (Table 5) and O_2 (Table 6) as oxidant under stabilized conditions. Interestingly, all the thiophenols afforded good to excellent yields in short reaction time at room temperature. The results have been shown in

Table 5. S–S homocoupling using H_2O_2 in the presence of Ce(IV)-Leucine@MCM-41							
Entry	Substrate	Product	Time (min)	Yield (%) ^a	M.p (°C)		
1	Br	4a	80	95	88-91		
2	SH	4b	65	98	59		
3	SH N	4c	40	97	176-178		
4	N SH N	4d	120	95	163-167		
5	SH	4e	40	91	70		
6	SH	4f	50	94	39		
7	SH N	4g	35	96	91		
8	HS COOH	4h	30	92	104		
9	SH COOH	4i	75	93	280-283		
10	SH	4j	60	95	135		

^a Isolated yield.

Table 6. S-S homocoupling using molecular O2 in the presence of Ce(IV) Leucine@MCM-41

Entry	Substrate	Product	Time (min)	Yield (%) ^a	M.p (°C)
1	Br	2a	95	92	90
2	SH	2b	70	91	60
3	SH N	2c	50	90	177-180
4	N SH	2d	120	91	165-167
5	SH	2e	45	95	67
6	SH	2f	60	92	40
7	SH N	2g	50	94	90-92
8	нs соон	2h	35	91	102
9	SH COOH	2i	80	90	280-282

10	SH	2j	70	88	134
^a Isolated	yield.				

Subsequently, we proposed a reasonable mechanism for this homocoupling of aryl thiols to disulfanes over our catalyst (Fig. 8). The reaction proceeds through radical pathway where O_2 acts as the initiator. It binds with the complexed Ce and further attachment of two successive thiol molecules follows an internal rearrangement to leave behind the disulfane product.



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Fig. 8 Proposed mechanism for oxidation of thiols in presence of Ce(IV)-Leucine@MCM-41 as catalyst.

3.3 Study of catalyst reusability

In green and sustainable catalysis reusability study of the catalyst is an obvious measure. This study was done with our catalyst in both the reactions with a larger batch size. Initially, 0.5 gm iodobenzene was reacted with S_8 in presence of 200 mg catalyst. After completion of reaction, the catalyst was recovered by filtration, washed well with ethyl acetate for several times, dried at 100 °C for 3h and reused in further cycles. Similar procedure was followed with 4-methyl thiophenol in the disulphide formation with O_2 . The results have been shown in Fig. 9. The catalyst was so efficient that we used it for a successive 5 times and 7 times respectively for the two reactions with slight change in catalytic activity.



Fig. 9 Reusability of Ce(IV)-Leucine@MCM-41 in the synthesis of diphenyl sulfide and 1,2 dip-tolyldisufane

3.4 Hot filtration and leaching test

To determine the heterogeneity of the catalyst, a hot filtration test was conducted for the synthesis of diphenyl sulfide by the reaction of iodobenzene and S_8 under optimized conditions. After a time lag of half period, a 43% yield was obtained from the reaction. But in the next half time of the reaction, the catalyst was separated from the reaction mixture by filtration and allowed to continue under identical reaction conditions. It was noteworthy that the overall yield of the reaction was only 45% after complete time thus verifying the heterogeneous property of the catalyst. This also confirmed that the active site Ce (IV) was not been leached out the whole matrix. An ICP-AES study of the filtered reaction mixture confirmed the leached content of Ce (IV) was only 0.15% of the original load which is catalytically inactive.

Conclusion

In summary, we report herein an improved and competent methodology for the synthesis of aryl thioethers and symmetric disulfanes over Ce anchored L-Leucine capped mesoporous MCM-41 as a high surface area, reusable, and highly efficient catalyst affording moderate to high yields in short time. The novel catalyst was synthesized following a post functionalization approach upon the templated synthesized MCM-41. It was physicochemically characterized by FESEM, EDX, ICP-AES, XRD, FT-IR, TGA and N₂ adsorption desorption measurements. The catalyst was isolated from the reaction mixture simply by filtration and reused several times with constant efficacy.

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Graphical Abstract

An efficient clean methodology for the synthesis of aryl thioethers and aromatic disulfides catalyzed over Ce(IV)-Leucine complex immobilized mesoporous MCM-41

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Anchored Ce(IV) on the surface of MCM-41 mesoprous silica was used for the synthesis of aryl thioethers and aromatic disulfides.

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