

Synthesis and characterization of indium and thallium immobilized on isonicotinamide-functionalized mesoporous MCM-41: Two novel and highly active heterogeneous catalysts for selective oxidation of sulfides and thiols to their corresponding sulfoxides and disulfides

Somayeh Molaei | Mohammad Ghadermazi

Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj, Iran

Correspondence

Mohammad Ghadermazi, University of Kurdistan, Department of Chemistry, Faculty of Science, Sanandaj, Iran.
Email: mghadermazi@yahoo.com

Two highly ordered isonicotinamide (INA)-functionalized mesoporous MCM-41 materials supporting indium and thallium (MCM-41-INA-In and MCM-41-INA-Tl) have been developed using a covalent grafting method. A surface functionalization method has been applied to prepare Cl-modified mesoporous MCM-41 material. Condensation of this Cl-functionalized MCM-41 with INA leads to the formation of MCM-41-INA. The reaction of MCM-41-INA with $\text{In}(\text{NO}_3)_3$ or $\text{Tl}(\text{NO}_3)_3$ leads to the formation of MCM-41-INA-In and MCM-41-INA-Tl catalysts. The resulting materials were characterized using various techniques. These MCM-41-INA-In and MCM-41-INA-Tl catalysts show excellent catalytic performance in the selective oxidation of sulfides and thiols to their corresponding sulfoxides and disulfides. Finally, it is found that the anchored indium and thallium do not leach out from the surface of the mesoporous catalysts during reaction and the catalysts can be reused for seven repeat reaction runs without considerable loss of catalytic performance.

KEYWORDS

functionalized MCM-41, indium and thallium, isonicotinamide, selective oxidation

1 | INTRODUCTION

The functionalization of metal catalysts on solid supports has recently attracted great attention owing to the sustainable green chemistry applications it offers. Many homogeneous catalysts demonstrate higher catalytic activity and selectivity than their heterogeneous counterparts because of their solubility in reaction media, which increases catalytic site accessibility for the substrate.^[1,2] When homogeneous catalysts are used, their recycling is often difficult and there is also product contamination observed. Recently, the replacement of homogeneous liquid catalysts by heterogeneous solid catalysts with good

recyclability has been widely applied.^[3] Several procedures for heterogenization of homogeneous catalysts have been developed which are mostly based on inorganic support systems, dendrimers or organic polymers. It is commonly recognized that covalent functionalization of complexes on inorganic supports gives the best recycling outcomes.^[4–11] Among the most efficient supports are the group of MCM materials, developed by Mobil since 1992, particularly MCM-41 that is usually selected as a potential support material for heterogeneous catalysts due to its high surface area, ordered structure of hexagonal channels, regular pore size distribution, good mechanical stability and surface nature. Organometallic

TABLE 1 Efficiency of more commonly used hydrogen peroxide in the presence of various catalysts

| Entry | Substrate | Catalyst/solvent | Substrate | >Time (min) | >Yield (%) |
|-------|---------------------------------------|---|--|-------------|------------|
| 1 | Oxidation of sulfides ^[38] | Silica vanadic acid (SVA)/ CH ₃ CN | Ph-S-CH ₂ Ph | 10 | 93 |
| | | | PhCH ₂ -S-CH ₂ Ph | 13 | 91 |
| | | | Ph-S-Me | 5 | 94 |
| | | | Ph-S-Ph | 40 | 88 |
| | | | Ph-S-CH ₂ CH ₂ (OH) | 25 | 91 |
| | | | Me-S-CH ₂ CH ₂ (OH) | 20 | 90 |
| 2 | Oxidation of sulfides ^[17] | SBA-15@Creatinine@Y/ solvent-free | Ph-S-Me | 60 | 96 |
| | | | PhCH ₂ -S-CH ₂ Ph | 4 | 90 |
| | | | Ph-S-Et | 30 | 94 |
| | | | CH ₃ CH ₂ CH ₂ -S-CH ₂ CH ₂ CH ₃ | 4 | 91 |
| | | | Ph-S-CH ₂ CH ₂ (OH) | 2 | 93 |
| | | | Ph-S-CH ₂ Ph | 10 | 92 |
| 3 | Oxidation of sulfides ^[39] | VO-2A3HP-MCM-41/ solvent-free | Ph-S-Me | 120 | 96 |
| | | | Ph-S-Ph | 1800 | 86 |
| | | | CH ₃ CH ₂ CH ₂ -S-CH ₂ CH ₂ CH ₃ | 100 | 98 |
| | | | Ph-S-CH ₂ CH ₂ (OH) | 15 | 90 |
| | | | Me-S-CH ₂ CH ₂ (OH) | 60 | 98 |
| | | | | | |
| 4 | Oxidation of sulfides ^[40] | MCM-41@XA@Ni(II)/ solvent-free | Ph-S-Me | 60 | 90 |
| | | | PhCH ₂ -S-CH ₂ Ph | 90 | 88 |
| | | | Ph-S-CH ₂ CH ₂ (OH) | 60 | 93 |
| | | | Me-S-CH ₂ CH ₂ (OH) | 43 | 95 |
| | | | CH ₃ CH ₂ CH ₂ -S-CH ₂ CH ₂ CH ₃ | 50 | 95 |
| | | | | | |
| 5 | Oxidation of thiols ^[41] | Zr-oxide@MCM-41/ethanol | PhCH ₂ -SH | 50 | 95 |
| | | | <i>p</i> -MePh-SH | 30 | 99 |
| | | | <i>o</i> -COOHPh-SH | 35 | 96 |
| | | | Ph-SH | 30 | 98 |
| | | | OHCH ₂ CH ₂ -SH | 30 | 97 |
| | | | COOHCH ₂ -SH | 40 | 90 |
| 6 | Oxidation of thiols ^[42] | Fe ₃ O ₄ /salen of Cu(II)/ ethanol | PhCH ₂ -SH | 60 | 90 |
| | | | <i>p</i> -MePh-SH | 15 | 97 |
| | | | <i>o</i> -COOHPh-SH | 120 | 91 |
| | | | OHCH ₂ CH ₂ -SH | 30 | 91 |
| | | | COOHCH ₂ -SH | 15 | 98 |
| | | | | | |
| 7 | Oxidation of thiols ^[43] | Fe ₃ O ₄ @S-ABENZ@VO/ CH ₂ Cl ₂ | <i>p</i> -MePh-SH | 15 | 97 |
| | | | <i>o</i> -COOHPh-SH | 105 | 98 |
| | | | <i>p</i> -BrPh-SH | 100 | 99 |
| 8 | Oxidation of thiols ^[36] | Co-salen-MNPs/ethanol | PhCH ₂ -SH | 60 | 99 |
| | | | <i>p</i> -MePh-SH | 60 | 98 |
| | | | <i>o</i> -COOHPh-SH | 60 | 99 |
| | | | OHCH ₂ CH ₂ -SH | 2 | 91 |
| | | | COOHCH ₂ -SH | 10 | 97 |
| | | | | | |
| 9 | Oxidation of alcohols ^[44] | VHPW/MCM-41/NH ₂ / toluene | PhCH ₂ -OH | 8 | 97 |
| | | | <i>p</i> -MePhCH ₂ -OH | 8 | 96 |
| | | | <i>m</i> -MePhCH ₂ -OH | 8 | 96 |
| | | | PhCHOH-Me | 8 | 93 |
| | | | PhCH ₂ CH ₂ -OH | 8 | 90 |
| | | | | | |
| 10 | Oxidation of alcohols ^[45] | PPh ₄ [MoO(O ₂) ₂ (HPEOH)]/ CH ₃ CN | PhCH ₂ -OH | 24 h | 63 |
| | | | Me-CHOH-Me | 20 h | 93 |
| | | | CH ₃ CH ₂ CH ₂ CH ₂ -OH | 15 h | 60 + 20 |
| | | | HO-CH ₂ CH ₂ CH ₂ -OH | 11 h | 88 |
| | | | | | |

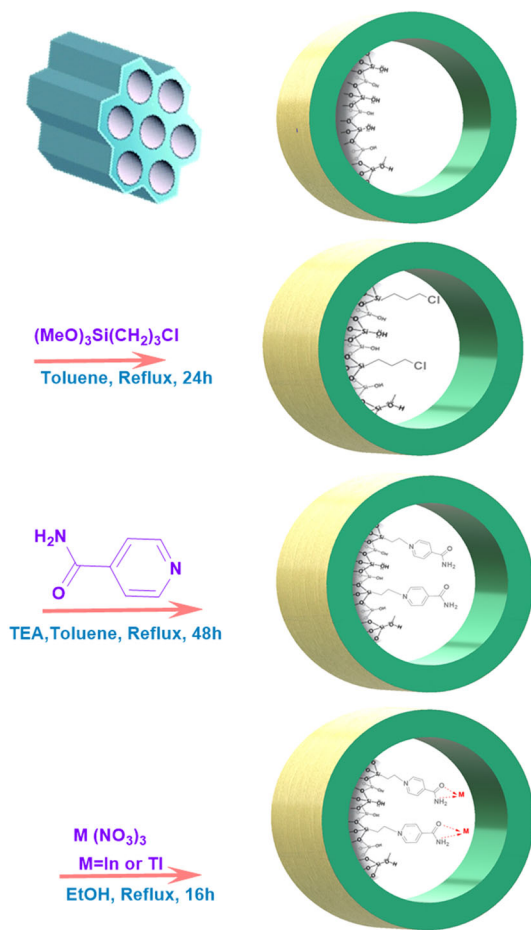
(Continues)

TABLE 1 (Continued)

| Entry | Substrate | Catalyst/solvent | Substrate | >Time (min) | >Yield (%) | |
|-------|--|---|--|-------------|------------|-----|
| 11 | Oxidation of alcohols ^[46] | PW(0.16)-NH ₂ -IL(0.4)-SBA-15/solvent-free | Ph-CHOH-Me | 6 h | 97 | |
| | | | Ph-CHOH-Ph | 6 h | 95 | |
| | | | CH ₃ CH ₂ CH ₂ -CHOH-CH ₃ | 6 h | 69 | |
| | | | PhCH ₂ -OH | 6 h | 92 | |
| | | | CH ₃ CH ₂ -CHOH-CH ₂ -CH ₃ | 6 h | 88 | |
| 12 | Oxidation of alcohols ^[47] | SiW ₉ Al ₃ /solvent-free | <i>p</i> -MePhCH ₂ -OH | 7 h | 100 | |
| | | | PhCH ₂ -OH | 5 h | 100 | |
| | | | <i>p</i> -ClPhCH ₂ -OH | 6 h | 100 | |
| | | | <i>p</i> -O ₂ NPhCH ₂ -OH | 12 h | 74 | |
| | | | <i>p</i> -H ₃ COPhCH ₂ -OH | 6 h | 100 | |
| 13 | Thiocyanation of organic compounds ^[48] | Silica vanadic acid (SVA)/KSCN/H ₂ O | <i>o</i> -MePh-NH ₂ | 1 h | 92 | |
| | | | <i>m</i> -MePh-NH ₂ | 1 h | 85 | |
| | | | <i>m</i> -BrPh-NH ₂ | 1.5 h | 80 | |
| | | | <i>m</i> -F ₃ CPh-NH ₂ | 1.25 h | 92 | |
| | | | <i>o</i> -F ₃ CPh-NH ₂ | 1 h | 89 | |
| | | | Ph-N(CH ₃) ₂ | 2 h | 90 | |
| 14 | Thiocyanation of organic compounds ^[49] | Graphene oxide/KSCN/H ₂ O | Ph-NH ₂ | 3 h | 90 | |
| | | | <i>o</i> -H ₃ COPh-NH ₂ | 2 h | 93 | |
| | | | <i>m</i> -H ₃ COPh-NH ₂ | 2 h | 87 | |
| | | | <i>o</i> -MePh-NH ₂ | 2 h | 89 | |
| | | | <i>o</i> -ClPh-NH ₂ | 5 h | 80 | |
| | | | Ph-N(CH ₃) ₂ | 3 h | 85 | |
| 15 | Thiocyanation of organic compounds ^[50] | SBSA (5%)/KSCN/H ₂ O | Ph-N(CH ₂ CH ₂ -OH) ₂ | 30 | 78 | |
| | | | Ph-N(CH ₃) ₂ | 14 | 95 | |
| | | | Ph-N(CH ₂ CH ₃) ₂ | 10 | 92 | |
| 16 | Thiocyanation of organic compounds ^[51] | Fe ₃ O ₄ -IL-HSO ₄ KSCN/Water:Ethanol(1:4) | Ph-N(CH ₂ CH ₂ -OH) ₂ | 2 h | 75 | |
| | | | Ph-N(CH ₃) ₂ | 2 h | 96 | |
| | | | Ph-N(CH ₂ CH ₃) ₂ | 85 | 92 | |
| 17 | Oxidative aromatization of Hantzsch 1,4-dihydropyridines ^[52] | Silica vanadic acid (SVA)/CH ₃ CN | 2,6-Dimethyl-1,4-dihydropyridine | | | |
| | | | R4 | R3,5 | | |
| | | | H | COMe | >10 | >97 |
| | | | Me | COMe | >18 | >95 |
| | | | Ph | COMe | >60 | >50 |
| | | | H | COOEt | >10 | >95 |
| | | | Me | COOEt | >13 | >90 |
| | | | Et | COOEt | >45 | >90 |
| 18 | Oxidative aromatization of Hantzsch 1,4-dihydropyridines ^[53] | H ₆ PMo ₉ V ₃ O ₄₀ /acetic acid | 2,6-Dimethyl-1,4-dihydropyridine | | | |
| | | | R4 | R3,5 | | |
| | | | H | COOEt | >30 | >98 |
| | | | Me | COOEt | >70 | >97 |
| | | | Et | COOEt | >20 | >99 |
| | | | Ph | COOEt | >70 | >96 |
| | | | 4-MePh | COOEt | >75 | >98 |
| | | | 4-ClPh | COOEt | >300 | >80 |

complexes can be reacted with silanol groups through covalent bonds to create inorganic-organic hybrid nanocomposites. Such hybrid nanocomposites can incorporate some beneficial features of both organic and inorganic components into the mesoporous support with

reactive and mechanical properties that are different from either of the completely organic or inorganic species. The strong covalent bonds thus increase the lifetime of the catalyst, the performance of these inorganic-organic hybrid materials is improved and the leaching of



SCHEME 1 Schematic depiction of preparation of catalysts

catalytically active sites can be avoided.^[12–20] Various indium and thallium compounds can promote a number of reactions such as C–C bond formations,^[21]

n-*tert*-butoxycarbonylation of amines,^[22] acylation of alcohols, phenols and thiols, geminal diacylation of aldehydes^[23] and Suzuki cross coupling.^[24] Indium is often selected as the metal centre due to its low toxicity and high chemoselectivity. What makes indium compounds attractive in ‘green’ chemistry is their benefits over most of the metal compounds in terms of their stability in air or in a humid environment.^[25,26] The aim of the work reported here was to highlight the outstanding efficiency of indium for oxidation of thiols and sulfides in comparison with a neighbouring element in the periodic table (thallium). Thallium is also unique in group IIIb as a soft acid on the hard acid–soft base classification of Pearson.

In the research reported here, indium and thallium were immobilized on isonicotinamide (INA)-functionalized mesoporous MCM-41 through covalent bonding, to provide two recyclable catalytic systems with high activity that could provide more economic sustainability. The novelty of the current research lies in the synthesis of two novel inorganic–organic hybrid materials and the use of indium and thallium as the active sites of catalysts in the oxidation of sulfides and thiols to their corresponding sulfoxides and disulfides for the first time. All reactions proceeded to give excellent yields within quite short reaction times.

The selective oxidation of sulfides to sulfoxides is a basic and significant functional group transformation because organic sulfoxides are useful synthetic intermediates for the manufacture of various chemically and biologically important compounds, and sulfoxide reactions are outstanding in drug metabolism and medicinal chemistry. Likewise, disulfides are significant in biology,

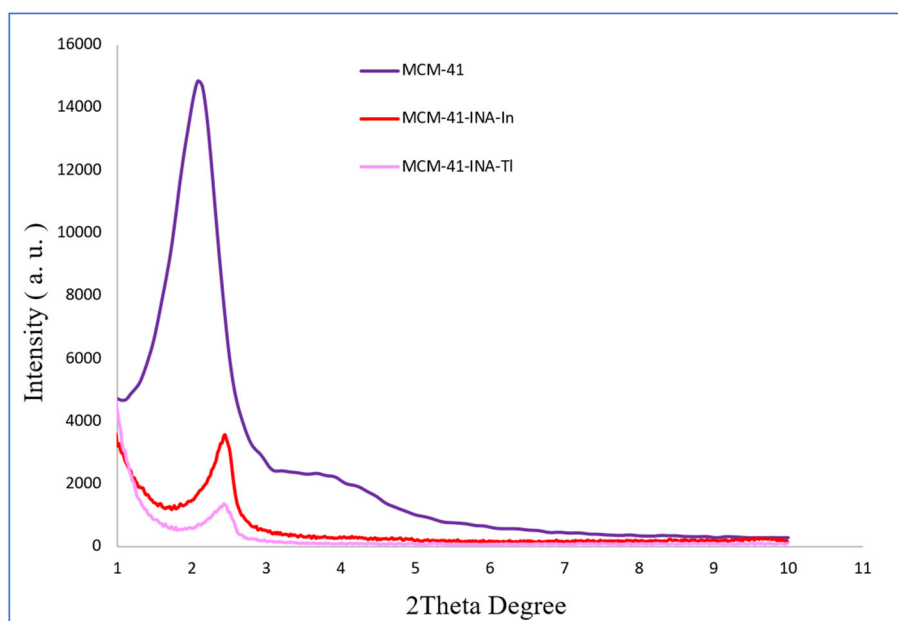


FIGURE 1 XRD analysis of MCM-41, MCM-41-INA-In and MCM-41-INA-Tl

industrial procedures and organic synthesis.^[27–34] So, many procedures involving different catalysts and various oxidants have been presented to carry out these transformations. There is a continuing requirement for procedures that are easy, mild, effective and especially selective.^[35–37] Due to the environmentally friendly character of hydrogen peroxide (H_2O_2), its effective oxygen content and low cost, oxidation using H_2O_2 as an oxidant is preferred.^[38] The efficiency of more commonly used H_2O_2 reactions in the presence of various catalysts is presented in Table 1.

2 | EXPERIMENTAL

2.1 | Characterization

X-ray diffraction (XRD) patterns were acquired using an MPD diffractometer with $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDS) measurements were conducted with an EDS-equipped SEM instrument (FESEM-TESCAN MIRA3) operating at 30 kV. Elemental analyses were performed using inductively coupled plasma optical emission spectrometry (ICP-OES) with a Varian 730-ES elemental analyser. Fourier transform infrared (FT-IR) spectra were recorded with a Bruker VRTEX 70 spectrophotometer. Thermogravimetric analysis (TGA) was carried out with a Shimadzu DTG-60 thermogravimetric analyser.

2.2 | MCM-41 preparation

Pristine MCM-41 was prepared by a template approach.^[54] In a typical synthesis, NaOH (2 M, 3.5 ml) and 1.0 g of cetyltrimethylammonium bromide were added to deionized water (480 ml), and heated at 80°C under stirring. When a homogeneous solution was obtained, 5 ml of tetraethyl orthosilicate was introduced dropwise with constant stirring for 2 h. Then the slurry was collected and washed with deionized water. After that, the powder was dried and calcined at 550°C (5 h).

2.3 | Modification MCM-41 with 3-chloropropyltrimethoxysilane group

A mixture of 1.0 g of MCM-41 and 3-chloropropyltrimethoxysilane (1.5 ml) was refluxed in toluene (40 ml) for 24 h. Then the powder was collected, washed with *n*-hexane and dried in an oven at 75°C to afford the modified MCM-41 (MCM-41-Cl).

TABLE 2 Textural properties of MCM-41 and metal-grafted MCM-41

| Sample | BET surface area ($\text{cm}^2 \text{g}^{-1}$) | Pore diameter by BJH method (nm) | Pore volume ($\text{cm}^3 \text{g}^{-1}$) |
|---------------|--|----------------------------------|---|
| MCM-41 | 1200.0 | 2.4 | 1.255 |
| MCM-41-INA-In | 1022.1 | 1.21 | 1.066 |
| MCM-41-INA-Tl | 855.8 | 1.21 | 1.192 |

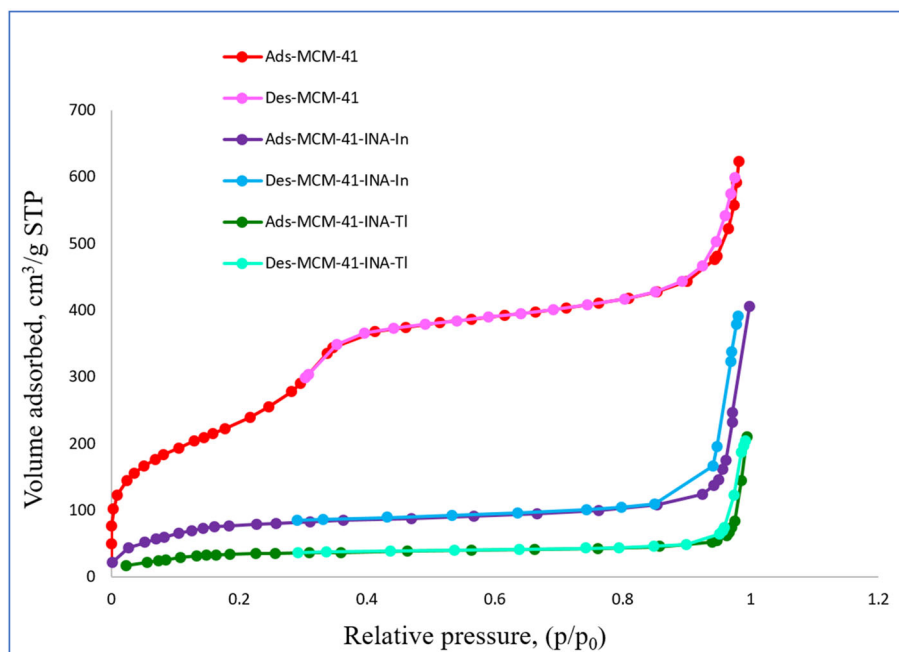


FIGURE 2 Nitrogen adsorption–desorption of MCM-41, MCM-41-INA-In and MCM-41-INA-Tl

2.4 | Immobilization of INA onto MCM-41-Cl

A mixture of triethylamine (3 ml), INA (2 mmol, 0.244 g) and MCM-41-Cl (1.0 g) in 40 ml of toluene was refluxed for 48 h. The resulting powder was then collected and washed with deionized water. After that, the powder was dried in an oven at 75°C to afford the desired product (MCM-41-INA).

2.5 | Preparation of indium and thallium catalysts

MCM-41-INA (1 g) was suspended into $\text{In}(\text{NO}_3)_3$ (2.5 mmol, 0.752 g) or $\text{Tl}(\text{NO}_3)_3$ (2.5 mmol, 0.975 g) in 40 ml of ethanol. The mixture was refluxed for 16 h. The powder was collected and washed with ethanol. After washing, the powder was dried in an oven at 75°C to afford each catalyst (MCM-41-INA-M). A schematic of the preparation of these catalysts is displayed in Scheme 1.

2.6 | Oxidation of sulfides

Into a reaction vessel were placed the catalyst (0.005 g), hydrogen peroxide (0.6 ml) and sulfide (1 mmol). At room temperature, the mixture was stirred. After completion of the reaction (the development of the reaction was observed with TLC), the catalyst was collected by centrifugation. The organic product was separated with ethyl acetate, washed several times with water and dried over anhydrous Na_2SO_4 . Finally, the solvents were removed to afford pure product.

2.7 | Oxidation of thiols

Into a reaction vessel were placed the catalyst (0.007 g), hydrogen peroxide (0.6 ml), thiol (1 mmol) and ethanol (3 ml). At room temperature, the mixture was stirred. After completion of the reaction (the development of the reaction was observed with TLC), the catalyst was collected by centrifugation. The organic products were extracted with dichloromethane and washed several times with water. The combined extracts were dried over anhydrous Na_2SO_4 . Finally, the organic solvents were evaporated, and pure product was obtained.

2.8 | Spectral data

Methylphenyl sulfoxide (Table 6, entry 1). ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 2.95 (s, 3H), 7.44–7.49 (m, 2H), 7.54–7.56 (m, 1H), 7.80–7.86 (m, 2H).

2,2'-Sulfinyldiacetic acid (Table 6, entry 3). ^1H NMR (400 MHz, DMSO, δ , ppm): 4.35–4.37 (m, 4H), 7.35 (br. s, 2H, 2 COOH).

2,2'-Dithiodibenzoic acid (Table 9, entry 1). ^1H NMR (400 MHz, DMSO, δ , ppm): 7.27–7.28 (m, 2H), 7.36–7.40 (m, 2H), 7.49–7.58 (m, 2H), 7.73–7.76 (m, 2H).

Dibenzyl disulfide (Table 9, entry 3). ^1H NMR (400 MHz, DMSO, δ , ppm): 3.88 (s, 2H), 4.16 (s, 2H), 7.28–7.33 (m, 4H), 7.34–7.40 (m, 6H).

3 | RESULTS AND DISCUSSION

3.1 | Catalyst characterization

MCM-41 was characterized from its small-angle powder XRD pattern. The sharp diffraction peak can be attributed to (100), and the two weaker diffraction peaks can be

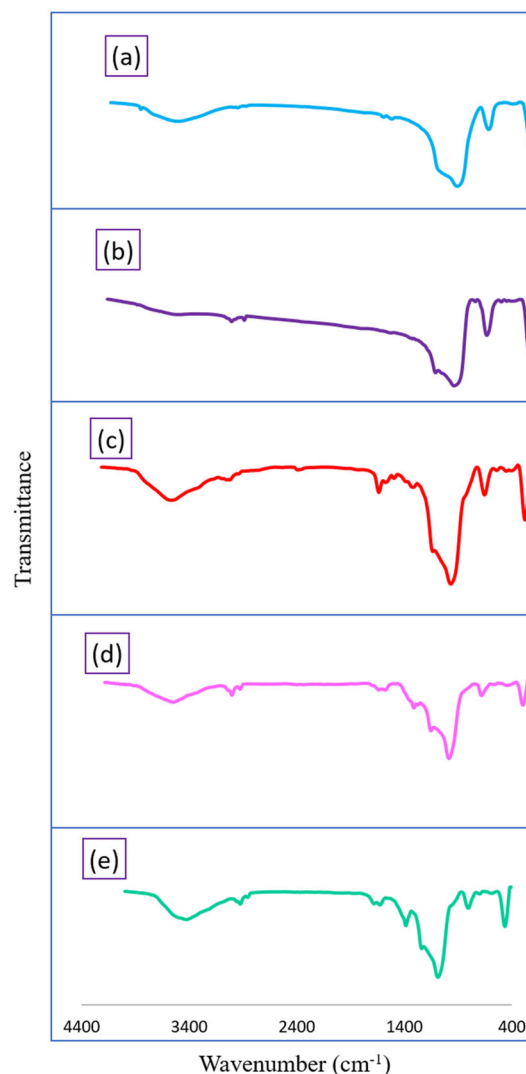


FIGURE 3 FT-IR spectra of (a) MCM-41, (b) MCM-41-Cl, (c) MCM-41-INA, (d) MCM-41-INA-In and (e) MCM-41-INA-Tl

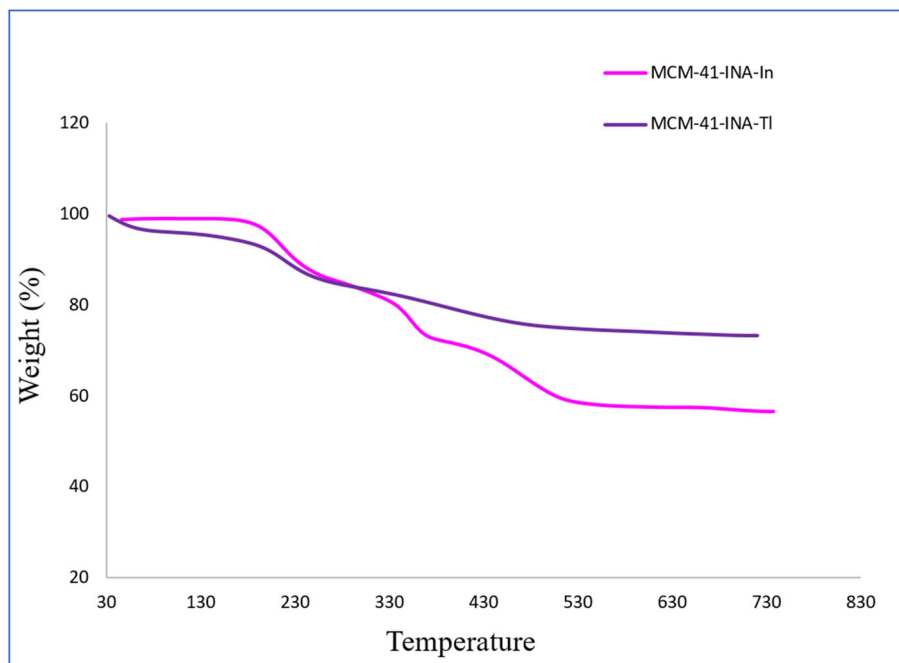


FIGURE 4 TGA curves of MCM-41, MCM-41-INA-In and MCM-41-INA-Tl

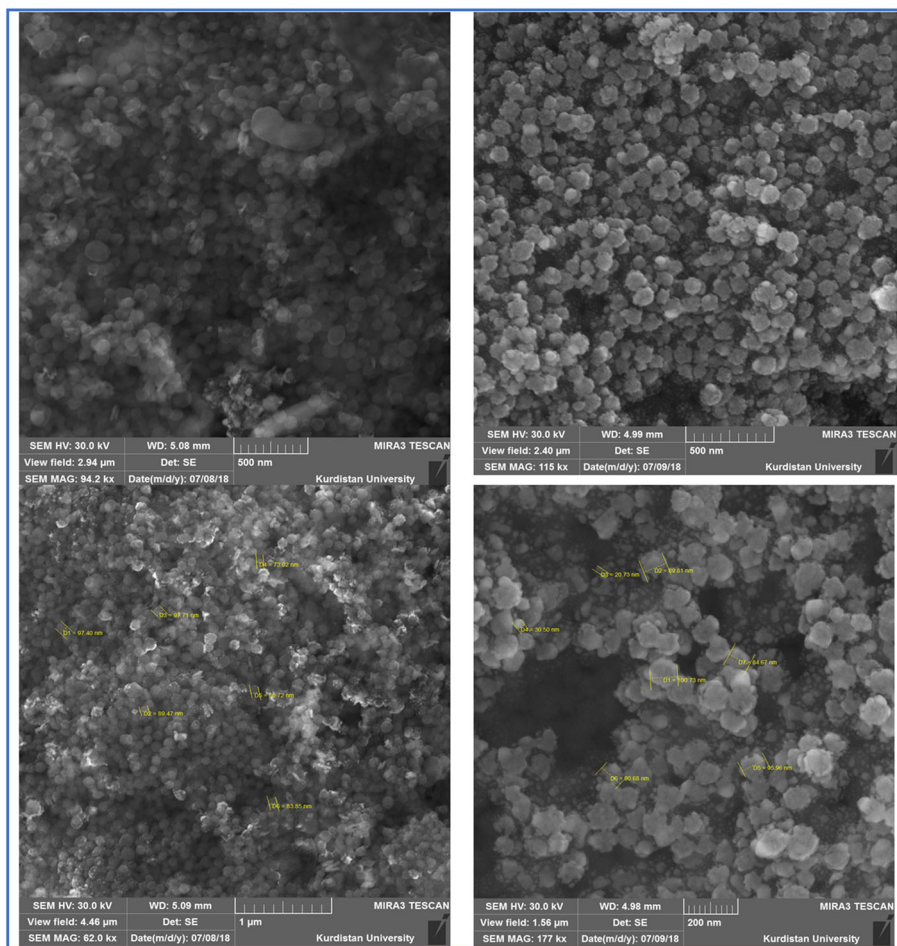


FIGURE 5 SEM images of MCM-41-INA-In (left) and MCM-41-INA-Tl (right)

attributed to (110) and (200) reflections,^[15] as shown in Figure 1. These peaks are typically characteristic of a two-dimensional hexagonal MCM-41 structure.^[12,55] After functionalization of MCM-41, the sharp diffraction peak is still seen in the XRD patterns of MCM-41-INA-In and MCM-41-INA-Tl, which clarifies the preservation of the hexagonal structure in these samples. However, the peak intensities decrease, resulting from the grafting of metal complexes inside the walls with a reduction of local order.^[56]

The materials MCM-41,^[15] MCM-41-INA-In and MCM-41-INA-Tl display type IV nitrogen adsorption isotherms (Figure 2), characteristic of mesoporous materials, implying that the mesostructures of the materials are retained.^[12] It can also be clearly seen that functionalization of the parent MCM-41 leads to a

decrease in the nitrogen gas adsorption uptake. These results indicate that the metal complexes had been successfully incorporated into the mesoporous channels. The textural parameters of the materials, according to Barrett–Joyner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) plots, decrease after the immobilization stage^[57] (Table 2).

The FT-IR spectra of MCM-41, MCM-41-Cl, MCM-41-INA, MCM-41-INA-In and MCM-41-INA-Tl are presented in Figure 3. The spectrum of MCM-41 shows bands for the O–H stretching vibration of Si–OH and bending vibration of H₂O at 3427 and 1654 cm^{−1}, respectively. The bands corresponding to the Si–O–Si asymmetric and symmetric stretching and bending vibrations can be observed at 1093, 802 and 451 cm^{−1}, respectively.^[58] The FT-IR spectrum of MCM-41-Cl exhibits

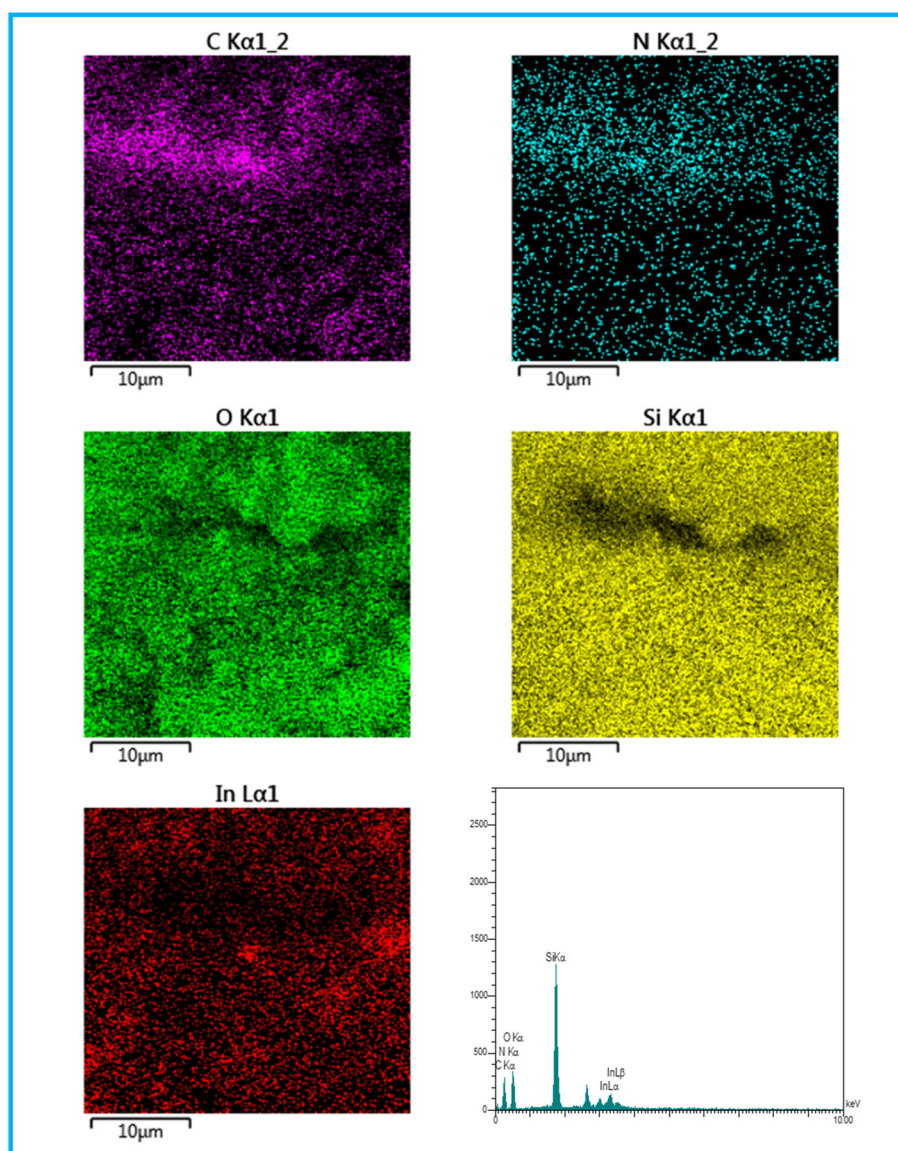


FIGURE 6 EDS elemental mapping images of MCM-41-INA-In catalyst

bands corresponding to the C&H stretching vibration of 3-chloropropyltriethoxysilane at 2956 and 2866 cm^{-1} .^[12] A new band at 1683 cm^{-1} in the FT-IR spectrum of MCM-41-INA was assigned to the C&O vibration of INA, suggesting the successful grafting of INA onto the MCM-41 surface. Free INA showed asymmetric and symmetric stretching vibrations of &NH₂ group at 3370 and 3187 cm^{-1} . Peaks due to carbonyl (C&O) and &CN stretching frequencies were observed at 1668 and 1391 cm^{-1} , respectively. Bands assigned to pyridine ring vibrations of free INA appeared at 1595 cm^{-1} .

A notable negative shift of the carbonyl frequency occurs in complexes of amides and other carbonyl donors. Similarly, the $\nu(\text{NH})$ frequencies of the uncoordinated INA have a slight positive shift. When the

pyridine ring nitrogen is involved in complex formation, certain vibrational modes increase in frequency.^[59] The FT-IR spectrum of MCM-41-INA exhibits bands for C&O and &NH₂ stretching at 1687 and 3430 cm^{-1} , respectively, which have been shifted to higher frequencies. Bands corresponding to pyridine ring vibrations in the spectrum of MCM-41-INA appear at 1612 cm^{-1} . The FT-IR spectrum of MCM-41-INA demonstrates all characteristics of INA coordinated through the ring nitrogen.

The FT-IR spectra of MCM-41-INA-In and MCM-41-INA-Tl mesoporous materials exhibit bands for C&O stretching centred at 1651 and 1653 cm^{-1} , respectively, which have been shifted to lower frequencies. These results confirm that In and Tl have been grafted into the pore channels of MCM-41-INA.^[60]

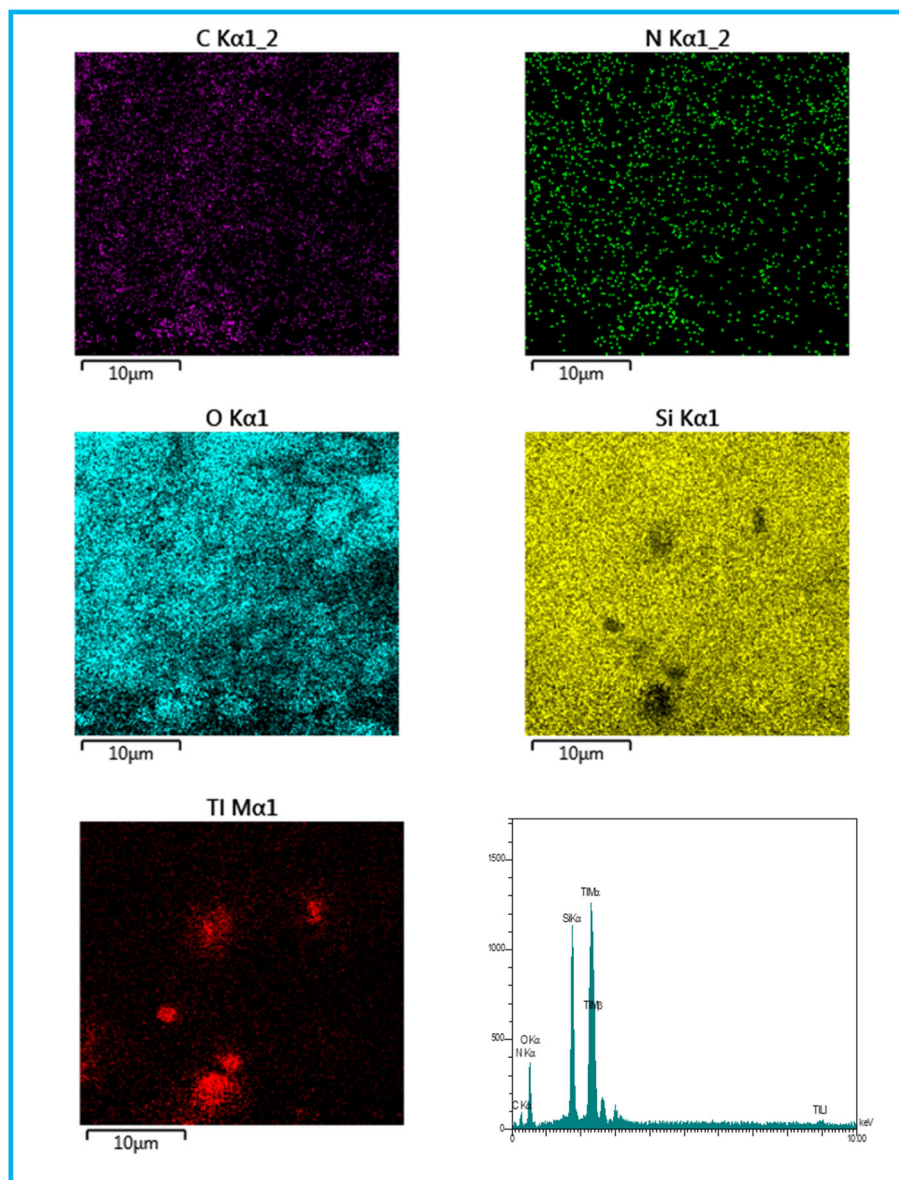


FIGURE 7 EDS elemental mapping images of MCM-41-INA-Tl catalyst

The results of TGA of MCM-41-INA-In and MCM-41-INA-Tl are depicted in Figure 4. For the two samples, the weight loss from 25 to 190°C is attributable to the removal of physically adsorbed water. A further weight loss from 200 to 400°C can be ascribed to desorption of the water on the silica surface. Furthermore, the weight loss from 400 to 550°C is assigned to the decomposition of the organic species.^[61]

SEM images for MCM-41-INA-In and MCM-41-INA-Tl are presented in Figure 5. It can be observed that the samples have a uniform spherical morphology. Furthermore, the MCM-41-INA-In and MCM-41-INA-Tl catalysts were investigated using mapping images, and the results are shown in Figures 6 and 7. C, N, Si and O, and each of In and Tl are uniformly dispersed in these catalysts. The content of metal was also in accordance with ICP-OES analysis, which was 1.6 and 2.1 mmol g⁻¹ for MCM-41-INA-In and MCM-41-INA-Tl, respectively.

3.2 | Catalytic studies

To compare per site activity of homogeneous and heterogeneous reactions (Table 3), oxidation of dibenzyl sulfide under solvent-free conditions at room temperature was selected as a model reaction. At first, the catalytic reaction was performed without any catalyst (Table 3, entry 1). No reaction was observed under this

TABLE 3 Testing of various catalysts for oxidation of dibenzyl sulfide^a

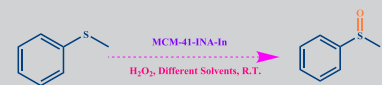
| Entry | Catalyst | Time (h) | Yield (%) ^b |
|-------|-----------------------------------|----------|------------------------|
| 1 | No catalyst | 3.5 | 0 |
| 2 | MCM-41 | 3.5 | 0 |
| 3 | MCM-41-Cl | 3.5 | 0 |
| 4 | MCM-41-INA | 3.5 | 0 |
| 5 | INA | 3.5 | 0 |
| 6 | In(NO ₃) ₃ | 3.5 | 55 |
| 7 | Tl(NO ₃) ₃ | 3.5 | 60 |
| 8 | In supported on MCM-41 | 3.5 | 45 |
| 9 | Tl supported on MCM-41 | 3.5 | 51 |
| 10 | INA-In | 3.5 | 65 |
| 11 | INA-Tl | 3.5 | 69 |
| 12 | MCM-41-INA-In | 3.5 | 88 |
| 13 | MCM-41-INA-Tl | 2.5 | 90 |

^aReaction conditions: dibenzyl sulfide (1 mmol), H₂O₂ (0.6 ml) and catalyst under solvent-free conditions.

^bIsolated yield of product.

condition. We carried out the reaction using MCM-41, MCM-41-Cl and MCM-41-INA (Table 3, entries 2–4) as the catalysts. Again, no reaction took place under these conditions after 3.5 h. When the reaction was performed in the presence of homogeneous-phase INA (Table 3, entry 5), no product was obtained after 3.5 h. Then the oxidation was carried out using In(NO₃)₃ and Tl(NO₃)₃ as catalysts (Table 3, entries 6 and 7), and the conversion of dibenzyl sulfide was 55 and 60%, respectively. This result clearly proves that the presence of In and Tl is essential for this transformation. But they cannot be reused because of the homogeneous nature of In(NO₃)₃ and Tl(NO₃)₃. When these homogeneous catalysts are grafted into MCM-41, without INA and 3-chloropropyltrimethoxysilane (Table 3, entries 8

TABLE 4 Effect of various parameters for the synthesis of methylphenyl sulfoxide in the presence of MCM-41-INA-In catalyst using H₂O₂^a

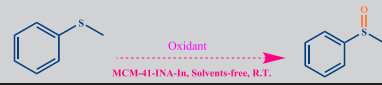


| Entry | Solvent | Catalyst (mg) | H ₂ O ₂ (ml) | Time (min) | Yield (%) ^b |
|-------|------------------|---------------|------------------------------------|------------|------------------------|
| 1 | Solvent free | 5 | 0.6 | 45 | 95 |
| 2 | EtOH | 5 | 0.6 | 180 | 83 |
| 3 | Ethyl acetate | 5 | 0.6 | 240 | 80 |
| 4 | Acetonitrile | 5 | 0.6 | 280 | 76 |
| 5 | <i>n</i> -Hexane | 5 | 0.6 | 350 | 54 |
| 6 | Solvent free | 7 | 0.6 | 45 | 97 |
| 7 | Solvent free | 3 | 0.6 | 75 | 91 |
| 8 | Solvent free | 5 | 0.8 | 30 | 97 |
| 9 | Solvent free | 5 | 0.4 | 85 | 82 |
| 10 | Solvent free | 5 | 0.2 | 120 | 76 |

^aReactions conditions: sulfide (1 mmol), H₂O₂, catalyst and solvent (3 ml).

^bIsolated yield.

TABLE 5 Testing of various oxidants for oxidation of methylphenyl sulfide^a



| Entry | Oxidant | Time (min) | Yield (%) |
|-------|-------------------------------|------------|-----------|
| 1 | H ₂ O ₂ | 45 | 95 |
| 2 | Molecular oxygen/air | 180 | 88 |
| 3 | Sodium percarbonate | 1440 | 76 |

^a19 mmol of oxidant; other reaction conditions same as those for Table 4.

and 9), the conversion of the reaction was reduced. Loading of the metals is decreased in these cases compared with the homogeneous counterparts. After that, we used the coordination complexes of the ligand with In and Tl ions as the catalysts under homogeneous conditions (Table 3, entries 10 and 11), and the product yield increased compared with the use of $\text{In}(\text{NO}_3)_3$ and $\text{Tl}(\text{NO}_3)_3$. The ligand coordinates with In or Tl ions in such a way that the In and Tl act as active catalytic sites. Finally, to prepare two heterogeneous catalysts, $\text{In}(\text{NO}_3)_3$ and $\text{Tl}(\text{NO}_3)_3$ were grafted into mesoporous channels of MCM-41-INA (Table 3, entries 12 and 13), and the product yield markedly increased. Large surface area facilitates the diffusion of organic molecules into the mesoporous channels of functionalized MCM-41 material for interaction with the In and Tl ions.

The catalytic performances of MCM-41-INA-In and MCM-41-INA-Tl were examined in the oxidation of sulfide with H_2O_2 at room temperature. To investigate the influence of catalyst dosage, solvent and amount of oxidant on the catalytic performance, methylphenyl sulfide was selected as a model substrate, and the results are collected in Table 4. The influence of the solvent on the catalytic performance of the MCM-41-INA-In catalyst was initially studied. Acetonitrile, ethanol, ethyl acetate and *n*-hexane were used as solvents; however, a higher conversion was achieved under solvent-free conditions. Then, the influence of catalyst dosage was studied. On decreasing the catalyst amount from 0.005 to 0.003 g, the conversion decreased; but with an increase of catalyst dosage, conversion enhanced slightly. So, 0.005 g of catalyst was selected as the optimum catalyst dosage. Finally,

TABLE 6 Oxidation of sulfides into sulfoxides in the presence of MCM-41-INA-In and MCM-41-INA-Tl^a

| Entry | Substrate | Product | MCM-41-INA-In Time (min); yield (%) | MCM-41-INA-Tl Time (min); yield (%) |
|-------|-----------|---------|--|--|
| 1 | | | 45; 95 | 40; 96 |
| 2 | | | 75; 90 | 70; 92 |
| 3 | | | 5; 93 | 5; 96 |
| 4 | | | 15; 95 | 15; 97 |
| 5 | | | 5; 92 | 5; 95 |
| 6 | | | 10; 90 | 10; 94 |
| 7 | | | 200; 88 | 150; 90 |
| 8 | | | 20; 91 | 20; 92 |
| 9 | | | 15; 90 | 15; 93 |
| 10 | | | 180; 89 | 180; 92 |
| 11 | | | 30; 92 | 25; 91 |

^aReactions conditions: sulfide (1 mmol), H_2O_2 (0.6 ml) and catalyst (5 mg).

the effect of the amount of H_2O_2 was investigated. It can be observed that the yield of product is increased by adding H_2O_2 .

The effect of various oxidants on the efficiency of the oxidation of sulfides was studied using the model reaction. Hydrogen peroxide, molecular oxygen/air and sodium percarbonate were selected as oxidants. As evident from Table 5, when the reaction was performed using hydrogen peroxide, a maximum conversion took place in a shorter reaction time.

Under the optimized reaction conditions, oxidation of other sulfides was performed in the presence of MCM-41-INA-In and MCM-41-INA-Tl (Table 6). In all reactions, good to excellent yields were achieved with excellent selectivity to target products.

For another part of our study, we evaluated the catalytic performance of MCM-41-INA-In and MCM-41-INA-Tl in the oxidation of thiols with H_2O_2 at room temperature. The reactions were optimized according to the oxidation of 2-mercaptobenzoic acid through the study of the effect of catalyst dosage, solvent and amount of oxidant (Table 7). At first, the effects of catalyst dosage were studied. Increasing the catalyst amount from 0.003 to 0.007 g caused an increase in conversion. However, a further increase of catalyst amount had only a slight influence on the conversion. So, 0.007 g of catalyst was selected as the effective amount. Then, the influence of various solvents was investigated. Acetonitrile, ethanol, ethyl acetate and *n*-hexane were used as solvents; a higher yield was obtained in ethanol in comparison with the other solvents. Finally, we investigated the influence of the amount of H_2O_2 . It was evident that the product yield was increased by adding H_2O_2 .

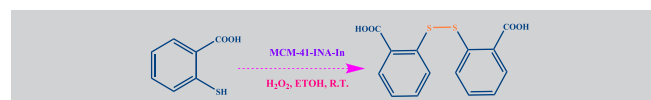
The effect of various oxidants on the efficiency of the oxidation of thiols was investigated using the model reaction. Hydrogen peroxide, molecular oxygen/air and sodium percarbonate were selected as oxidants and the results are summarized in Table 8. When the reaction was carried out using hydrogen peroxide, a maximum conversion took place in a shorter reaction time.

We then investigated the catalytic performance of MCM-41-INA-In and MCM-41-INA-Tl in the oxidation of other thiols (Table 9). In all reactions, good to excellent yields were achieved with excellent selectivity to target products.

3.3 | Homoselectivity and chemoselectivity of oxidation of sulfides

To study homoselectivity and chemoselectivity of oxidation of sulfides, the reaction was performed in the presence of 2,2'-disulfaneyldibenzoic acid and

TABLE 7 Optimization of reaction conditions for oxidative coupling of thiol using 2-mercaptobenzoic acid with H_2O_2 catalysed by MCM-41-INA-In^a

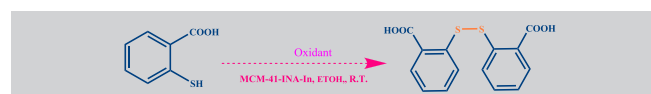


| Entry | Solvent | Catalyst (mg) | H_2O_2 (ml) | Time (min) | Yield (%) ^b |
|-------|------------------|---------------|---------------|------------|------------------------|
| 1 | EtOH | 3 | 0.6 | 15 | 90 |
| 2 | EtOH | 5 | 0.6 | 12 | 93 |
| 3 | EtOH | 7 | 0.6 | 8 | 96 |
| 4 | EtOH | 9 | 0.6 | 7 | 97 |
| 5 | Solvent free | 7 | 0.6 | 20 | 90 |
| 6 | Ethyl acetate | 7 | 0.6 | 20 | 85 |
| 7 | Acetonitrile | 7 | 0.6 | 25 | 82 |
| 8 | <i>n</i> -Hexane | 7 | 0.6 | 35 | 78 |
| 9 | EtOH | 7 | 0.8 | 5 | 97 |
| 10 | EtOH | 7 | 0.4 | 15 | 90 |
| 11 | EtOH | 7 | 0.2 | 27 | 78 |

^aReaction conditions: thiol (1 mmol), H_2O_2 , catalyst and solvent (3 ml).

^bIsolated yield.

TABLE 8 Testing of various oxidants for oxidation of 2-mercaptobenzoic acid^a



| Entry | Oxidant | Time (min) | Yield (%) |
|-------|----------------------|------------|-----------|
| 1 | H_2O_2 | 15 | 90 |
| 2 | Molecular oxygen/air | 45 | 91 |
| 3 | Sodium percarbonate | 1080 | 87 |

^a19 mmol of oxidant; other reaction conditions same as those for Table 7.

2-(phenylthio)ethanol with H_2O_2 and molecular oxygen/air as two oxidants.

When 2,2'-disulfaneyldibenzoic acid was subjected to oxidation (Table 6, entry 11), homoselective monosulfoxidation took place, and further oxidation to disulfoxidation or mono-sulfonation did not take place in the presence of H_2O_2 and molecular oxygen/air as two oxidants (Scheme 2).

Also, there is chemoselectivity in the oxidation of 2-(phenylthio)ethanol (Table 6, entry 8). For this substrate, the sulfide functional group was converted to sulfide, but alcohol oxidation did not occur during the conversion, and the primary hydroxyl group remained intact in the course of the reaction in the presence

TABLE 9 Oxidative coupling of thiols into disulfides in the presence of MCM-41-INA-In and MCM-41-INA-Tl^a

| | | | MCM-41-INA-In Time (min); yield (%) | MCM-41-INA-Tl Time (min); yield (%) |
|-------|-----------|---------|---|---|
| Entry | Substrate | Product | | |
| 1 | | | 8; 96 | 5; 96 |
| 2 | | | 4; 95 | 2; 97 |
| 3 | | | 20; 91 | 15; 92 |
| 4 | | | 10; 94 | 8; 96 |
| 5 | | | 2; 92 | 1; 95 |
| 6 | | | 4; 94 | 4; 95 |
| 7 | | | 10; 93 | 5; 96 |
| 8 | | | 5; 94 | 5; 94 |
| 9 | | | 5; 92 | 3; 94 |
| 10 | | | 3; 94 | 3; 95 |

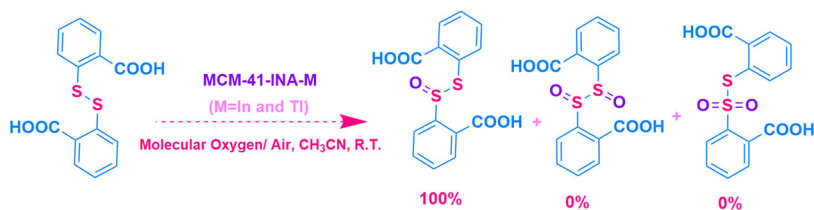
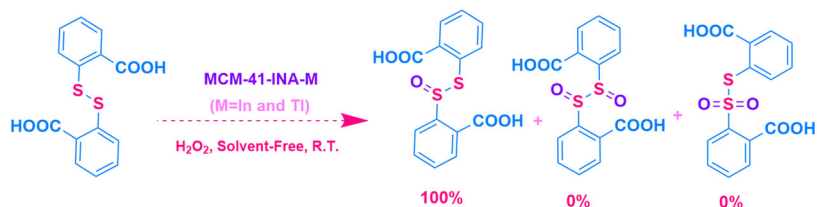
^aReactions conditions: thiol (1 mmol), H₂O₂ (0.6 ml), catalyst (7 mg) and ethanol (3 ml).

of H₂O₂ and molecular oxygen/air as two oxidants (Scheme 3).

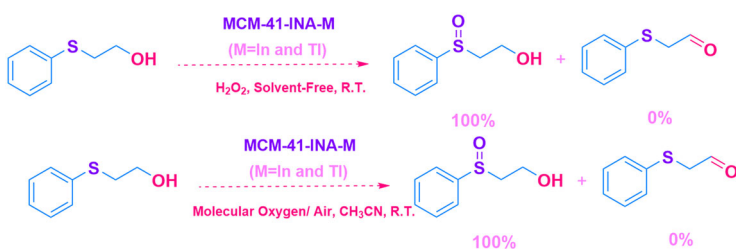
3.4 | Reusability of catalysts

The reusability of the MCM-41-INA-In and MCM-41-INA-Tl catalysts was evaluated in the oxidation of dibenzyl sulfide and in the oxidation of mercaptosuccinic acid under the optimum conditions for seven runs and the results are presented in Figure 8. After each

catalytic cycle, the catalyst was collected by centrifugation, washed with water followed with ethyl acetate and dried at 100°C. As shown in Figure 8, the catalysts were found to maintain their activity after seven runs. This could be attributed to the low leaching of indium and thallium from the catalysts in the reaction. Also, the SEM images (Figure 9) and FT-IR spectra (Figure 10) of MCM-41-INA-In and MCM-41-INA-Tl after seven runs indicate that the structures of the novel MCM-41-INA-In and MCM-41-INA-Tl catalysts have been retained.



SCHEME 2 Homoselective oxidation of 2,2'-disulfanediyldibenzoic acid to its mono-sulfoxide derivative in the presence of H₂O₂ and molecular oxygen/air as two oxidants



SCHEME 3 Chemoselective sulfoxidation of 2-(phenylthio)ethanol in the presence of H₂O₂ and molecular oxygen/air as two oxidants

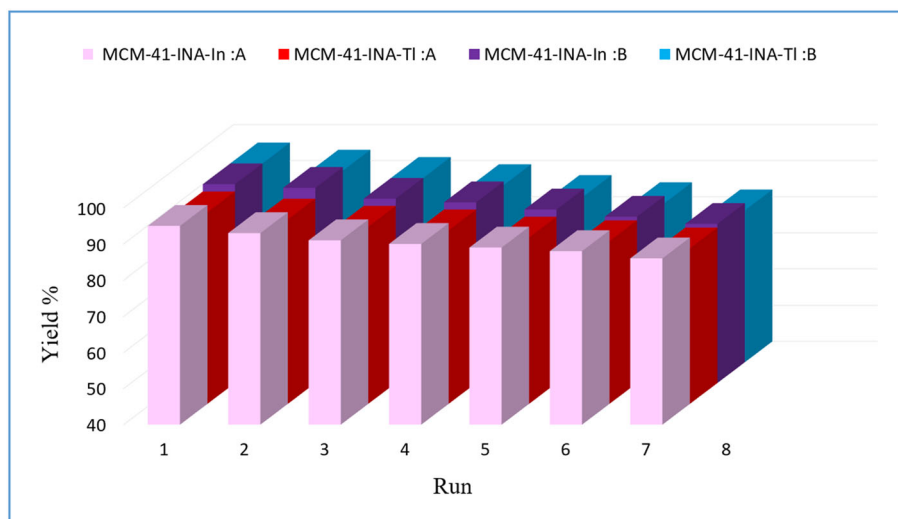


FIGURE 8 Reusability of MCM-41-INA-In and MCM-41-INA-Tl catalysts for oxidation of dibenzyl sulfide (A) and oxidation of mercaptosuccinic acid (B)

ICP-OES analysis of spent MCM-41-INA-Tl was conducted to determine the amounts of metal after each reaction run. The results are presented in Table 10.

The catalytic performance of MCM-41-INA-In and MCM-41-INA-Tl in the oxidation of dipropylsulfane and oxidation of phenylmethanethiol was compared

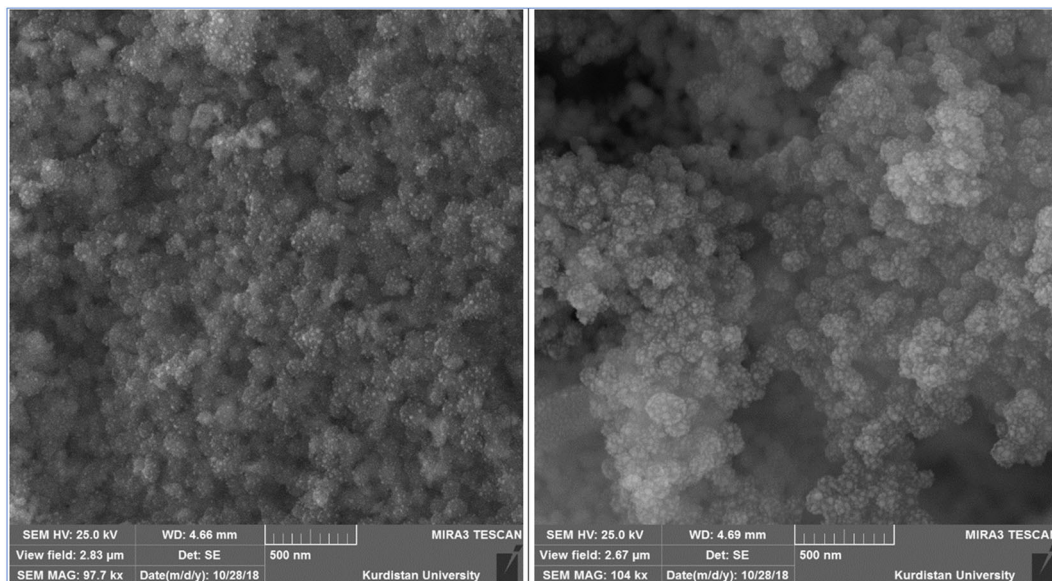


FIGURE 9 SEM images of recovered MCM-41-INA-In (left) and MCM-41-INA-Tl (right)

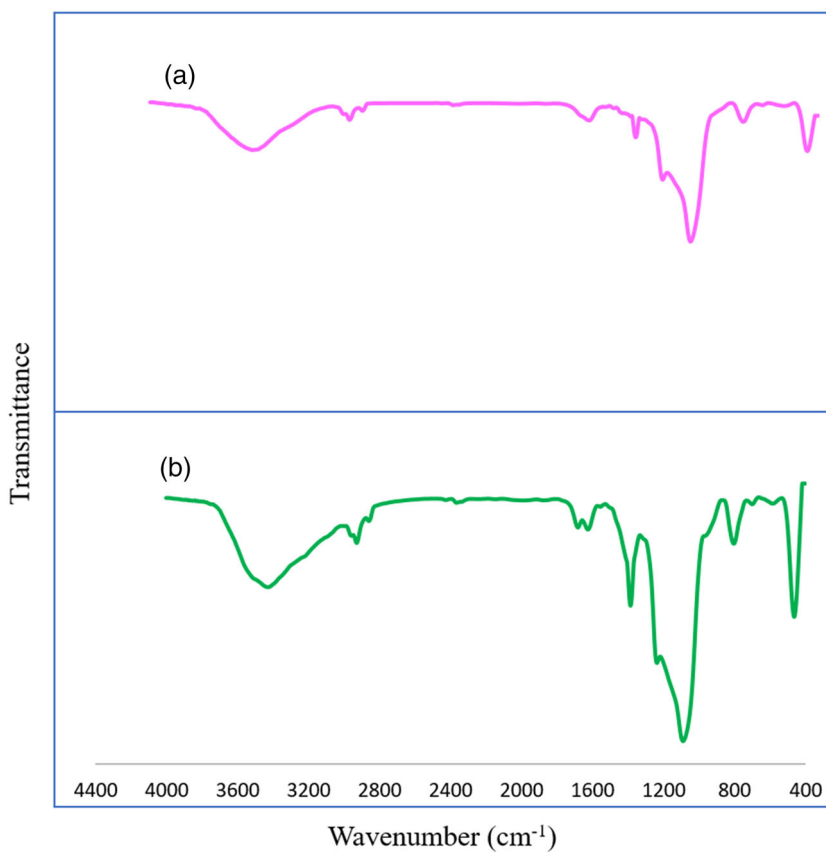


FIGURE 10 FT-IR spectra of recovered (a) MCM-41-INA-In and (b) MCM-41-INA-Tl

TABLE 10 Recycling of MCM-41-INA-Tl catalyst used in oxidation of dibenzyl sulfide

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--------------------------------------|------|------|------|------|------|------|------|
| Metal amount (mmol g ⁻¹) | 2.03 | 2.00 | 1.96 | 1.93 | 1.88 | 1.83 | 1.79 |

TABLE 11 Comparison of MCM-41-INA-In and MCM-41-INA-Tl catalysts for oxidation of dipropylsulfane and oxidation of phenylmethanethiol with previously reported catalysts

| Entry | Substrate | Catalyst:amount | Solvent | Temp. (°C) | Time (min) | Yield (%) |
|-------|--------------------|---|----------------|-----------------|------------|--------------------|
| 1 | Dipropylsulfane | VO-salen-MCM-41:15 mg | Ethanol | RT ^a | 15 | 94 ^[62] |
| 2 | Dipropylsulfane | Cu-Salen-MCM-41:20 mg | Ethanol | RT ^a | 27 | 92 ^[63] |
| 3 | Dipropylsulfane | Fe ₃ O ₄ @PTA-VO(IV):15 mg | Solvent-free | RT ^a | 12 | 97 ^[64] |
| 4 | Dipropylsulfane | VO-2A3HP-MCM-41:4 mg | Solvent-free | RT ^a | 100 | 98 ^[39] |
| 5 | Dipropylsulfane | Fe ₃ O ₄ -AMPD-Cu:5 mg | Solvent-free | RT ^a | 25 | 93 ^[65] |
| 6 | Dipropylsulfane | Fe ₃ O ₄ -Adenine-Ni:5 mg | Solvent-free | RT ^a | 65 | 95 ^[66] |
| 7 | Dipropylsulfane | VO-AMPD@SBA-15:4 mg | Solvent-free | RT ^a | 35 | 98 ^[67] |
| 8 | Dipropylsulfane | MCM-41-INA-In:5 mg | Solvent-free | RT ^a | 5 | 92 (this work) |
| 9 | Dipropylsulfane | MCM-41-INA-Tl:5 mg | Solvent-free | RT ^a | 5 | 95 (this work) |
| 10 | Phenylmethanethiol | Fe ₃ O ₄ -Adenine-Zn:5 mg | Ethyl acetate | RT ^a | 90 | 96 ^[68] |
| 11 | Phenylmethanethiol | Boehmite-SSA:2 mg | Ethyl acetate | RT ^a | 75 | 97 ^[69] |
| 12 | Phenylmethanethiol | VO@MCM-41-Cys:8 mg | Neat condition | RT ^a | 60 | 98 ^[56] |
| 13 | Phenylmethanethiol | DSA@MNPs:4 mg | Ethanol | RT ^a | 60 | 90 ^[70] |
| 14 | Phenylmethanethiol | Ni-SMTU@boehmite:8 mg | Ethanol | RT ^a | 225 | 95 ^[71] |
| 15 | Phenylmethanethiol | Zn-2A3HP-MCM-41:10 mg | Ethanol | RT ^a | 65 | 93 ^[72] |
| 16 | Phenylmethanethiol | MCM-41@creatinine@La:5 mg | Ethanol | RT ^a | 65 | 96 ^[73] |
| 17 | Phenylmethanethiol | Fe ₃ O ₄ @MCM-41@Ni-P2C:10 mg | Ethanol | RT ^a | 35 | 92 ^[74] |
| 18 | Phenylmethanethiol | MCM-41-INA-In:7 mg | Ethanol | RT ^a | 30 | 91 (this work) |
| 19 | Phenylmethanethiol | MCM-41-INA-Tl:7 mg | Ethanol | RT ^a | 20 | 92 (this work) |

^aRoom temperature.

with that of previously reported catalysts (Table 11). The MCM-41-INA-In and MCM-41-INA-Tl catalysts provide the highest activity for oxidation of dipropylsulfane and oxidation of phenylmethanethiol compared with the other catalysts.

4 | CONCLUSIONS

We have successfully developed two novel indium- and thallium-grafted functionalized mesoporous MCM-41 materials using a post-grafting method. Surface functionalization and INA condensation followed by indium or thallium impregnation resulted in indium- and thallium-grafted functionalized mesoporous MCM-41. These novel mesoporous MCM-41-INA-In and MCM-41-INA-Tl catalysts showed excellent catalytic performance in the oxidation of sulfides and thiols to their corresponding sulfoxides and disulfides at room temperature under mild conditions. Some attractive features of these protocols are high yields, short reaction times and inexpensive and simple procedure. These catalysts showed only slight leaching of indium or thallium and

can be reused for seven successive reaction runs without considerable loss of catalytic performance.

ORCID

Somayeh Molaei  <https://orcid.org/0000-0001-6040-4830>
 Mohammad Ghadermazi  <https://orcid.org/0000-0001-8631-6361>

REFERENCES

- [1] F. Dehghani, A. R. Sardarian, M. Esmaeilpour, *J. Organometal. Chem.* **2013**, 743, 87.
- [2] Y. Zhu, L. P. Stubbs, F. Ho, R. Liu, C. P. Ship, J. A. Maguire, N. S. Hosmane, *ChemCatChem* **2010**, 2, 365.
- [3] F. Liu, L. Wang, Q. Sun, L. Zhu, X. Meng, F.-S. Xiao, *J. Am. Chem. Soc.* **2012**, 134, 16948.
- [4] W. Xie, L. Hu, *Food Chem.* **2016**, 197, 92.
- [5] W. Xie, C. Zhang, *Food Chem.* **2016**, 211, 74.
- [6] W. Xie, C. Qi, *J. Agric. Food Chem.* **2013**, 61, 3373.
- [7] W. Xie, X. Yang, M. Fan, *Renewable Energy* **2015**, 80, 230.
- [8] C. del Pozo, A. Corma, M. Iglesias, F. Sánchez, *Organometallics* **2010**, 29, 4491.
- [9] N. U. Silva, C. I. Fernandes, T. G. Nunes, M. S. Saraiva, C. D. Nunes, P. D. Vaz, *Appl. Catal. A* **2011**, 408, 105.

- [10] E. Tyrrell, L. Whiteman, N. Williams, *J. Organometal. Chem.* **2011**, *696*, 3465.
- [11] S. Molaei, T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, *Appl. Organometal. Chem.* **2019**, *33*, e4649.
- [12] M. Vasconcellos Dias, M. S. Saraiva, P. Ferreira, M. J. Calhorda, *Organometallics* **2015**, *34*, 1465.
- [13] E. P. Reddy, L. Davydov, P. G. Smirniotis, *J. Phys. Chem. B* **2002**, *106*, 3394.
- [14] S. Molaei, T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, *Polyhedron* **2018**, *156*, 35.
- [15] S. Molaei, T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, *Micropor. Mesopor. Mater.* **2018**, *272*, 241.
- [16] S. Molaei, T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, *Catal. Lett.* **2018**, *148*, 1834.
- [17] S. Molaei, T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, *Appl. Organometal. Chem.* **2019**, *33*, e4649.
- [18] M. Nikoorazm, A. Ghorbani-Choghamarani, M. Ghobadi, S. Massahi, *Appl. Organometal. Chem.* **2017**, *31*, e3848.
- [19] M. Khanmoradi, M. Nikoorazm, A. Ghorbani-Choghamarani, *Catal. Lett.* **2017**, *147*, 1114.
- [20] M. A. Zolfigol, S. Sajjadifar, A. Ghorbani-Choghamarani, F. Tami, *Res. Chem. Intermed.* **2018**, *44*, 7093.
- [21] G. Hilt, K. I. Smolko, *Angew. Chem.* **2001**, *40*, 3399.
- [22] S. V. Chankeshwara, A. K. Chakraborti, *Synthesis* **2006**, *2006*, 2784.
- [23] S. T. Kadam, S. S. Kim, *Synthesis* **2008**, *2008*, 3307.
- [24] S. A. Frank, H. Chen, R. K. Kunz, M. J. Schnaderbeck, W. R. Roush, *Org. Lett.* **2000**, *2*, 2691.
- [25] L. M. Aguirre-Díaz, M. Iglesias, N. Snejko, E. Gutiérrez-Puebla, M. Á. Monge, *CrystEngComm* **2013**, *15*, 9562.
- [26] A. F. Douglas, B. O. Patrick, P. Mehrkhodavandi, *Angew. Chem.* **2008**, *47*, 2290.
- [27] X.-T. Zhou, H.-B. Ji, Z. Cheng, J.-C. Xu, L.-X. Pei, L.-F. Wang, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 4650.
- [28] H. Zhang, G. Wang, *Tetrahedron Lett.* **2014**, *55*, 56.
- [29] H. B. Jeon, K. T. Kim, S. H. Kim, *Tetrahedron Lett.* **2014**, *55*, 3905.
- [30] N. Iranpoor, H. Firouzabadi, A. R. Pourali, *Synlett* **2004**, 347.
- [31] S. Rostamnia, B. Gholipour, H. G. Hosseini, *Process SAF Environ.* **2016**, *100*, 74.
- [32] S. Rostamnia, B. Gholipour, X. Liu, Y. Wang, H. Arandiyan, *J. Colloid Interface Sci.* **2018**, *511*, 447.
- [33] S. Rostamnia, H. Alamgholiloo, M. Jafari, R. Rookhosh, A. R. Abbasi, *Appl. Organometal. Chem.* **2016**, *30*, 954.
- [34] M. Nikoorazm, M. Ghobadi, *Silicon* **2018**. <https://doi.org/10.1007/s12633>.
- [35] M. Hajjami, S. Rahmani, *J. Porous Mater.* **2015**, *22*, 1265.
- [36] A. Ghorbani-Choghamarani, Z. Darvishnejad, B. Tahmasbi, *Inorg. Chim. Acta* **2015**, *435*, 223.
- [37] A. Ghorbani-Choghamarani, B. Tahmasbi, F. Arghand, S. Faryadi, *RSC Adv.* **2015**, *5*, 92174.
- [38] M. A. Zolfigol, A. Khazaei, M. Safaiee, M. Mokhlesi, R. Rostamian, M. Bagheri, M. Shiri, H. G. Kruger, *J. Mol. Catal. Chem.* **2013**, *370*, 80.
- [39] M. Nikoorazm, A. Ghorbani-Choghamarani, M. Khanmoradi, *Appl. Organometal. Chem.* **2016**, *30*, 236.
- [40] S. Nazarzadeh, A. Ghorbani-Choghamarani, E. Tahanpesar, *J. Iran. Chem. Soc.* **2018**, *15*, 649.
- [41] M. Hajjami, L. Shiri, A. Jahanbakhshi, *Appl. Organometal. Chem.* **2015**, *29*, 668.
- [42] A. Ghorbani-Choghamarani, B. Ghasemi, Z. Safari, G. Azadi, *Catal. Commun.* **2015**, *60*, 70.
- [43] S. Rezaei, A. Ghorbani-Choghamarani, R. Badri, A. Nikseresht, *Appl. Organometal. Chem.* **2018**, *32*, e3948.
- [44] X. Dong, D. Wang, K. Li, Y. Zhen, H. Hu, G. Xue, *Mater. Res. Bull.* **2014**, *57*, 210.
- [45] N. Gharah, S. Chakraborty, A. K. Mukherjee, R. Bhattacharyya, *Inorg. Chim. Acta* **2009**, *362*, 1089.
- [46] R. Tan, C. Liu, N. Feng, J. Xiao, W. Zheng, A. Zheng, D. Yin, *Micropor. Mesopor. Mater.* **2012**, *158*, 77.
- [47] J. Wang, L. Yan, G. Qian, S. Li, K. Yang, H. Liu, X. Wang, *Tetrahedron* **2007**, *63*, 1826.
- [48] A. Khazaei, M. A. Zolfigol, M. Safaiee, M. Mokhlesi, E. Donyadari, M. Shiri, H. G. Kruger, *Catal. Commun.* **2012**, *26*, 34.
- [49] D. Khalili, *New J. Chem.* **2016**, *40*, 2547.
- [50] S. Sajjadifar, *J. Org. Chem.* **2012**, *2*, 116.
- [51] E. Rezaei Nezhad, S. Karimian, S. Sajjadifar, *J. Sci. I. R. Iran.* **2015**, *26*, 233.
- [52] M. Safaiee, M. A. Zolfigol, M. Tavasoli, M. Mokhlesi, *J. Iran. Chem. Soc.* **2014**, *11*, 1593.
- [53] M. M. Heravi, F. Derikvand, S. Hassan-Pour, K. Bakhtiari, F. F. Bamoharram, H. A. Oskooie, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 3305.
- [54] F. Havasi, A. Ghorbani-Choghamarani, F. Nikpour, *Micropor. Mesopor. Mater.* **2016**, *224*, 26.
- [55] P. Selvam, V. M. Ravat, V. Krishna, *J. Phys. Chem. C* **2011**, *115*, 1922.
- [56] N. Noori, M. Nikoorazm, A. Ghorbani-Choghamarani, *Micropor. Mesopor. Mater.* **2016**, *234*, 166.
- [57] S. Bhunia, D. Saha, S. Koner, *Langmuir* **2011**, *27*, 15322.
- [58] J. N. Appaturi, M. R. Johan, R. J. Ramalingam, H. A. Al-Lohedan, *Micropor. Mesopor. Mater.* **2018**, *256*, 67.
- [59] S. Bayarı, A. Ataç, Ş. Yurdakul, *J. Mol. Struct.* **2003**, *655*, 163.
- [60] M. Nikoorazm, A. Ghorbani-Choghamarani, H. Mahdavi, S. M. Esmaili, *Micropor. Mesopor. Mater.* **2015**, *211*, 174.
- [61] M. Zare, Z. Moradi-Shoeili, P. Esmailpour, S. Akbayrak, S. Özkur, *Micropor. Mesopor. Mater.* **2017**, *251*, 173.
- [62] A. Jabbari, H. Mahdavi, M. Nikoorazm, A. Ghorbani-Choghamarani, *J. Porous Mater.* **2015**, *22*, 1111.
- [63] H. Mahdavi, M. Nikoorazm, A. Ghorbani-Choghamarani, S. Arshadi, *J. Porous Mater.* **2016**, *23*, 75.
- [64] M. Norouzi, A. Ghorbani-Choghamarani, *React. Kinet. Mech. Catal.* **2016**, *119*, 537.
- [65] M. Darabi, T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, *Transition Met. Chem.* **2017**, *42*, 703.
- [66] T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, *Appl. Organometal. Chem.* **2017**, *32*, e3974.
- [67] T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, S. Molaei, *Res. Chem. Intermed.* **2018**, *44*, 4259.

- [68] T. Tamoradi, A. Ghorbani-Choghamarani, M. Ghadermazi, *New J. Chem.* **2017**, *41*, 11714.
- [69] A. Ghorbani-Choghamarani, M. Hajjami, B. Tahmasbi, N. Noori, *J. Iran. Chem. Soc.* **2016**, *13*, 2193.
- [70] A. Ghorbani-Choghamarani, H. Rabiei, B. Tahmasbi, B. Ghasemi, F. Mardi, *Res. Chem. Intermed.* **2016**, *42*, 5723.
- [71] A. Ghorbani-Choghamarani, P. Moradi, B. Tahmasbi, *RSC Adv.* **2016**, *6*, 56458.
- [72] M. Nikoorazm, A. Ghorbani-Choghamarani, M. Khanmoradi, *J. Iran. Chem. Soc.* **2017**, *14*, 1215.
- [73] T. Tamoradi, M. Ghadermazi, A. Ghorbani-Choghamarani, *New J. Chem.* **2018**, *42*, 5479.
- [74] M. Nikoorazm, F. Ghorbani, A. Ghorbani-Choghamarani, Z. Erfani, *Phosphorus Sulfur Silicon Relat. Elem.* **2018**, *193*, 552.

How to cite this article: Molaei S, Ghadermazi M. Synthesis and characterization of indium and thallium immobilized on isonicotinamide-functionalized mesoporous MCM-41: Two novel and highly active heterogeneous catalysts for selective oxidation of sulfides and thiols to their corresponding sulfoxides and disulfides. *Appl Organometal Chem.* 2019;e4972. <https://doi.org/10.1002/aoc.4972>