

#### Article

# Efficient preparation of Zr(IV)-salen grafted mesoporous MCM-41 catalyst for chemoselective oxidation of sulfides to sulfoxides and Knoevenagel condensation reactions

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#### 1. Introduction

#### ABSTRACT

Zr(IV)-salen-MCM-41 was prepared by reaction of NH<sub>2</sub>-MCM-41 with salicylaldehyde to afford Schiff base ligands. Thereafter, ZrOCl<sub>2</sub>·8H<sub>2</sub>O was reacted with the Schiff base ligands for complex formation. The structural properties of the synthesized materials were investigated by a number of analytical techniques including X-ray diffraction, N<sub>2</sub> sorption-desorption, thermogravimetric analysis, Fourier transform infrared spectroscopy, inductively coupled plasma atomic emission spectroscopy, and energy dispersive X-ray spectroscopy. Catalytic studies of the mesoporous materials functionalized with Zr(IV)-Schiff base complexes were investigated and extended to selective oxidation of sulfides to sulfoxides and the Knoevenagel condensation reactions of aldehydes with malononitriles and ethyl cyanoacetate. Additionally, catalyst recycling of the Zr-salen-MCM-41 materials was also studied.

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M41S family mesoporous materials [1] have attracted considerable attention across a wide application sector as sorbents [2–5], heterogeneous catalysts [6–8], drug delivery vehicles [9,10], and separators [11]. Among the M41S derivatives, MCM-41 possessing a two-dimensional (2D) hexagonal mesostructure has attracted significant attention because of high surface areas, efficient surface functionalization, and large pore volumes. The catalytic efficiency of this material depends on the nature of the functionalization by grafting of organic compounds via Si–C bond formation. The abundance of surface hydroxyl groups on MCM-41 permits reactions with desired organic compounds, leading to organic-inorganic mesoporous hybrid materials [12]. Typically, the functionalization of mesoporous materials is performed in one of three ways: (1) post-synthetic modification of the pore surface of a purely inorganic silica material (grafting); (2) *in situ* addition of a functional organosiloxane to the corresponding silica material (co-condensation); and (3) functionalization by organic groups bridging into the pore walls by bissilylated organosilica precursors (periodic mesoporous organosilicas). Functionalizing with amine-containing groups is one of many ways to graft useful functionality into the mesoporous silica to afford mesoporous catalysts [13].

Selective oxidation of sulfides to sulfoxides is an important transformation in synthetic organic chemistry because sulfoxides are useful functional groups in numerous pharmaceutically and biologically active compounds. In addition, sulfoxides are important synthetic intermediates for the production of molecules, especially by C–C bond formation [14,15].

Numerous reports highlight synthetic methods for the oxi-

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dation of sulfides to sulfoxides, based on metal intermediate catalysts, such as Fe [16], Au [17], Ti [18], Cu [19], Co [20], Mn [21], Zr [22], Mo [23], Zn [24], V [25], Ru [26], Ta [27], and W [28]. These works represent considerable progress; however, all suffer from one or more disadvantages including long reaction time, low product yield, tedious acidic work-up, generation of environmentally unfavorable by-products, additional synthetic steps to remove or recover the expensive catalyst, and difficulties in preventing over-oxidation. Hence, a new methodology is required to design suitable catalysts that can overcome such drawbacks.

The Knoevenagel condensation reaction, discovered by Knoevenagel [29] in 1896, involves the condensation of aldehydes with a C-H acidic methylene activated group. The Knoevenagel condensation is widely employed in the synthesis of important chemical intermediates, such as coumarin derivatives because of their biological activities [30]. Furthermore, the Knoevenagel condensation reaction has been used for the preparation of cosmetics, perfumes, and substituted alkenes. Generally, the reaction requires both a solvent and a catalyst. Examples of acidic and basic catalysts, such as ionic liquids [31], porous calcium hydroxyapatite [32], silica-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles bearing 3-aminopropyl functional groups [33], Fe<sub>3</sub>O<sub>4</sub> nanoparticle-supported amino acids [34], carbamic acid ammonium salts [35], zinc chloride [36], cation-exchanged zeolites [37], montmorillonite KSF [38], and magnesium fluoride [39], have been reported. In the presence of acid catalysts the Knoevenagel condensation reaction can accelerate because of increasing aldehyde electrophilicity. To accomplish a cleaner Knoevenagel synthesis, great effort has been made to prepare heterogeneous catalysts.

Designing suitable supports to immobilize metal-Schiff base complexes remains an important and relevant topic in the field of heterogeneous catalysis. A number of solid material supports, such as polymers, carbon nanotubes, ionic liquids, zeolites, and mesoporous silicas, including SBA-15, have widely been investigated. Among them, mesoporous materials have attracted extensive attention for the immobilization of metal-salen complexes owing to their high surface area, large pore size together, and facile functionalization of the silica walls. The mesoporous material-supported metal-salen complexes have proven to be highly efficient catalysts for the synthesis of a variety of valuable organic compounds. Briefly, among the mesoporous material-supported metal-salen complex catalyzed systems, zirconium Schiff base complex-modified SBA-15 was applied as a heterogeneous catalyst for the synthesis of a library of N-containing pyrazine-based heterocycles [40]. Other works have shown that pyrazine-based heterocycles synthesized in the presence of SBA-15-supported Fe(III)-Schiff base [41] and Mn(salen)/C<sub>3</sub>N<sub>2</sub>-Schiff-SBA-15 and Mn(salen)/C<sub>4</sub>N<sub>2</sub>-Schiff-SBA-15 were reported as useful for the epoxidation of alkenes [42]. Additionally, the Sizuki C-C cross-coupling reaction over Pd-salen MCM-41 has been reported [43]. In another work, the Pd(II)-Schiff base complex-functionalized MCM-41 behaved as a highly active catalyst toward the Suzuki-Miyaura cross-coupling reaction [44]. Oxidation of sulfides and oxidative coupling of thiols were performed using immobilized Ni or

Cd complexes on MCM-41 as heterogeneous catalysts [45]. Furthermore, [Ru(salen)(NO)] complex-modified SBA-15 used in the hydrogenation of ketones to the corresponding alcohols has been reported [46]. Co(II)-Schiff base functionalized MCM-41 was synthesized and used as a catalyst for styrene oxidation with  $H_2O_2$  [47]. Additionally, Cr(III) alanine-salicylaldehyde Schiff base complex immobilized on mesoporous silica gels, MCM-41, and SBA-15 were promising catalysts for the epoxidation of styrene [48].

This investigation reports the synthesis, characterization, and catalytic properties of a MCM-41 mesoporous silica-supported Zr(IV) complex applied to efficient Knoevenagel condensation reactions and the chemoselective oxidation of sulfides to sulfoxides.

#### 2. Experimental

#### 2.1. Chemicals

Analytical grade hexadecyltrimethylammonium bromide (CTAB), HCl (37%), NaOH, tetraethyl orthosilicate (TEOS), aldehydes, sulfides, H<sub>2</sub>O<sub>2</sub> (30%), malononitrile, and ethyl cyanoacetate were all purchased from Aldrich and Merck and used without further purification. De-ionized distilled water was used in the preparation of all solutions. The known products were characterized by physical data with those of authentic samples. Unknown compounds were identified by their <sup>1</sup>H NMR and <sup>13</sup>CNMR spectra (Bruker NMR-Spectrometer FX 400Q).

#### 2.2. Synthesis of Zr(IV)-salen-MCM-41

MCM-41 was synthesized according to a previous literature method [49–51]. Briefly, MCM-41 was prepared by the reaction of TEOS (1 mmol) as the silica source and CTAB (0.1 mmol) in a basic solution of NaOH (0.3 mmol) and H<sub>2</sub>O (60 mL). The gel mixture was then crystallized under hydrothermal treatment at 110 °C for 60 h in a Teflon-lined autoclave. The resultant solid was recovered by filtration, washed with de-ionized water and dried in air. The collected product was calcined at 550 °C for 7 h to remove the polymeric surfactant, CTAB.

Modification of mesoporous MCM-41 to *n*-propylamine-MCM-41 was conducted according to Ref. [52]. In a typical procedure, 27 mmol of 3-aminopropyl triethoxysilane (APTES) was stirred with MCM-41 (4.8 g) in *n*-hexane (96 mL) at 80 °C for 24 h under a N<sub>2</sub> atmosphere. The resulting solid NH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-MCM-41 was filtered, washed several times with *n*-hexane and dried in vacuum. Thereafter, NH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-MCM-41 (1 g) was added to salicylaldehyde (1 mmol) in absolute ethanol (20 mL) and stirred for 5 h under reflux conditions under a N<sub>2</sub> atmosphere. The solution slowly became yellow, indicating the formation of the Schiff base. The yellow solid imine product was isolated after ethanol removal.

Further modification was required to form the Zr(IV)-imine complex of MCM-41.  $ZrOCl_2 \cdot 8H_2O$  (2 mmol) was added to a suspension of imine-MCM-41 (1 g) in acetonitrile (30 mL) at room temperature under a  $N_2$  atmosphere. The mixture was

stirred for 6 h. The solid product was filtered, washed with water and then dried in an oven, obtaining a peach-colored Zr(IV)-salen-MCM-41 (Scheme 1).

#### 2.3. Catalyst characterization

The crystalline structures of the synthesized samples were examined by X-ray diffraction (XRD) using a GBC-Difftech MMA diffractometer. The Ni-filtered Cu  $K_{\alpha}$  ( $\lambda = 0.154$  nm) radiation was used at an acceleration voltage of 35 kV and a current of 34.2 mA. The diffraction angle was scanned from 1° to 10°,  $2\theta$ at a rate of 1°/min. To determine the textural properties, Fourier transform infrared (FT-IR) analyses were performed using an FT-IR spectrophotometer Vertex 70 (Bruker, Germany) in the range of 400-4000 cm<sup>-1</sup>. Thermogravimetric analysis (TGA, PerkinElmer Pyris Diamond, UK) was determined from ambient temperature to 800 °C using a ramp rate of 10 °C/min. To determine the textural properties, N<sub>2</sub> adsorption-desorption isotherms were measured using a BEL sorp-mini II volumetric adsorption analyzer. All of the samples were degassed at 100 °C under an Ar gas flow for 3 h prior to analysis. The specific surface area of the synthesized materials was evaluated using the BET model and the pore size distribution was calculated by the BJH model. Energy dispersive X-ray spectroscopy (EDX, FESEM-TESCAN MIRA3) studies of Zr(IV)-salen-MCM-41 confirm the presence of zirconium in the catalyst.

#### 2.4. General procedure for the oxidation of sulfides to sulfoxides

 $H_2O_2$  (30%, 0.4 mL) was added to a mixture containing sulfide (1 mmol) and catalyst (Zr(IV)-Schiff base-MCM-41, 0.03 g) at 35 °C under solvent-free conditions. The reaction mixture was stirred until completion of the reaction as monitored by thin-layer chromatography (TLC). After complete conversion of the reactant, the product was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and the residue purified by chromatography (eluting with 4:1 hexane/acetone).

### 2.5. General procedure for the synthesis of arylidene malononitriles and arylidene ethylcyanoacrylates

A mixture of malononitrile (2 mmol) or ethyl cyanoacetate (2 mmol), an aromatic aldehyde (1 mmol), and catalyst (Zr(IV)-Schiff base-MCM-41, 0.05 g) in water (3 mL) was stirred at 35 °C for a desired time. The reaction was monitored





by TLC. Upon completion of the reaction, the mixture was decanted and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure. Recrystallized absolute ethanol and water further purified the product.

#### 2.6. Characterization data of selected compounds

Tetrahydrothiopheneoxide (**2b**, Table 4). IR (ATR) cm<sup>-1</sup>: 1034 (S=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 2.21–2.3 (m, 4H), 3.02–3.11 (m, 4H).

Diethyl sulfoxide (**2f**, Table 4). IR (ATR) cm<sup>-1</sup>: 1066 (S=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 1.39–1.43 (q, *J* = 3.2, 3H), 2.98– 3.01 (q, *J* = 3.2, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ: 7.75, 47.30.

2-(4-Bromo-benzylidene)-malononitrile (**3e**, Table 7). IR (ATR) cm<sup>-1</sup>: 3050–2900, 2226, 1576, 1487, 614. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.27 (s, 1H), 7.68–7.72 (d, 2H), 7.77–7.79 (d, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 159.6, 134.2, 132.9, 131.1, 130.8, 114.6, 113.5, 84.6.

2-(4-Methyl-benzylidene)-malononitrile (**3g**, Table 7). IR (ATR) cm<sup>-1</sup>: 3037–2927, 2223, 1587, 1451. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 2.48 (s, 3H), 7.35 (d, 2H), 7.73 (s, 1H), 7.82 (d, 2H, *J* = 7.2).

Ethyl-2-cyano-3-(4-methylphenyl)acrylate (**3h**, Table 7). IR (ATR) cm<sup>-1</sup>: 3030–2904, 2216, 1722, 1473, 1593, 1092, 1264. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 1.41 (t, 3H), 2.44 (s, 3H), 4.39 (q, 2H, *J* = 7.06), 7.32 (d, 2H), 7.91 (d, 2H, *J* = 8.4), 8.22 (s, 1H).

Ethyl-2-cyano-3-(3-hydroxyphenyl)acrylate (**3j**, Table 7). IR (ATR) cm<sup>-1</sup>: 3372, 2984, 2222, 1698, 1491, 1595, 1179, 1239. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 1.41 (t, 3H, *J* = 7.2), 4.4 (q, 2H), 6.17 (s, 1H), 7.10 (d, 1H, *J* = 6.8), 7.37 (d, 1H), 7.44 (s, 1H), 7.60 (m, 1H), 8.22 (s, 1H). <sup>1</sup><sup>3</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 157.6, 156.4, 133.7, 131.7, 125.7, 122.2, 117.4, 104, 64, 15.3.

2-(3-Nitro-benzylidene)-malononitrile (**3k**, Table 7). IR (ATR) cm<sup>-1</sup>: 3108–2867, 2226, 1611, 1595, 1524, 1353. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.80 (m, 1H), 7.90 (d, 1H, *J* = 2.4), 8.35 (s, 1H), 8.49 (d, 1H), 8.67 (s, 1H).

2-(4-Ethoxy-benzylidene)-malononitrile (**3p**, Table 7). IR (ATR) cm<sup>-1</sup>: 3000–2900, 2219, 1587, 1473, 1174, 1263. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 1.48 (t, 3H, *J* = 12.66), 4.16 (q, 2H), 7.00 (d, 2H), 7.65 (s, 1H), 7.90 (d, 2H, *J* = 8.4). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 160, 134.6, 124.9, 116.6, 115.6, 114.5, 79.3, 65.44, 15.7.

2-(4-Methoxy-benzylidene)-malononitrile (**30**, Table 7). IR (ATR) cm<sup>-1</sup>: 3050–2900, 2220, 1603, 1568, 1276, 1179. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 3.94 (s, 3H), 7.02 (d, 2H), 7.67 (s, 1H), 7.92 (d, 2H, *J* = 8). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 166.8, 160, 134.6, 125.1, 116.3, 115.6, 114.5, 79.6, 57, 30.

#### 3. Results and discussion

#### 3.1. Structural features of the synthesized catalyst

The low-angle XRD patterns of the synthesized and functionalized MCM-41 materials are presented in Fig. 1. The diffractograms reveals that a one-dimensional hexagonal mesoporous p6mm structure of MCM-41 was synthesized. In the



Fig. 1. Low-angle XRD patterns of the synthesized materials.

MCM-41 diffractogram it is clearly discernible that a very sharp diffraction peak (100) at  $2\theta = 2.64^{\circ}$  and two additional high-order reflections (110, 200) with lower intensities at 4.60° and 5.47°, respectively, are observed [53]. The *d*-spacing values for these peaks are 33.46, 19.21, and 16.16 Å, respectively. The unit cell parameter ( $a_0$ ) of 38.64 Å was calculated using the following equation [54]:

$$a_0 = 2d100/\sqrt{3}$$
 (1)

A significant difference was observed in the intensity of the peaks in the XRD diffractogram through each functionalization of MCM-41. These results provide further evidence that functionalization occurred mainly inside the mesopore channels. They also confirm that the integrity of the hexagonal symmetry long-range order was retained after several stages of functionalization and oxidation reactions.

 $N_{\rm 2}$  adsorption-desorption isotherm data revealed that all samples exhibited type IV isotherms typical of mesoporous porosity (Fig. 2) possessing hysteresis loops with parallel and almost horizontal branches, classified as H4-type according to the IUPAC nomenclature.

Furthermore, a distinct inflection in the  $p/p_0$  range from 0.25 to 0.35 represents the characteristic capillary condensation of nitrogen inside the parent MCM-41 and amine-function-



Fig. 2. Nitrogen adsorption (solid symbols)-desorption (open symbols) isotherms of synthesized materials.

#### Table 1

Textural properties of synthesized materials obtained by  $N_{\rm 2}$  adsorption-desorption analysis.

Sample Name	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$D_{\rm BJH}$ (nm)	$V_{\rm total}$ (cm <sup>3</sup> /g)
MCM-41	986.16	3.65	0.711
Amine-MCM-41	810.68	2.46	0.758
Imine-MCM-41	201.36	1.41	0.177
Zr-imine-MCM-41	57.82	1.67	0.081

alized MCM-41 possessing a uniform pore size distribution. These results are in agreement with those previously reported [8,55]. Textural properties of the samples obtained by N<sub>2</sub> isotherms are summarized in Table 1. MCM-41 and amine-MCM-41 show high surface areas and pore volumes, which are typical of mesoporous materials. However, a decrease in the  $S_{\text{BET}}$  and  $D_{\text{B|H}}$  average pore diameter is observed with functionalization in imine-MCM-41 and Zr-imine-MCM-41. This result can be easily interpreted because of the presence of pendant functional groups on the surface that partially block the adsorption of nitrogen molecules. Such a significant decrease of textural properties of porous materials on grafting has already been reported [56,57]. A wall thickness of MCM-41, 2.14 Å, was calculated by the following equation [54]:

Wall thickness = 
$$a_0 - D_{B|H}$$
 (2)

FT-IR spectroscopy was employed to detect the presence of the functional binding groups in the amine-functionalized MCM-41 material, the imine analog, and the Zr(IV)-imine-MCM-41 catalyst together with the recovered catalysts after oxidation of sulfides and the Knoevenagel condensation reaction (Fig. 3). The vibration signals at ~1040 and 800 cm<sup>-1</sup> are typical Si–O–Si bands attributed to the asymmetric and symmetric stretching, respectively [58,59]. The presence of the peak close to 1630 cm<sup>-1</sup>, mainly from the NH<sub>2</sub> symmetric bending vibration, indicates the successful grafting of the or-



**Fig. 3.** FT-IR spectra of (1) amine-MCM-41, (2) imine-MCM-41, (3) Zr(IV)-MCM-41, (4) Zr(IV)-MCM-41 after oxidation reaction, and (5) Zr(IV)-MCM-41 after Knoevenagel reaction.

100

95

ganic amine onto the surface [60,61]. The absorbance of the C–N stretching vibration is normally observed around 1000–1300 cm<sup>-1</sup>. However, this peak cannot be resolved because of its overlap with the absorbance of the Si–O–Si stretch in the 970–1350 cm<sup>-1</sup>. A band residing at 1640 cm<sup>-1</sup> (MCM-41) could be assigned to the C=N bond of imine in the Schiff base mesoporous silica. After the complex preparation, FT-IR spectroscopy displays an imine bond shift to 1616 cm<sup>-1</sup>, confirming complex formation. The spectrum of the recovered Zr(IV)-imine-MCM-41 shows that the catalyst is stable during the reaction (Fig. 3(d) and (e)).

Based on inductively coupled plasma atomic emission spectroscopy (ICP-AES), the concentration of Zr(IV) in the complex Schiff base MCM-41 catalyst was 0.318 mmol/g. To investigate leaching of the Zr species, a leaching experiment was performed via oxidation of methylphenyl sulfide. In a representative test, the solid catalyst Zr(IV)-salen-MCM-41 was recovered by filtration, and the filtrate was analyzed for Zr(IV) content using ICP-AES. The concentration of Zr(IV) obtained was determined to be 0.275 mmol/g, resulting in a decrease of 13%.

EDX of the Zr(IV)-salen-MCM-41 showed that the mass percents of C, N, Si, O, and Zr are 12.59%, 1.88%, 38.47%, 42.96%, and 4.10%, respectively (Fig. 4). These peaks suggest successful complexation of zirconium with the Schiff base of MCM-41 mesoporous support.

The TGA curves of the synthesized materials are presented in Fig. 5. The thermogram of the calcined MCM-41 shows three individual steps of weight loss. The first distinct weight loss is 1.76% in the region of 25-120 °C associated with desorption of water. Thereafter, a second (120-600 °C) weight loss of 3.52% is observed, which is likely to be attributed to the decomposition of trace amounts of the residual template. The final weight loss (600-800 °C) of 1.32% results from water loss via further condensation of silanol groups. The thermogram of the amine-functionalized MCM-41 material shows a gradual weight loss up to 800 °C. The TGA curve of amine-MCM-41 shows four distinct weight loss regions (25-120, 120-300, 300-600, and 600-800 °C). The weight loss at the lower temperature, attributed to the desorption of physisorbed water held in the pores, is 7.18%. The weight losses in the second and third steps (13.85%) are associated with oxidative decomposition of the organic functional groups. At the higher temperature, the weight loss (1.37%) relates to the dehydroxylation of the sili-





Fig. 5. TGA curves of the synthesized materials.

800

cate networks. On the basis of elemental analysis, the amount of loaded functional amine groups was calculated to be 0.465 mmol/g of MCM-41. The TGA curve of the imine-MCM-41 material shows four steps of weight loss (25-120, 120-300, 300-600, and 600-800 °C). A weight loss of 2.16% is observed in the first step. Upon increasing the temperature, a weight loss equal to 19.87% for the second and third steps is observed. Water loss from additional condensation of the silanol groups finally results in the fourth step recording a weight loss of 1.61%. Hence, the amount of loaded imine as a functional group was calculated to be 0.501 mmol/g of MCM-41. Finally, The TGA curve of the Zr-imine-MCM-41 material shows four individual steps of weight loss (25-120, 120-280, 280-700, and 700–800 °C). A weight loss of 3.05% relates to the first step and a weight loss equal to 20.85% corresponds to the second and third steps. Finally, a 0.89% weight loss results at the higher-temperature fourth step.

#### 3.2. Catalytic activity

#### 3.2.1. Selective oxidation of sulfides to sulfoxides

In the present work various sulfides were oxidized to sulfoxides by  $H_2O_2$  (30%) in the presence of Zr(IV)-salen-MCM-41 as a catalyst under solvent-free conditions. The amount of the catalyst is a major factor affecting the oxidation yield. Thus, after screening catalyst loading levels (Table 2), the results show that 0.03 g of Zr(IV)-salen-MCM-41 gave the optimal loading of catalyst (Table 2, entry 6).

#### Table 2

Optimization of Zr(IV)-salen-MCM-41 as a catalyst for selective oxidation of methyl phenyl sulfide under solvent-free conditions.

Entry	Catalyst (g)	Time (h)	Yield <sup>a</sup> (%)
1	_	5	60
2	0.01	2	70
3	0.015	2	78
4	0.02	2	80
5	0.025	2	85
6	0.03	2	93 b
7	0.04	3.5	75

Reaction conditions: methyl phenyl sulfide 1 mmol,  $\rm H_2O_2$  0.4 mL.  $^a$  Purification by preparative TLC.  $^b$  Isolated yield.

Table 3
Oxidation of methyl phenyl sulfide under varying solvents.

Entry	Solvent	Yield <sup>a</sup> (%)
1	Acetone	15
2	Dichloromethane	20
3	H <sub>2</sub> O	35
4	<i>n</i> -Hexane	40
5	Ethanol	70
6	Acetonitrile	70
7	Solvent-free	93 <sup>b</sup>

Reaction conditions: methylphenyl sulfide 1 mmol,  $H_2O_2$  0.4 mL, Zr(IV)-salen-MCM-41 0.03 g, 35 °C.

<sup>a</sup> Purification by preparative TLC. <sup>b</sup> Isolated yield.

Furthermore, during the optimization of the reaction conditions in choosing an appropriate solvent, the methylphenyl sulfide was subjected to oxidation by  $H_2O_2$  in the presence of the synthesized catalyst in varying solvents. As is evident from Table 3, the optimum condition is under solvent-free conditions, which was then applied throughout the remainder of this investigation.

According to the obtained results, the optimized reaction conditions were selected to determine the scope of the functionalized MCM-41 catalyzed by the oxidation reaction. In this light a wide range of aliphatic and aromatic sulfides were subjected to oxidation to their corresponding sulfoxides in the presence of 0.03 g of Zr(IV)-salen-MCM-41. The results are summarized in Table 4.

As shown in Table 4 in all cases, the reaction proceeded effectively to give the corresponding sulfoxides in satisfactory yields. In this report, aromatic and aliphatic sulfides oxidize successfully in the presence of Zr(IV)-salen-MCM-41 as a catalyst. To investigate the reaction mechanism, the oxidation reaction of methylphenyl sulfide by H<sub>2</sub>O<sub>2</sub> in the presence of the Schiff base of MCM-41 and without interference of Zr(IV) was examined (Table 4, entry 2). The reaction did not proceed to completion and therefore the presence of the metal is obviously necessary. In another study, the reaction of methylphenyl sulfide was performed in the presence of the Zr(IV)-salen complex. The over-oxidation to sulfone occurred at the beginning of the reaction (Table 4, entry 3). Additionally, a catalyst was synthesized on the surface of a non-porous silica. After catalyst preparation, the catalytic properties were examined in the oxidation of methyl phenyl sulfide under the same conditions but in the presence of the new catalyst. The progress of the reaction was monitored by TLC. The reaction failed to complete after 120 min and furthermore, sulfone was formed. The yield of methylphenyl sulfoxide was 51% (Table 4, entry 4). Interestingly, this reaction, which performed in the presence of modified MCM-41 (Table 4, entry 1) at the same time on stream (120 min), gave a yield of 93%. Therefore a significant differ-

#### Table 4

Oxidation of sulfides to sulfoxides with  $H_2O_2$  catalyzed by Zr(IV)-salen-MCM-41 under solvent-free conditions.

R <sub>1</sub> ∕ <sup>S</sup> ∖R <sub>2</sub> 1a−i	$\frac{\text{Cat. (0.03 g), H}_2\text{O}_2 (0.4 \text{ mL})}{35 \text{ °C, solvent-free}}$	$\begin{array}{c} 0\\ \\ R_1 \\ \\ \mathbf{S}\\ \mathbf{R}_2 \\ \mathbf{2a-i} \end{array}$	R <sub>1</sub> , R <sub>2</sub> =	alkyl or aryl
Entry	Substrate	Product	Time (min)	Isolated yield (%)
1	SS_	2a	120	93
2	S S	2a	240 a	60 <sup>b</sup>
3	s_	2a	135	63 <sup>b,c</sup>
4	s_	2a	120	51 <sup>b,d</sup>
5	$\langle s \rangle$	2b	30	89
6	s s	2c	20	99
7	<sup>™</sup> s <sup>™</sup> s	2d	45	86
8	s	2e	10	77
9	$\sim$	2f	40	98
10	$\overline{S}$	2g	30	95
11	$\sim s$	2h	160	90
12	∕ <sup>s</sup> ∕OH	2j	10	98

Reaction condition: sulfide 1 mmol,  $H_2O_2$  0.4 mL, Zr(IV)-salen-MCM-41 0.03 g, 35 °C. <sup>a</sup> Blank run using Schiff base-MCM-41 as the catalyst without Zr. <sup>b</sup>Purification by preparative TLC. <sup>c</sup> Zr(IV)-salen was used as a catalyst. <sup>d</sup> Zr(IV)-salen-silica was used as a catalyst.

ence in yields is observed.

A plausible oxidation reaction mechanism is shown in Scheme 2 [62]. The role of Zr(IV) in the modified MCM-41 catalyst is to form the active oxidant-sulfide complex. Finally, transfer of oxygen to sulfur leads to the formation of the sulfoxide.

#### 3.2.2. Knoevenagel condensation reaction

First, to optimize the reaction conditions, the reaction of 2-nitrobenzaldehyde (1 mmol) and malononitrile (2 mmol) in the presence of varying loadings of catalyst was selected as a model reaction. The results are summarized in Table 5. As shown, a higher yield and shorter reaction time were obtained using 0.05 g of Zr(IV)-salen-MCM-41. No improvement in the reaction efficiency was observed upon increasing the Zr(IV)-salen-MCM-41 loading to 0.08 g.

In a separate study, the condensation of 2-nitrobenzaldehyde and malononitrile in the presence of Zr(IV)-salen-MCM-



Scheme 2. Proposed mechanism for the oxidation of sulfides to sulfoxides.

#### Table 5

Optimization of the Zr(IV)-salen-MCM-41 catalyst for the synthesis of 2-(2-nitro-benzylidene)-malononitrile in water at 35 °C.

Entry	Catalyst (g)	Time (min)	Isolated yield (%)
1	_	200	98
2	0.03	50	88
3	0.05	30	99
4	0.08	15	91

Reaction conditions: 2-nitrobenzaldehyde 1 mmol, malononitrile 2 mmol, H2O 3 mL, 35 °C.

41 was examined under varying solvents at 35 °C. As Table 6 indicates, the optimum results were obtained when the reaction was performed in water.

To assess the efficiency and scope of the functionalized mesoporous silica catalyst in the preparation of arylidene malononitriles and arylidene ethylcyanoacrylate, the condensation of various aldehydes with malononitrile and ethyl cy-

#### Table 6

Knoevenagel condensation reaction of 2-nitrobenzaldehyde and malononitrile under varying solvents.

Solvent	Time (min)	Isolated yield (%)
Solvent-free	180	88
H <sub>2</sub> O	30	99
Ethanol	150	83
H <sub>2</sub> O/PEG (1:1)	40	86
_		

Reaction conditions: 2-nitrobenzaldehyde 1 mmol, malononitrile 2 mmol, solvent 3 mL, 35 °C.

anoacetate was examined in the presence of Zr(IV)-salen-MCM-41 in water at 35 °C. The corresponding results are presented in Table 7. It was observed that the desired products were produced in excellent yields (90%–99%) and the Zr(IV)-salen-MCM-41 is a highly efficient, general and mild modified mesoporous catalyst for the Knoevenagel condensation. Malononitrile was more reactive than ethyl cyanoacetate.

#### Table 7

Knoevenagel condensation reaction of active methylene compounds with functionalized aromatic aldehydes.

		CHO +	$\langle CN - Cat. (0.05) \rangle$	g) →	←CN + H <sub>2</sub> O	
		R \/ X =	$X H_2O, 35$ CN, COOEt	3a-n		
Entry	Aldehyde	Х	Product	Time (min)	Isolated vield (%)	M.P. a (°C)
	CHO	CN	3a	60	96	70–75 (83 [63])
4		CN	3a	130	45 b	71-75 (83 [63])
1		CN	3a	120	60 c	73-76 (83 [63])
	CHO	COOEt	3b	330	98	47-50 (52 [63])
		CN	30	60	95	156-160 (164 [63])
2		COOEt	3d	300	99	83-87 (87 [63])
	CI CHO					
		CN	3e	70	97	156–158 (153–156 [63])
3		COOEt	3f	400	99	88-94
	 Br CHO ↓					
4		CN	3g	80	97	132–134 (132–133 [64])
	Me	COOEt	3h	360	99	87–92 (88–91 [64])
	CHO L	CN	3i	5	95	150-153
5		COOEt	3i	5	99	79-84
	CHOOH		,			
6		CN	3k	35	99	100–103 (104–105 [63])
0	NO <sub>2</sub>	COOEt	31	130	99	121–126 (128–132 [63])
	$\downarrow$ NO <sub>2</sub>	CN	3m	30	99	136-140 (141-142 [63])
7		COOEt	3n	90	98	89–94 (96 [63])
	СНО					
8		CN	30	250	96	107–110 (115 [63])
	OMe CHO					
9		CN	3p	150	99	127-132
	OEt	-	- 1			

Reaction conditions: aldehydes 1 mmol, malononitrile or ethyl cyanoacetate 2 mmol, Zr(IV)-salen-MCM-41 0.05 g, water 3 mL, 35 °C. <sup>a</sup> The data in parentheses are reported in the literature. <sup>b</sup> Zr(IV)-salen was used as a catalyst. <sup>c</sup> Zr(IV)-salen-silica was used as a catalyst. Additionally, to show the important role of MCM-41 as a support, Zr(IV)-salen was prepared without any support and immobilized on non-porous silica. The catalytic activity of these prepared catalysts was tested in the synthesis of benzylidene malononitrile (Table 7, entry 1). As mentioned, in the presence of Zr(IV)-salen, a yield of only 45% was attained, whereas in the presence of Zr(IV)-salen supported on non-porous silica the product yield increased to 60% even with a shorter reaction time. These results show that MCM-41, as a mesoporous compound that offers inherent textural properties such as high surface area and large pore volume, has great potential as a support for the Knoevenagel condensation reaction.

For any heterogeneous system, an additional important factor is to determine the recycling and reusability properties. The experimental design further encompassed the reusability of Zr(IV)-salen-MCM-41 for the oxidation of sulfides and the Knoevenagel condensation reaction (Table 8). In both cases, the catalyst could be easily separated and recovered by simple filtration. The recovered catalyst, after washing with CH<sub>2</sub>Cl<sub>2</sub> and H<sub>2</sub>O followed by drying, was used in a subsequent run. A minimal decrease in activity was observed. As expected, the reactions proceeded with similar yields to the first run.

#### 4. Conclusions

Zr(IV)-salen-MCM-41 was successfully synthesized and efficiently used as a solid acid catalyst for the selective oxidation of sulfides to sulfoxides and synthesis of arylidene malononitriles and arylidene ethylcyanoacrylate via the Knoevenagel condensation reaction. Notably, this functionalized MCM-41 can be recycled several times to obtain similar product yields. This work offers several advantages including clean and mild reaction conditions, use of green solvent or solvent-free conditions implemented across a wide range of substrates, operational simplicity and a facile work-up procedure.

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#### Table 8

Reusability of Zr(IV)-salene-MCM-41 in the sulfide oxidation and Knoevenagel condensation.

	Isolated yield (%)			
Run	Tetrahydothiophen	2-(3-Nitro-benzylidene)-		
	oxide <sup>a</sup>	malononitrile <sup>b</sup>		
1	89	99		
2	90	98		
3	88	97		
4	83	95		

 $^a$  Reaction conditions: tetrahydrothiophene 1 mmol,  $H_2O_2$  0.4 mL, catalyst 0.03 g, 30 min, 35 °C, solvent-free.

 $^{\rm b}$  Reaction conditions: 3-nitrobenzaldehyde 1 mmol, malononitrile 2 mmol, catalyst 0.05 g, 35 min, water 3 mL, 35 °C.

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#### Graphical Abstract

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## Efficient preparation of Zr(IV)-salen grafted mesoporous MCM-41 catalyst for chemoselective oxidation of sulfides to sulfoxides and Knoevenagel condensation reactions

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Zirconium-imine-MCM-41 catalyst was prepared by reaction of NH<sub>2</sub>-MCM-41 with salicylaldehyde to afford the Schiff base ligands. Then zirconyl chloride octahydate was added to Schiff base ligands for complex formation. This Zr(IV)-Schiff base mesoporous material can be used as a solid acid catalyst for the selective oxidation of sulfides to sulfoxides and Knoveonagel condensation reaction of aldehydes.



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