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# Anchorage of a ruthenium complex into modified MOF: synergistic effects for selective oxidation of aromatic and heteroaromatic compounds<sup>†</sup>

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The structure of IRMOF-3 was modified with pyridine-2-aldehyde and then the Schiff base moieties were used to anchor ruthenium complex to this metal–organic framework. The prepared catalyst was characterized by X-ray powder diffraction (XRD), diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and FTIR methods. The results show that the prepared catalyst acquires a high potential for selective oxidation of aromatic and heteroaromatic compounds under mild conditions and easy workups.

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#### 1. Introduction

MOFs possess unique properties among the various classes of microporous and mesoporous materials generating interests for many applications. MOFs are remarkable for applications in gas adsorption,1 separations,2 and catalysis,3,4 mostly because of their chemical tunability, high porosities, and adequate thermal stability.<sup>5</sup> In fact MOFs bridge the gap between zeolites and mesoporous materials. MOF pore systems range from ultramicropore to mesopore. Unique features of MOFs also include exceptionally high porosities, well-defined crystalline structures, designable channel surface functionalities, framework flexibility, and flexible dynamic behavior in response to guest molecules. The broad choice of structure that facilitates pore size tunability would be a great opportunity for the design of MOFs with pore openings suitable for generating size and shape selectivity. However, MOFs still have several issues to be solved. Thermal, hydrothermal and chemical stability are among the issues. Also, high material costs due to the use of organic linkers that are not commercially available from industry are concerned. This principle was also used in the covalent functionalization of various MOFs by carrying out organic reactions directly on MOF crystals. Catalytic oxidation is widely used in the manufacture of bulk and fine chemicals from organic hydrocarbons in liquid phase as well as gas phase.6-8 Liquid phase oxidations generally employ soluble metal salts or complexes in combination with oxidants such as O<sub>2</sub> (or air), H<sub>2</sub>O<sub>2</sub>, or organic hydroperoxides (TBHP). But, heterogeneous solid catalysts have also been given some attention in liquid

phase oxidations since they have advantages such as facile recovery and recycling, and amenability to continuous operation as compared to their homogeneous counterparts.7 The MOF encapsulation approach invites comparison to earlier studies of oxidative catalysis by zeolite-encapsulated Fe(porphyrin)9,10 as well as Mn(porphyrin) systems.11,12 The rational design of perfect nanoporous catalysts that have a resemblance to redox enzymes could be a hope in the field of oxidation catalysis. Direct oxidation of arenes is an easy and effective method, and much research have been carried out to develop practical methods which would be applicable to various arenes.13,14 The common oxidation of arenes requires a large excess of metal oxidant such as chromium(vi) oxide. Since the metal residues are environmentally undesirable and often cause problems during reaction and work-up, improvement of selective arene oxidations requiring only a catalytic amount of metal reagent in combination with an appropriate stoichiometric oxidant is a great challenge. Direct oxidation to diones has been reported in low yields by the oxidation with highly toxic osmium tetroxide.15 From an economical point of view, sodium periodate (NaIO<sub>4</sub>) is inexpensive, readily available and generally in this type of oxidation preferred to other. Although NaIO<sub>4</sub> is not an atom efficient and environmentally benign oxidant because it gives stoichiometric amounts of inorganic waste, however it use for oxidation of stable cancerous polyaromatic arenes is unavoidable. In the previously reported methods ruthenium oxide species play a key role for this type of oxidation.<sup>16-21</sup> To overcome the prolonged reported reaction times we oxidized various arenes and heteroaromatic compounds by using ultrasonic irradiation. The results were surprising, since previous works with Ru-catalyzed oxidations of arenes had resulted in either dicarboxylic acids, tetracarboxylic acids or dioles.<sup>22</sup> The advantage of ultrasound is forming acoustic cavitations in liquids, resulting in the initiation or enhancement of the

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chemical activity in the solution. Moreover, MOFs appear to be one of the excellent candidates as oxidative catalysis due to their frameworks which contain a larger content of reducible metal ions than zeolite frameworks.23-27 Here we show that a wellknown MOF material, can be subjected to a sequence of chemical reactions suitable for complexation of ruthenium. IRMOF-3 represents a good model for a post-synthetic covalent modification study. Current research includes heterogenization of homogeneous catalysts, through covalent attachment to inorganic-organic matrices such as IRMOF-3 with mutual advantages of both homogenous and heterogeneous catalysis. Our synthesized catalyst exhibits catalytic activity as a reusable and green catalyst in oxidation of arenes and several heteroaromatic compounds. It also could be used for desulfurization of gas oil reactions containing heteroaromatic impurities. With further exploration of this system, we developed a new Rucontaining catalyst, IRMOF-3-PI-Ru, exploiting post-synthesis modification strategy of MOF.

#### 2. Experimental

#### 2.1. Materials and apparatus

2.1.1. Instrumentation. Ultrasonication was performed in a TECNO-GAZ Tecna 3 ultrasonic cleaner with a frequency of 50/ 60 Hz and a normal power of 250 W. The reaction flask was located in the water bath of the ultrasonic cleaner, and the temperature of the water bath was controlled by a current of water at room temperature. IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer. XRD measurements were performed on a Philips PW1840 diffractometer with Cu-Ka radiation (1.5418 Å), scan rate  $0.1^{\circ} 2\theta \text{ s}^{-1}$  and within a range of  $2\theta$  of 4–60°. Scanning electronmicrographs were taken on a LEO 1430 VP instrument. The metal contents were analyzed using inductively coupled plasma (ICP; Labtam 8440 plasma lab). <sup>1</sup>H NMR spectra were obtained on a BrukerDRX-500 Avance spectrometer and13 C NMR spectra were obtained on a BrukerDRX-125 Avance spectrometer. Chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR spectra were expressed in ppm downfield from tetramethylsilane. Melting points were measured on a Büchi Melting Point B-540 instrument and are uncorrected. Elemental analyses were made by a Carlo-Erba EA1110 CNNO-S analyzer and agreed with the calculated values.

**2.1.2.** Materials. All materials were purchased from Merck and Sigma-Aldrich and used without further purification.  $Ru_3(CO)_{12}$  (99%) was purchased from Acros.

2.1.3. Preparation of IRMOF-3. IRMOF-3,  $Zn_4O(C_8H_5NO_4)_3$  was synthesized according to the literature with slight modifications.<sup>28</sup> 0.9683 g zinc nitrate tetrahydrate and 0.2293 g of 2-amino-1,4-benzenedicarbocyclic acid were added to 30 mL of solvent *N'*,*N*-dimethyl formamide (DMF). The resulting suspension was stirred for 3 h at room temperature then heated under autogeneous pressure at 105 °C for 24 h in a Teflon-lined autoclave. After decanting the hot mother liquor and rinsing with DMF, the product was immersed in CHCl<sub>3</sub> for 3 days, during which the activation solvent was decanted and freshly replenished three times. The solvent was removed under vacuum at room temperature, yielding pale yellow cube-shaped crystals (yield over 90% based on 2-aminoterephthalic acid). To

increase the yield of products and reduction of wastes that formed during the preparation of IRMOF-3, in addition to the stirring and rising temperature of the reaction, the time was also increased from 24 h to 60 h. However increasing a time of reaction was only improveds the better crystal growth *e.g.* for IRMOF-3 after 36, 48 and 60 h, no improve in the yield of product was observed. Elemental analysis was performed on samples outgassed under vacuum (120 °C, 12 h).  $Zn_4O(ATA)_3$ : (% calcd/found), C 35.4/35.5, H 1.86/1.9, N 5.16/5.21, FT-IR: 3369 (br), 1620 (sh), 1568 (s), 1419 (s), 1385 (s), 1258 (m), 1155 (w), 1064 (w), 948 (w), 898 (w), 836 (w), 768 (m), 582 (w), 517 (w).

**2.1.4.** Synthesis of IRMOF-3-PI,  $[Zn_4O(ATA)_{3-x} (PITA)_x]$ (PITA = 2-pyridyl-imine terephthalate). The isoreticular functionalized IRMOF-3-PI was synthesized according to the reported procedure.<sup>29</sup> (0.428 g) of pyridine-2-aldehyde was first dissolved in 15 mL of dry CH<sub>3</sub>CN. To this solution, freshly prepared desolvated IRMOF-3 (1 g) was immersed, and it was then allowed to stand for 5 days under an inert (nitrogen) atmosphere. After 5 days, the resulting pale yellow colored solid was collected by centrifugation, washed with dry CH<sub>3</sub>CN, and dried *in vacuo* at 120 °C. Elemental analysis was performed on samples outgassed under vacuum (120 °C, 12 h). Anal. calcd for Zn<sub>4</sub>O(ATA)<sub>2.79</sub> (PITA)<sub>0.21</sub>: (% calc/found), C 37.20/37.10, H 1.93/1.92, N 5.50/5.45.

2.1.5. Synthesis of IRMOF-3-PI-Ru, [Zn<sub>4</sub>O(ATA)<sub>3-x</sub>(PITA- $Ru(CO)_4$ ]. To obtain isoreticular metalation, a mixture of Ru<sub>3</sub>(CO)<sub>12</sub> (0.3 mmol, 0.053 g) and 1 g of IRMOF-3-PI in anhydrous CH<sub>2</sub>Cl<sub>2</sub> was stirred under reflux condition at 40 °C for the time specified. Where upon, the yellow crystalline material became brown within several minutes. After 12 h, the brownish yellow-colored material was washed three times with 10 mL portions of CH<sub>2</sub>Cl<sub>2</sub>. The crystals were then immersed in dry CH<sub>2</sub>Cl<sub>2</sub>, and the solvent was refreshed every 24 h for 3 days to yield IRMOF-3-PI-Ru. The solid phase was washed repeatedly through Soxhlet extraction with ethanol and acetone and dried at 60 °C overnight, leading to ruthenium anchored IRMOF-3-PI as a brownish powder. The amount of ruthenium metal in catalyst was found to be 2.62 w% based on ICP analysis. Elemental analysis was performed on samples outgassed under vacuum (120 °C, 12 h). Anal. calcd for Zn<sub>4</sub>O(ATA)<sub>2.79</sub> (PITA-Ru(CO)<sub>4</sub>)<sub>0.21</sub> (% calcd/found), C 35.5/35.4, H 1.86/1.90, N 5.28/ 5.2. The amount of Ru in the final solid was determined by the atomic absorption spectrometer: calcd: Ru 2.56%; found, Ru 2.6% (2.4 ×  $10^{-2}$  mol%).

**2.1.6.** Synthesis of MOF-5. MOF-5 were prepared following the procedure reported previously.<sup>30–32</sup> FTIR spectra of MOF-5, two sharp peaks were obtained at 1580 and 1373 cm<sup>-1</sup>. Several small peaks were seen in the range of 1225 to 950 cm<sup>-1</sup>, 900 to 670 and 500 cm<sup>-1</sup>. A broad peak at 3395 cm<sup>-1</sup> (ESI S1†). Diffraction peaks at around  $2\theta = 6.9^{\circ}$  and  $9.87^{\circ}$  are readily recognized from the XRD pattern (ESI S2†). The observed diffraction peaks agree with the MOF-5.<sup>30</sup>

**2.1.7.** Synthesis of MIL-101. MIL-101 was synthesized according to reported procedure.<sup>33</sup> The sample was washing several times, drying at 100 °C. FTIR spectra and the XRD patterns of MIL-101 are plotted in (ESI S3 and S4†). The main diffraction peaks were at  $2\theta = 3.25, 5.10, 8.41, 9.02, 16.49, 17.40$ ,

and relative diffraction intensities of the prepared sample was found to be the same as the standard data for MIL-101.<sup>19,34</sup>

# 2.2. General procedure for oxidation of aromatic and heteroaromatic compounds under ultrasonic irradiation conditions

2.2.1. Ultrasonic assisted IRMOF-3-PI-Ru catalyzed oxidation of aromatic (arenes) and heteroaromatic (benzothiophene) compounds. A 20 mL flask was charged with CH<sub>2</sub>Cl<sub>2</sub> (4 mL), H<sub>2</sub>O (5 mL), CH<sub>3</sub>CN (4 mL), pyrene (202.25 mg, 1 mmol) and NaIO<sub>4</sub> (1 g, 4.68 mmol, ~4 eq.). IRMOF-3-PI-Ru (10 mg) was added into the flask and the dark brown suspension was irradiated at room temperature for 50 min. At first, the mixture of dichloromethane and water was found inactive when tested as a catalyst for the oxidative cleavage of pyrene in the CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O/IO<sub>4</sub><sup>-</sup> system. However, when CH<sub>3</sub>CN was added to this inactive system, it rapidly lead to pyrene-4,5-dione formation. Addition of water, on the other hand is unavoidable for it is the only solvent that dissolves sodium metaperiodate. It is also well known that addition of CH<sub>3</sub>CN to reaction mixtures in which catalysis had ceased (due to precipitation of the ruthenium catalyst in the course of an oxidation) results in dissolution of the precipitate and restoration of full catalytic activity. It should be noted that CH<sub>3</sub>CN and water alone are not effective; the third solvent component, CH<sub>2</sub>Cl<sub>2</sub>, plays an important role.<sup>21</sup> The reaction mixture was poured into 50 mL of water and the organic phase was separated. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  10 mL). The CH\_2Cl\_2 extracts were combined with the organic phase, washed with brine  $(3 \times 10 \text{ mL})$  and dried over anhydrous sodium sulfate to give a dark orange solution. The solution was concentrated under reduced pressure and the mixture was purified by preparative TLC (n-hexane : EtOAc, 10:3), pyrene-4,5-dione as main product was obtained at room temperature with a 74% yield. A similar procedure was applicable for the other reported products listed in Table 3.

2.2.2. General procedure for oxidation of solid sulfides to their corresponding sulfoxides and sulfones under ultrasonic irradiation conditions. To a mixture of sulfide (1 mmol) and 30% aq.  $H_2O_2$  (1 mmol) in EtOH (4 mL), catalyst (10 mg) was added and the mixture was irradiated in the presence of ultrasound at room temperature for the time specified. Completion of the reaction was indicated by TLC (*n*-hexane/EtOAc, 10 : 4). After completion, the reaction mixture was cooled to 5 °C. The catalyst precipitated as solid at the bottom layer and was easily separated by filtration. The product was at the upper liquid layer. The organic layer decanted and the solution was concentrated under reduced pressure to afford the essentially crud products. Further purification was achieved by short column chromatography on silica gel with *n*-hexane : EtOAc as eluent.

#### 3. Results and discussion

#### 3.1. Catalyst synthesis and characterization

Following the procedure reported previously<sup>28</sup> and were activated by guest exchange with  $CHCl_3$ ,<sup>30</sup> followed by vacuum drying at 120 °C prior to further treatment.



**Scheme 1** Procedure for obtaining MOFs containing the ruthenium Schiff base complex.

The free  $NH_2$  groups were thus modified by covalent modification *via* a simple condensation reaction, producing a 2-pyridylimine (R-N=C-C<sub>5</sub>H<sub>4</sub>N) moiety, useful as a bidentate ligand.<sup>29,35-37</sup> Pyridylimine formation activated the framework toward metal sequestering, demonstrated by anchoring Ru to the wall of IRMOF-3. The preparative procedure is summarized in Scheme 1.

The FTIR spectra of IRMOF-3, IRMOF-3-PI, and IRMOF-3-PI-Ru were measured in the KBr pellet (Fig. 1).

The observed peaks for IRMOF-3 are confirmed by comparing with FTIR vibration bands in literatures.<sup>28</sup> In the FTIR spectrum of IRMOF-3-PI appearance of a new band at 1655 cm<sup>-1</sup> ( $\nu_{C=N}$ ), that were absent in the case of IRMOF-3, clearly indicates that the IRMOF-3 framework has been organically modified as shown in Fig. 1.

In IRMOF-3-PI-Ru, the vibration bands for both the azomethine group and the C=N moiety of the pyridine ring shifted to the lower frequency range and are not well-resolved due to overlapping with the band that appeared for the bending vibration mode of the -NH<sub>2</sub> group. Upon complexation of Ru with the ligand, the C=N stretching frequency is shifted to lower frequency ( $\nu_{C=N} = 1650 \text{ cm}^{-1}$ ) indicating formation of Ru complex (Fig. 1). In addition, a broad band at 1968 cm<sup>-1</sup> ( $\nu_{C=O}$ )



Fig. 1 FTIR spectra of IRMOF-3, IRMOF-3-PI and IRMOF-3-PI-Ru.

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Fig. 2 X-ray diffraction patterns of IRMOF-3, IRMOF-3-PI and IRMOF-3-PI-Ru.

which represent the stretching vibrations of carbon monoxide groups (CO). This is related to the decomposition of this metal cluster with conventional heating to afford  $Ru(CO)_4$  and subsequently coordination to the imine nitrogen (Scheme 1).

Powder X-ray diffraction patterns of IRMOF-3, IRMOF-3-PI, and catalyst IRMOF-3-PI-Ru were recorded (Fig. 2). The resulting XRD pattern and related indexes (*hkl*) of the crystal IRMOF-3



Fig. 3 Diffuse reflectance spectroscopy (DRS) of IRMOF-3-PI and. IRMOF-3-PI-Ru.

showed the characteristic peak at  $2\theta = 6.8^{\circ}$  (200), 9.6° (220) and 13.7° (400). However, another peak appeared at 15.35° (420), 19.39° and 24.62°. The corresponding *hkl* indices of the most important diffraction peaks are indicated. The XRD pattern of IRMOF-3 corresponds well with the literature data, indicating that the desired material is obtained.<sup>38-40</sup> Comparison of the X-ray powder diffraction patterns of IRMOF-3, IRMOF-3-PI, and IRMOF-3-PI-Ru showed that peak patterns of IRMOF-3 were not altered. This clearly shows that the framework structure of IRMOF-3 remained intact upon organic functionalization as well as metal complex formation in IRMOF-3 (Fig. 2).

Diffuse Reflectance Spectroscopy (DRS) of the catalyst IRMOF-3-PI-Ru was performed on the solid catalyst (Fig. 3). The DRS spectrum featured a strong band at 362 nm, which can be ascribed to the charge transfer transition arising from  $\pi$ -electron interactions between the metal and ligand. A comparison between spectrums of IRMOF-3-PI and IRMOF-3-PI-Ru, shows that the molecule remains unchanged during the process of anchoring (Fig. 3).

The SEM images (Fig. 4a and b), shows that the IRMOF-3 and IRMOF-3-PI-Ru have a highly crystalline structure, and Ru is located within the network (Fig. 4). The SEM image of IRMOF-3 indicates that the particles have cubic topological ordered with a crystal size of  $\sim$ 50–100 nm (Fig. 4a). The SEM image of the prepared catalyst is shown in Fig. 4b. The particle size according to Scherrer equation calculated from the XRD data was  $\sim$ 19 nm.



Fig. 5 Nitrogen adsorption–desorption isotherms of IRMOF-3 on the top and IRMOF-3-PI-Ru on the bottom.



Fig. 4 SEM images of (a) IRMOF-3, (b) IRMOF-3-PI-Ru and TEM image of IRMOF-3-PI-Ru (c).

Table 1 Optimization of reaction conditions for oxidation of arenes and heteroaromatic compounds<sup>a</sup>

	e 2	MOF-3-PI-Ru CH <sub>2</sub> Cl <sub>2</sub> : H <sub>2</sub> O 4 : 5 Za			), , , , , , , , , , , , , , , , , , ,	>
Entry	Catalyst (mg)	Ru content <sup><math>b</math></sup> (mg)	NaIO <sub>4</sub> /arene	Time (min)	T (°C)	Yield (%)
1	Without catalyst (0)	0.00	12/1	360	50	5
2	IRMOF-3-PI-Ru <sup><math>c</math></sup> (5)	0.12	4/1	60	r.t	65
3	IRMOF-3-PI-Ru (10)	0.24	4/1	50	r.t	74
4	IRMOF-3-PI-Ru (15)	0.36	4/1	50	r.t	74
5	IRMOF-3-PI-Ru (25)	0.60	4/1	50	r.t	75
6	IRMOF-3-PI-Ru (35)	0.84	4/1	50	r.t	76
-	1.					

<sup>a</sup> Isolated yield. <sup>b</sup> Measured by ICP. <sup>c</sup> Preliminary activation of the as-prepared IRMOF-3-PI-Ru under vacuum at 120 °C.



Scheme 2 Proposed mechanism for the oxidation of pyrene

However, the particle dimension obtained by SEM image indicated to be  $\sim$ 50–100 nm. This difference can be attributed to the aggregation of the particles (Fig. 4a and b).

TEM analyses indicate that the continuous 3D pore structure of the IRMOF-3 is robust enough to survive the PI-Ru

incorporation process and so offers an excellent matrix to support highly dispersed PI-Ru species. The places with darker contrast could be assigned to the presence of PI-Ru particles and located in the IRMOF-3 cavities (Fig. 4c).

The nitrogen adsorption-desorption isotherms of IRMOF-3 and catalyst IRMOF-3-PI-Ru are shown in Fig. 5. The nitrogen sorption study revealed that the BET surface area of IRMOF-3 was 2450 m<sup>2</sup> g<sup>-1</sup> (pore volume = 1.01 cm<sup>3</sup> g<sup>-1</sup>). IRMOF-3-PI-Ru shows the BET surface area of a value of 1374  $m^2 g^{-1}$  with pore volume of 0.77 cm<sup>3</sup> g<sup>-1</sup>. Change in surface area as well as pore volume IRMOF-3-PI-Ru was smaller than IRMOF-3. It seems space occupied by the Schiff-base moiety has not changed substantially after complex formation with ruthenium (ESI S5<sup>†</sup>).

#### 3.2. Catalytic activity studies

This catalyst is an excellent heterogeneous system for rapid oxidation of arenes and functionalized sulfides to sulfoxides and sulfones with NaIO4 under mild conditions. It is remarkable that the reaction tolerates oxidatively sensitive functional groups and the sulfur atom is selectively oxidized. The influence of different reaction parameters on the efficiency of the oxidation process was evaluated in the model reaction depicted in Table 1. Typical results for the ultrasonic-assisted IRMOF-3-PI-Ru-catalyzed oxidation of arenes: a mixture of arene (1 mmol)

Table 2 The catalytic activity tests of IRMOF-3-PI-Ru in a comparison with several homogeneous and heterogeneous prepared catalysts in the presence of ultrasonic

Entry	Catalyst (mg)	NaIO <sub>4</sub> (1a(1b)(2a))/arene	Time (min) 1a(1b)(2a)	<i>T</i> (°C) 1a(1b)(2a)	Yield <sup><i>a</i></sup> (%) 1a(1b)(2a)
1	IRMOF-3-PI- $Ru^{b}$ (10)	4(8)(4)/1	50(75)(65)	r.t(40)(r.t)	74(55)(65)
2	IRMOF-3 (10)	4(8)(4)/1	90(120)(110)	r.t(40)(r.t)	40(30)(60)
3	$RuCl_3 \cdot nH_2O(10)^c$	4(8)(4)/1	120(150)(120)	r.t(50)(r.t)	55(40)(59)
4	$Ru_3(CO)_{12}$ (10)	4(8)(4)/1	120(150)(120)	r.t(50)(r.t)	50(40)(55)
5	$MOF-5^d$ (10)	4(8)(4)/1	110(130) (120)	r.t(40)(r.t)	45(30)(55)
6	MIL-101 $^{e}$ (10)	4(8)(4)/1	120(150)(180)	r.t(40)(r.t)	40(30)(50)

<sup>a</sup> Isolated yield. <sup>b</sup> Preliminary activation of the as-prepared IRMOF-3-PI-Ru under vacuum at 120 °C. <sup>c</sup> Reported previously.<sup>22 d</sup> Activated at 120 °C and 180 °C, respectively. <sup>e</sup> Activated at 120 °C and 180 °C, respectively.

and NaIO<sub>4</sub> (1 g, 4.68 mmol, 4 eq.) in a system consisting of  $H_2O$ ,  $CH_2Cl_2$ ,  $CH_3CN$  (5, 4, 4 mL) with different catalytic amounts and of IRMOF-3-PI-Ru in a comparison with several homogeneous and heterogeneous catalysts.

Although the precise mechanism of the reaction awaits further studies, by analogy with the previous works on rutheniumcatalyzed oxidation of similar compounds<sup>22</sup> a proposed mechanistic pathway for the oxidation of pyrene is presented in Scheme 2.

K-region oxidation of pyrene has been studied extensively because of its suspected role in the carcinogenicity of fused arenes. One of the oxidation products, pyrene-4,5-dione (1a), is also important because it serves as an intermediate in the preparation of other fused-ring molecules, which are of interest

Table 3 Ultrasonic assisted IRMOF-3-PI-Ru catalyzed oxidation of arenes and heteroaromatic compounds							
				Irradiated		Non irradiated	
Entry	Substrate	Products <sup>a</sup>	$T(^{\circ}C)$	Time (min)	$\operatorname{Yield}^{b}(\%)$	Time (min)	$\operatorname{Yield}^{b}(\%)$
1			r.t(40)	50(75)	74(55)	220(270)	60(50)
2			r.t	60	65	240	65
3	3	3a C	r.t	60	80	240	80
4	4		r.t	60	80	240	85
5	5	5a CHO	r.t	60	60	360	60
6	6	6a COOH	r.t	60	80	240	80
7	7	соон 7а	r.t	60	95	240	95
8	8	Ba	r.t	60	95	240	95
9	9	9a 0' <sup>S</sup> 0	r.t	45	98	200	98
10		10a 0 <sup>5</sup> 0	r.t	45	90	220	90
11	11		r.t	45	88	240	88
12	12	12a 0 <sup>8</sup> 0	r.t	45	85	240	85

Table 4 (	Comparison of IRMOF-3-PI-Ru with	other catalysts for the selective	oxidation of sulfides in the presence of ultrasonic <sup>a</sup>
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			Sulfoxide (b) <sup><i>d</i></sup>		Sulfone (a) <sup>d</sup>	
Entry	Catalyst (mg)	$H_2O_2^{\ b}$ (TBHP) <sup>c</sup> : sulfide (mol)	Time (min)	Yield <sup>e</sup> (%)	Time (min)	Yield <sup>e</sup> (%)
1	Without catalyst (—)	12:1	360	50(75)	_	_
2	IRMOF-3-PI-Ru (5)	2(3.4):1	2(2)	96(96)	55(55)	82(80)
3	IRMOF-3-PI-Ru (10)	2(3.4):1	2(2)	96(96)	55(55)	92(92)
4	IRMOF-3-PI-Ru (15)	2(3.4):1	2(2)	96(96)	55(55)	92(92)
5	IRMOF-3 (10)	2(3.4):1	120(120)	70(60)	360(360)	70(70)
6	$\operatorname{RuCl}_{3}(10)$	2(3.4):1	15(15)	95(95)	80(80)	90(90)
7	$Ru_3(CO)_{12}$ (10)	2(3.4):1	22(25)	96(96)	80(80)	90(90)
8	MOF-5 (10)	2(3.4):1	120(120)	96(96)	360(360)	90(90)
9	MIL-101 $^{f}(10)$	2(3.4):1	150(150)	96(96)	450(450)	90(90)

<sup>*a*</sup> Reaction scale: 1-benzothiophene (1 mmol), oxidant and with catalysts (10 mg) in 3 mL solvent. <sup>*b*</sup> Using 30% aq. H<sub>2</sub>O<sub>2</sub>. <sup>*c*</sup> *tert*-Butyl hydroperoxide (TBHP) was indicated in parentheses in table. <sup>*d*</sup> See ESI S5 and ref. 41–43. <sup>*e*</sup> Isolated yield. <sup>*f*</sup> The selective oxidation of sulfides without ultrasonic conditions.<sup>44</sup>

from both a theoretical and a practical point of view. Further oxidation of pyrene-4,5-dione gives pyrene-4,5,9,10-tetraone (1b), which has been used in metal complex formation and as a monomer in step growth polymerizations.<sup>21</sup>

The model reaction was applied to the oxidation of pyrene 1. Pyrene-4,5-dione 1a was obtained at room temperature with 4 equiv. of  $NaIO_4$  in 74% yield and irradiation at 40 °C for 75 min using 8 equiv. of  $NaIO_4$  afforded pyrene-4,5,9,10-tetraone 1b in 55% yield. Treatment of chrysene 2 under the same condition to 1a gave 2a in good yield (Table 1).

The catalytic behavior of IRMOF-3-PI-Ru for the selective oxidation of pyrene 1 to pyrene-4,5-dione 1a, pyrene-4,5,9,10-tetraone 1b and chrysene 2 to chrysene-5,6-dione 2a in a comparison with several homogeneous and heterogeneous prepared catalysts was shown in Table 2.

In order to increase the yield of products various amount of catalyst were employed. It was found that the best results were obtained in the presence of 10 mg of IRMOF-3-PI-Ru larger amount of catalyst, however, had no significant effect on the yield.

According to the same conditions to the oxidation of pyrene 1, anthracene 3, phenanthrene 4, naphthalene 5, biphenyl 6, *trans*stilbene 7, 1,1-diphenyl-ethylene 8 in Table 3 gave corresponding anthracene-9,10-dione 3a, phenanthrene 9,10-dione 4a, phthalaldehyde 5a, benzoic acid 6a–7a, benzophenone 8a in good yields. The catalytic activity of the system toward heteroaromatic compounds led to the interesting results. 1-Benzothiophene (BT), dibenzothiophene (DBT), 4,6-dimethyldi-benzothiophene (4,6-DMDBT) and 4-methyldibenzothiophene (4-MDBT) gave corresponding sulfones 9a, 10a, 11a and 12a, respectively in a high yield. The results are summarized in Table 3.

Although several studies on the oxidation of sulfides by various catalysts, especially industrial catalysts, but due to highperformance MOFs are few studies in this area can be seen. So in continuation of our work on the catalytic properties of catalysts, herein, the catalytic behavior of IRMOF-3-PI-Ru and several prepared catalysts for the selective oxidation of sulfides to sulfoxides and sulfonesis reported in Table 4. The aromatic sulfides selected for these studies include; BT, DBT, 4,6-DMDBT and 4-MDBT. In order to examine the scope of this process, and to demonstrate the diversity of the IRMOF-3-PI-Ru, the optimized conditions were applied to 1-benzothiophene as shown in Table 4.

The effect of kind of catalysts on the oxidation of heteroaromatic compounds has been investigated. Six catalysts such as IRMOF-3-PI-Ru, IRMOF-3, RuCl<sub>3</sub>, Ru<sub>3</sub>(CO)<sub>12</sub>, MOF-5, MIL-101 were selected. Catalytic amounts of catalysts were irradiated in the presence of ultrasound in an open vessel at room

Table 5Study of the solvent and optimization of reaction conditions for oxidation of heterosulfides <sup>a</sup>								
Entry	Solvent	Temp (°C)	$H_2O_2$ (TBHP) : sulfide	Sulfoxide (b)		Sulfone (a)		
				Time (min)	$\operatorname{Yield}^{ab}(\%)$	Time (min)	Yield <sup>ab</sup> (%)	
1	EtOH	r.t	4(10):1	<2(2)	96(95)	55(55)	95(95)	
2	EtOH	r.t	3(5):1	<2(2)	96(95)	55(55)	92(92)	
3	EtOH	r.t	2(3.4):1	2(2)	96(96)	55(55)	92(92)	
4	EtOH	40	2(3.4):1	2(2)	96(96)	55(55)	92(92)	
5	MeOH	r.t	2(3.4):1	2(2)	96(96)	55(55)	92(92)	
6	THF	r.t	2(3.4):1	4(4)	94(94)	60(60)	90(90)	
7	Toluene	r.t	2(3.4):1	2(2)	96(96)	55(55)	92(92)	
8	$CH_3CN$	r.t	2(3.4):1	2(2)	96(96)	60(60)	92(92)	

<sup>*a*</sup> Reaction scale: 1-benzothiophene (1 mmol), oxidant and catalysts (10 mg) in 3 mL solvent. <sup>*b*</sup> Isolated yield.

temperature. The disappearance of the starting materials and appearance of target products were monitored by TLC. In order to optimize the reaction conditions, oxidation reaction of 1benzothiophene as a model compound was examined using 30% aq. H<sub>2</sub>O<sub>2</sub> (or TBHP) under various reaction conditions (Table 4). One of the main factors in the oxidative system was the amount of H<sub>2</sub>O<sub>2</sub> (or TBHP) and catalyst. Thus, it was of great interest to explore the influence of the H<sub>2</sub>O<sub>2</sub> (or TBHP) dosages on removal of sulfide. With equal molar amounts of H<sub>2</sub>O<sub>2</sub> (or TBHP) and 1 benzothiophene, the corresponding oxidize compounds 1-benzothiophene 1-oxide and 1-benzothiophene 1,1-dioxide respectively were produced with 100% selectivity. According to the results in Table 4, optimal reaction conditions were achieved at H<sub>2</sub>O<sub>2</sub> (or TBHP) dosages to sulfide 2:1 (or 3.4:1) respectively and 10 mg of IRMOF-3-PI-Ru at room temperature was used. To compare the relative reactivity of six prepared different catalysts, the oxidation of 1-benzothiophene was carried out under the same reaction conditions (Table 4, entries 3, 5-9). The data indicate that IRMOF-3-PI-Ru is considerably more efficient catalyst than others. At the end of the reaction, the catalyst was recovered by cooling the reaction mixture to 5 °C, dried in vacuum and weighed.

Solid sulfur compounds are insoluble in aqueous media, it was necessary to use a co-solvent that solubilizes these compounds in water. In this study, EtOH was used as the cosolvent since it is green and biologically less objectionable in the environment compared to other solvents. Table 5 entries 6– 8 indicate that the metal organic framework moiety plays a significant role as Phase Transfer Catalyst (PTC). A comparison between EtOH and several other solvents was shown in Table 5.

Based on the above results, the catalytic prototype can be seen in Scheme 3.

For dibenzothiophene the corresponding dibenzothiophene *S*-oxide 98% yield and dibenzothiophene *S*,*S*'-dioxide 96% yield could be obtained in excellent yield in the presence of 10 mg of IRMOF-3-PI-Ru and 2:1,  $H_2O_2$  (or 3.4:1 TBHP) : sulfide ratio with trace over-oxidation product. In case of 4,6-dimethyldibenzothiophene under the same conditions gave corresponding 4,6-dimethyldibenzothiophene *S*-oxide 96% yield and 4,6-dimethyldibenzothiophene *S*,*S*'-dioxide 95% yield respectively. Also, 4-methyldibenzo thiophene gave corresponding 4-methyldibenzothiophene *S*-oxide 95% yield and 4-methyl dibenzothiophene *S*-oxide 95% yield and 4-methyl dibenzothiophene *S*-oxide 94% yield respectively. The oxidation



Fig. 6 Reusability of IRMOF-3-PI-Ru as catalyst in oxidation of 1-benzothiophene.

reactivity decreased in the order of DBT > 4,6-DMDBT > 4-MDBT > BT. BT exhibited the lowest reactivity due to the different electron density on the sulfur atom related to the other substrate. In summary, presented catalytic findings confirm that the MOF structure has a significant impact on the catalytic properties.

The merit of the present work in comparison with recently reported protocols<sup>44–49</sup> and other industrial catalysts, this is the amounts of the catalysts used, reaction times and yields of the products, selective oxidation under mild conditions, easy workups and reasonably nontoxic nature.

The recoverability and reusability of the catalyst (IRMOF-3-PI-Ru) was examined in the oxidation reaction of 1-benzothiophene 9a. The catalyst was separated after each run, washed with MeOH and acetone, dried in an oven at 60 °C, the recovered catalyst was reused in subsequent reactions without a significant decrease in activity even after five runs (Fig. 6).

According to the methodology suggested by Sheldon *et al.*,<sup>50</sup> we performed fast catalyst filtration tests for all the elaborated catalytic systems. We filtered the catalyst, *e.g.*, IRMOF-3-PI-Ru, after 22 min (*ca.* 50% 1-benzothiophene 9a conversion) and allowed the filtrate to react further. No further substrate conversion in the filtrate was observed after removal of the



Scheme 3 The oxidation catalytic prototype of sulfides to sulfoxides and sulfones.



Fig. 7 Catalyst filtration test for the oxidation of 1-benzothiophene.

catalyst in the oxidations over IRMOF-3-PI-Ru (an example is shown in Fig. 7), indicating that the observed catalysis is truly heterogeneous. A trace amount of ruthenium (less than 1 ppm) was determined in the filtrate by ICP-AES after oxidation with  $\rm H_2O_2.^{26,51}$ 

The recovered catalyst was then subjected to X-ray powder diffraction and FTIR spectral analysis study. Comparison of X-ray diffraction patterns (see Fig. S6†) and FTIR spectra (see Fig. S7†), of the pristine compound and recovered catalyst convincingly demonstrates the structural integrity of the compound retained after the reactions.

#### 4. Conclusions

In summary, we have succeeded in designing a new heterogeneous catalyst for oxidation reactions by anchoring a Ru Schiff base moiety into microporous IRMOF-3 by a post-synthetic method. The catalyst shows high activity toward selective oxidation of arenes and heteroaromatic compounds and for oxidation of sulfides to sulfoxides and sulfones. The possibility of easy recycling of the catalyst and mild reaction conditions make the catalyst cheap and highly desirable to address the environmental concerns.

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