

Copper-complexed dipyridyl-pyridazine functionalized periodic mesoporous organosilica as heterogeneous catalyst for styrene epoxidation

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Abstract

A new heterogenous catalyst has been synthesized by immobilization of a copper complex on dipyridyl-pyridazine functionalized periodic mesoporous organosilica (dppz-vPMO). This ordered support was firstly prepared by a co-condensation reaction between vinyltriethoxysilane and 1,2-bis(trimethoxysilyl)ethane and further post-functionalized through a hetero Diels-Alder reaction with 3,6-di-2-pyridyl-1,2,4,5-tetrazine. Techniques such as XRD, N₂ isotherms, TEM, ¹³C NMR, XPS and DRIFT, among others, were employed to characterize the surface functionalized materials. These results have proven the ordered mesostructure of the materials as well as the presence of novel nitrogen-chelating heterocyclic compounds in the pore surface after the post-modification process. Additionally, it has been confirmed the successful anchoring of a copper complex on the dipyridyl-pyridazine (dppz) ligands. The resulting material was evaluated as heterogenous catalyst in the epoxidation of styrene using *tert*-butylhydroperoxide (TBHP) as oxidant. Under optimized reaction conditions, Cu@dppz-vPMO showed a high styrene conversion (86.0 %) and a remarkable selectivity to styrene oxide (41.9 %). Indeed, this catalyst provided excellent catalytic results in terms of stability, reaction rate, conversion and selectivity compared to other bipyridine-like copper catalysts.

Keywords: periodic mesoporous organosilicas; Diels-Alder reaction; dipyridyl-pyridazine; copper complex; epoxidation reactions.

1. Introduction

Epoxidation of olefins is one of the most relevant reactions in organic synthesis since the resultant epoxide products are important and versatile intermediates for the synthesis of a wide variety of fine chemicals, pharmaceuticals, agrochemicals, and perfumes, among others[1–4]. While traditional methods for the synthesis of epoxides are characterized by using stoichiometric amounts of harmful oxidants (peracids) and generate enormous wastes[5–7], the recent synthetic methodologies in this field are focused to overcome them. Thus, the use of safer oxidizing agents, such as tert-butyl hydroperoxide (TBHP), molecular oxygen or hydrogen peroxide in the styrene epoxidation opens an economic and environmental alternative. However, their characteristic low reactivity and selectivity in this type of reaction when they are used alone has led to the use of such oxidants in combination with transition-metal catalysts[3,8]. Over the last decades, a wide variety of ions, oxides and complexes of transition metals have been explored through homogeneous catalytic processes. Despite these systems lead to high yields in the epoxidation reactions, their immobilization on solid supports have gained much more attention from an environmental and economical perspective due to their potential applications in industry[9–14]. Nowadays, the development of efficient heterogenized catalytic systems for the epoxidation of olefins remains a challenge[4,15–17]. Different types of porous materials, such as zeolites[18], polymers[19], mesoporous silicas[14], activated carbons[20] or MOFs[21] have been employed as supports of transition metal complexes for liquid phase epoxidation of olefins.

Studies on epoxidation reactions catalysed by heterogenized Schiff-bases and other Cu(II)-complexes catalysts have received a great deal of attention during recent

years. Depending on the support, different synthetic approaches have been adopted to integrate them on their framework for the oxidation of olefins. Thus, Spodine et al.[22] were the first who reported the synthesis of a MOF with Cu(II) centers coordinated to bipy (2,2'-bipyridine) and H₄btec (1,2,4,5-benzenetetracarboxylic acid) ligands as a heterogeneous catalyst for oxidation reactions. More recently, Cu species have been incorporated within the framework of a Ga-[23] and Zr-based metal organic framework[24] with bipyridine linkers by a post-synthetic modification method with CuCl₂ and CuBr₂, respectively. Furthermore, another family of ordered porous materials that have attracted a great interest due to their unique features are mesoporous organosilicas. The first attempts were based on the confinement of copper (II) complexes with bipyridine ligands in the mesoporous channels of MCM-41 for oxidation de alkenes[25,26]. Later, a more developed strategy involved the covalent attachment or grafting of organic compounds within the mesochannels of silica materials and subsequent complexation with copper. Most of the studies reported the functionalization of highly ordered 2D-hexagonal mesoporous silicas, such as MCM-41 and SBA-15 materials, with 3-aminopropyltriethoxysilane followed by its condensation with a suitable aldehyde to produce a coordinating Schiff-base ligand[27–29]. Although these heterogenous systems have shown to be effective for liquid phase oxidation of olefins, it is well known the drawbacks associated to grafting procedures. As an alternative to mesoporous organosilicas, the synthesis of periodic mesoporous organosilicas (PMOs) is able to produce well-ordered mesoporous structures with a uniform distribution of the organic functionality into the pore walls[30–32]. Since their discovery, a wide variety of metal and metal complexes have been directly integrated during the PMO synthesis or alternatively, through post-modification

processes for catalytic applications[33]. Copper complexes have been successfully supported on ionic liquid based PMO materials for the synthesis of propargylamines or polyhydroquinolines through the three-component coupling reaction of amines, aldehydes and alkynes[34] or Hantzsch reaction[35], respectively. More recently, Inagaki et al.[36] reported the immobilization of a Cu complex on a periodic mesoporous organosilica containing 2,2'-bipyridine ligands as bridging organic groups. The resulting catalysts were evaluated in the Mukaiyama epoxidation of cyclohexene as a model radical reaction. To the best of our knowledge, no more examples of copper supported PMO materials have been described.

As above-mentioned, the presence of organic moieties in the PMO framework allows these materials to be modified through organic reactions. One of the reactions that have been extensively investigated by our research group is the Diels-Alder reaction. The double bonds on the walls of an ethenylene-bridged PMO have acted as dienophiles for the Diels-Alder reaction with common dienes, such as cyclopentadiene and anthracene[37], pyrrole derivatives[38] and tetrazine[39,40]. This latter diene gave rise to dipyridyl-pyridazine moieties on the PMO surface, which can form interesting chelates with metal ions. Following this approach, we have recently investigated the synthesis of mesoporous silica materials decorated with dipyridyl-pyridazine (dppz) ligands, which were further attached to lanthanide (Ln^{3+}) complexes ($\text{Ln}^{3+} = \text{Er}^{3+}, \text{Yb}^{3+}, \text{Nd}^{3+}$ or $\text{Eu}^{3+}/\text{Tb}^{3+}$ mixture) and used as potential ratiometric thermometer materials[40,41].

Herein, we report the preparation of a novel periodic mesoporous organosilica (PMO) with ethane bridges in the silica framework and pendant vinyl groups in the pore channels, which was post-functionalized with dipyridyl-pyridazine moieties

through a hetero Diels-Alder reaction with 3,6-di-2-pyridyl-1,2,4,5-tetrazine. Subsequently, this material was grafted with a Cu^{2+} complex for producing a suitable heterogenous catalyst for epoxidation reactions.

2. Experimental

2.1. Synthesis of vinyl-functionalized ethylene-bridged PMO (vPMO)

Periodic mesoporous organosilica was synthesized according to the procedure described in literature for the synthesis of thiol-functionalized mesoporous ethane-silicas with some modifications[42]. Typically, Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, MW = 5800, Sigma–Aldrich) (0.5 g) and KCl (3.49 g) were dissolved in HCl solution (16.5 mL, 2M) and H_2O (3.75 mL) under vigorous stirring at 45 °C. Next, a mixture with a molar composition ratio of 80 % of 1,2-bis(trimethoxysilyl)ethane (BTME, 2.84 mmol) and 20 % of vinyltriethoxysilane (VTES, 0.71 mmol) was added dropwise to the above solution. The reaction mixture was stirred at 45 °C for 24 h and following aged at 100 °C under static conditions for 24 h. The white solid product was recovered by filtration and thoroughly washed with distilled water. To remove the surfactant, 1 g of as-synthesized material was refluxed in a solution containing 50 mL ethanol and 1 mL HCl solution (37%) for 24 h. This process is repeated twice, the white solid was recovered by filtration, washed with acetone and dried under vacuum at 100 °C. The material synthesized was named vPMO.

2.2. Post-functionalization of vPMO by Diels-Alder reaction with 3,6-di-2-pyridyl-1,2,4,5-tetrazine.

The organic ligand 3,6-di-2-pyridyl-1,2,4,5-tetrazine (dppz) was synthesized according to a previously reported procedure[40]. This compound was used as diene in the surface Diels-Alder reaction of vinyl-functionalized ethylene-bridged PMO. Thus, 0.6 g of

vPMO was added to a mixture containing 0.5 g of 3,6-di-2-pyridyl-1,2,4,5-tetrazine and 40 mL of dodecane. The reaction mixture was stirred at 150 °C for 13 days under inert atmosphere. The resulting material was collected by vacuum filtration and washed with chloroform. In order to remove possible unreacted diene physically adsorbed into the pores, the material was refluxed in chloroform during 24 h. This procedure was repeated twice. Then, the solid was collected by vacuum filtration and dried at 100 °C. Finally, the solid product was aromatized using NaNO₂ as oxidant to dehydrogenate the dihydropyridazine ring of the surface adduct. Thus, 0.15 g of material were dissolved in 7 mL of acetic acid and in small portions 0.21 g of NaNO₂ were added. The mixture was kept under stirring at 65 °C for 2 h. Then, the solid was recovered by vacuum filtration, washed with ethanol twice and dried at 100 °C overnight. The final material was named *dppz-vPMO*.

2.3. Immobilization of Cu complexes on the surface Diels-Alder adducts.

To immobilize Cu complexes on the surface of Diels-Alder adducts[24], 0.063 g of CuCl₂·2H₂O were dissolved in acetonitrile (15 mL) and then 0.1 g of *dppz-vPMO* were added to the solution. The mixture was stirred at room temperature for 24 h. Afterwards, it was filtered and washed several times with chloroform to guarantee the complete removal of any physisorbed copper salt. The material was dried under vacuum at 100 °C and named as *Cu@dppz-vPMO*.

2.4. Characterization techniques

X-ray powder diffraction (XRD) patterns were collected on a Bruker D8 Discover A25 diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with an applied voltage and current of 40 kV and 300 mA, respectively. Nitrogen adsorption experiments were carried out at -196 °C using an Autosorb-iQ MP/MP-XR instrument. Prior to the measurements, all the

samples were degassed at 120 °C for 24 h. Specific surface areas were calculated from the linear regions of Brunauer-Emmett-Teller (BET) plots ($P/P_0 = 0.1-0.20$). Pore size distributions were obtained using the density functional theory method (DFT) (DFT kernel: silica, cylindrical pores, nonlinear DFT (NLDFT) equilibrium model). Raman spectra were acquired with a Renishaw Raman instrument by excitation with green laser light (532 nm). High-resolution Transmission Electron Microscopy images were recorded on a JEOL JEM 1400 microscope at an accelerating voltage of 300 kV. The diffuse reflectance infrared Fourier transform spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer equipped with a diffuse reflectance environmental chamber (Harrick) connected to a temperature controller. The sample was heated in situ from room temperature to 150 °C under nitrogen. Spectra were collected between 1000 and 4000 cm^{-1} . The ^{13}C CP/MAS NMR spectra were recorded on a Bruker Avance III HD 400 WB spectrometer at 100.61 MHz. Chemical shifts were referenced to tetramethylsilane (TMS). X-ray photoelectron spectroscopy (XPS) were recorded on a SPECS Phoibos HAS 3500 150 MCD X-ray photoelectron spectrometer with a monochromatic Al anode (1486.7 eV). Accurate binding energies have been determined with respect to the position of Si 2p at 103.4 eV. XPS survey spectrum was collected at a pass energy of 60 eV, while high-resolution XPS spectra were obtained at a pass energy of 40 eV and a resolution of 0.1 eV. UV-vis spectra were recorded on an UV-visible diffuse reflectance spectrophotometer Varian Carey IE UV-vis equipped with a 110 nm integration sphere. ICP-MS analysis was performed on a Perkin Elmer NexION™ 350X ICP Mass Spectrometer”.

2.5. Epoxidation of styrene

Epoxidation reaction of styrene was carried out in a two necked round-bottom glass reactor equipped with a magnetic stirring bar and a reflux condenser. Toluene and

nitrobenzene were used as solvent and internal standard, respectively[24]. Typically, 50 mg of catalyst was added to a solution containing styrene (0.058 mL, 0.5 mmol), *tert*-butyl hydroperoxide (TBHP, 0.2 mL, 0.5 mmol), nitrobenzene (0.082 mL, 0.8 mmol) and toluene (2 mL). Afterwards, the reaction mixture was kept under stirring at 90 °C for 1 h. Sample aliquots (0.2 mL) were taken out from the mixture and diluted with toluene. The products were analysed and quantified in a Varian gas chromatograph with a capillary column (VF-1MS, 15 m x 0.25 mm ID) and a flame ionization detector (FID) and using standard compounds. After the reaction, the catalyst was filtered off, washed with acetonitrile and dried under vacuum at 90 °C, and then reused directly without further purification. The recyclability of the Cu@dppz-vPMO catalyst was investigated during five consecutive runs.

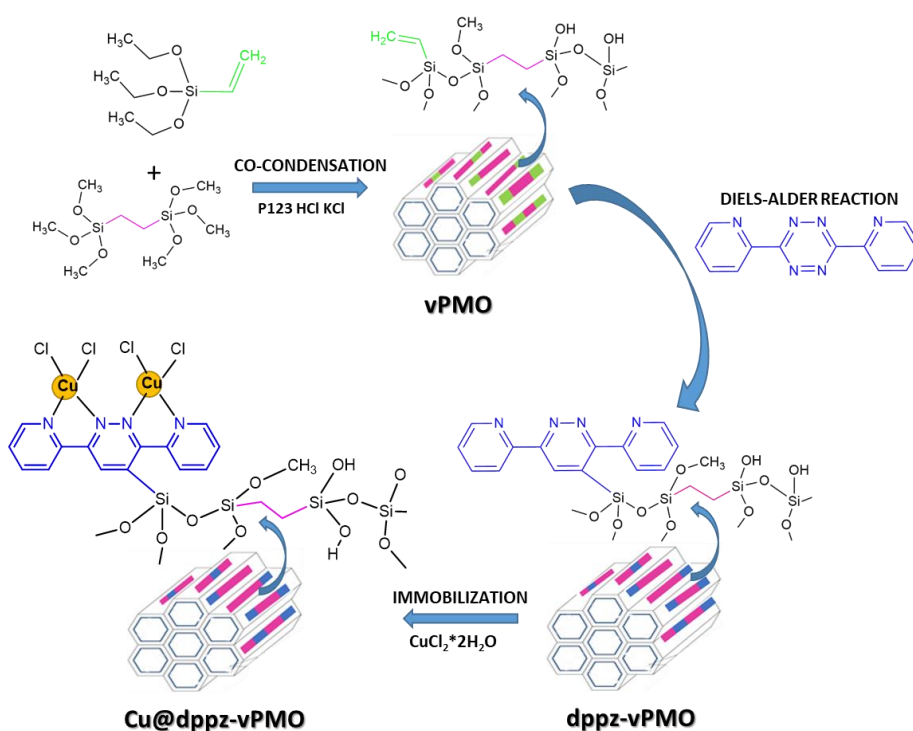
One blank reaction was carried out without adding any catalyst under the same experimental conditions.

3. Results and discussion

3.1. Synthesis and characterization of materials

The copper (II) complex was immobilized on dppz-vPMO support as illustrated on Scheme 1. Firstly, vinyl-functionalized ethylene-bridged PMO (vPMO) was prepared by co-condensation reaction between 1,2-bis(trimethoxysilyl)ethane (80 %) and vinyltriethoxysilane (20 %) using P123 as template under acidic conditions. Next, the pendant double bonds of vPMO acted as dienophiles in a hetero Diels-Alder reaction with a substituted tetrazine (3,6-di-2-pyridyl-1,2,4,5-tetrazine, dptz), giving rise to the formation of surface dipyridyl-pyridazine (dppz) units. Thus, the dppz-vPMO support was functionalized with nitrogen-based chelating heterocycles providing suitable ligands

for anchoring Cu(II) complexes. The copper complex on dipyridyl-pyridazine functionalized PMO was finally synthesized by coordinating the copper salt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) with dppz-vPMO support.



Scheme 1. Synthesis procedure of Cu@dppz-vPMO catalyst.

The XRD diffraction pattern of vinyl-functionalized ethylene-bridged PMO (vPMO) displayed a low peak (100) at $2\theta = 0.9$ and two small second-order (110) and (200) peaks at higher incidence angles, characteristic of materials with 2D-hexagonal pore mesostructure ($P6mm$) (Fig 1). After Diels-Alder reaction with 3,6-di-2-pyridyl-1,2,4,5-tetrazine, the resulting dppz-vPMO material showed a similar diffraction pattern, indicating that the mesoscopic ordering of the parent material remained intact after the surface modification reaction. Likewise, after immobilization of Cu-complexes on the dipyridyl-pyridazine units, the initial ordered mesoporous structure was preserved[41]. These results indicate the great stability of the pristine mesostructure after Diels-Alder

and immobilization reactions. Recently, Inagaki et al. reported that the mesostructure ordering of bipyridine-bridged PMO during the immobilization of Cu-complexes was damaged when the solid was dispersed in protic solvents, such as methanol and water[36].

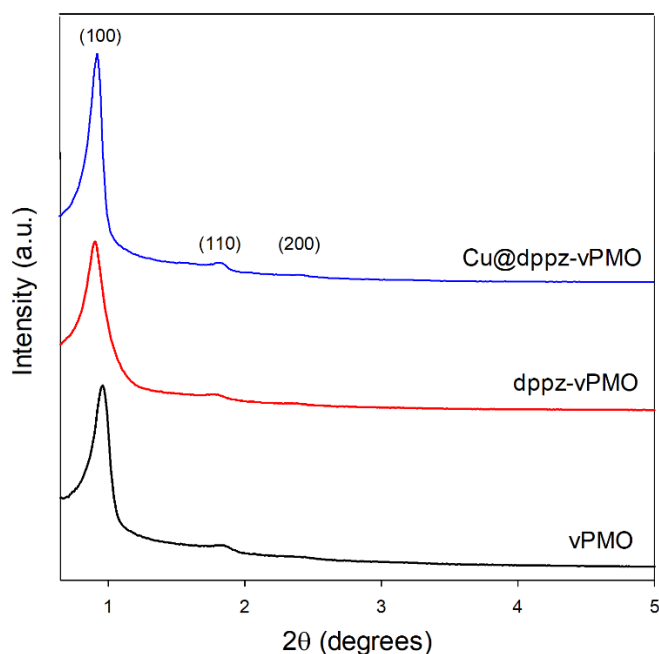


Fig 1. XRD patterns of vPMO, dppz-vPMO and Cu@dppz-vPMO.

The nitrogen adsorption-desorption isotherms of the different materials are shown in Fig 2. All materials exhibited type-IV isotherms with H1-type hysteresis loops at relative pressures of 0.5-0.7, confirming the presence of uniform cylindrical mesopores. The average pore diameter and narrow pore size distribution of the PMO materials confirmed the presence of pores in the mesopore range (Fig 2, right). Textural properties (S_{BET} , V_p and D_p) of the periodic mesoporous organosilica materials are listed in Table 1. vPMO has a high S_{BET} of $849 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.86 \text{ cm}^3 \text{ g}^{-1}$. After Diels-Alder reaction, a slight decrease of surface area and pore volume were appreciated. In addition, the immobilization of the copper complex on the surface Diels-Alder adducts gave rise to a higher decrease of S_{BET} ($421 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.50 \text{ cm}^3 \text{ g}^{-1}$). The pore wall thickness increased after Diels-Alder reaction with the tetrazine derivative due to the

volume occupied by the organic fragments. Similar results were previously reported in this type of reaction with the same diene and other dienophiles[39,40].

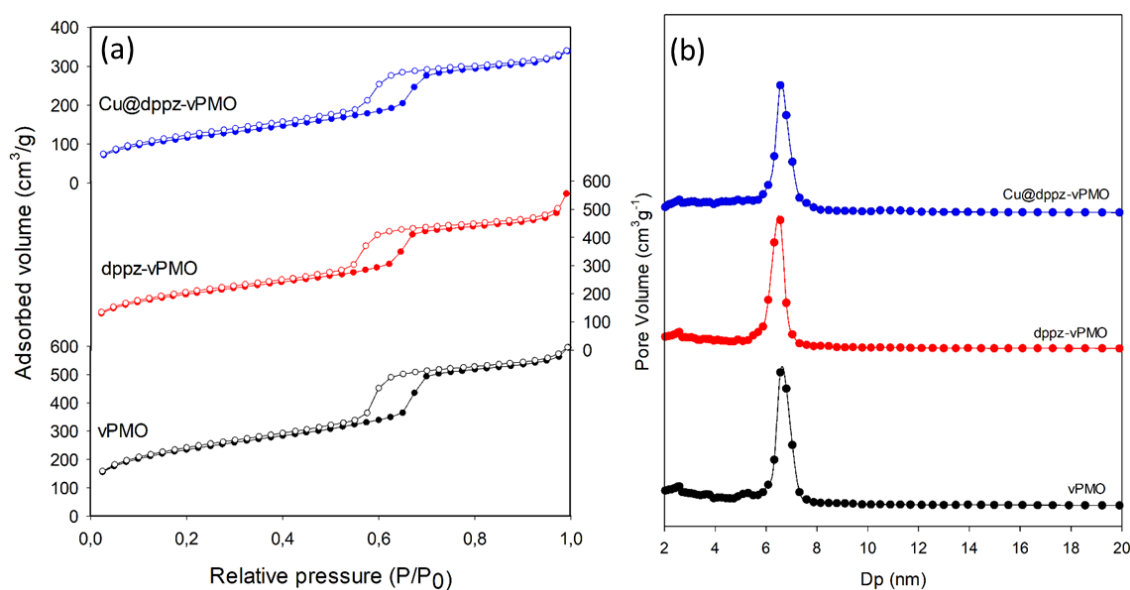


Fig 2. N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of periodic mesoporous organosilica materials.

Table 1. Physicochemical properties of synthesized periodic mesoporous organosilicas^a

Sample	d_{100} (nm)	a_0	S_{BET} (m ² g ⁻¹)	V (cm ³ g ⁻¹)	D^b (nm)	t^c (nm)
vPMO	9.2	10.6	849	0.86	6.6	4.0
dppz-vPMO	9.6	11.1	715	0.78	6.6	4.5
Cu@dppz-vPMO	9.7	11.2	421	0.50	6.6	4.6

^a d_{100} , (100) spacing; S_{BET} , BET surface area; V, pore volume; D, pore diameter; t, wall thickness.

^b calculated by the DFT method

^c calculated from $(a_0 - D)$, where $a_0 = 2d_{100}/\sqrt{3}$

In addition to the PXRD and nitrogen sorption measurements, TEM images corroborated the structural ordering of the synthesized materials (Fig 3). TEM images of vPMO

revealed the highly ordered hexagonally array of straight mesoporous channels. These uniform pore channels were retained after functionalization and complexation processes.

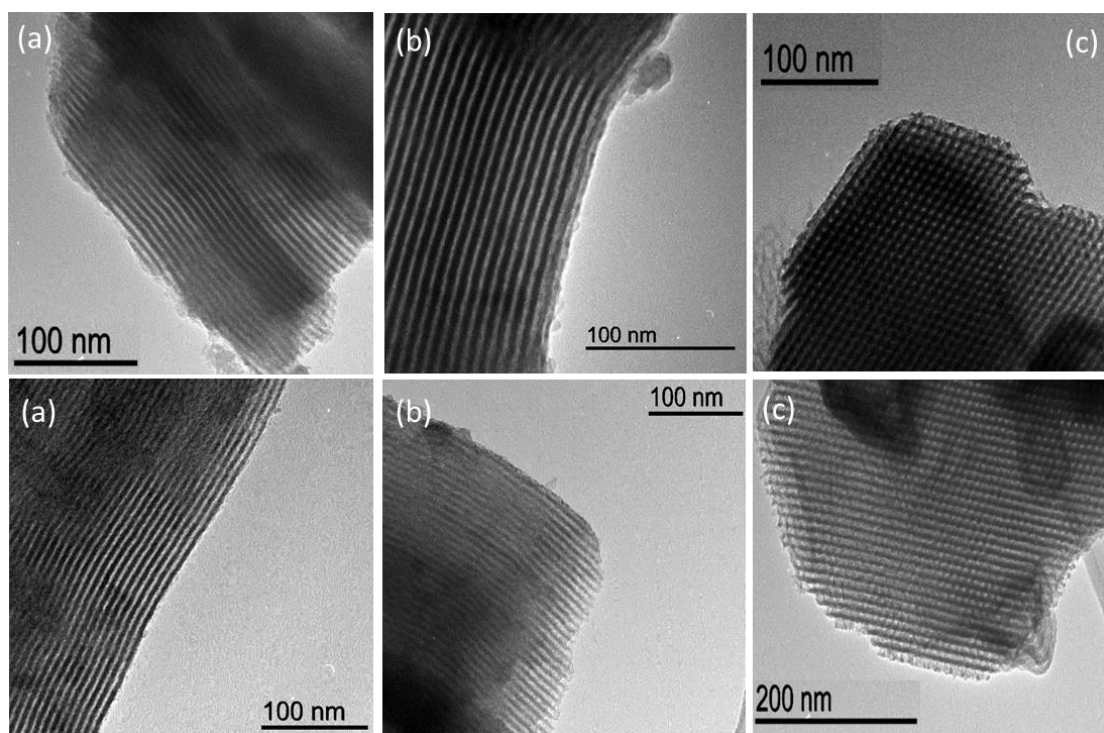


Fig 3. TEM images of vPMO (a), dppz-vPMO (b) and Cu@dppz-vPMO (c).

The presence of both organic moieties, i.e. bridging ethylene groups in the silica framework and vinyl groups in the channel pores, on the parent material as well as the resulting surface Diels-Alder adducts on dppz-vPMO have been confirmed by DRIFT and solid-state ^{13}C CP/MAS NMR measurements (Fig 4). DRIFT spectrum of vPMO (Fig 4a) showed bands at 3050 and 1591 cm^{-1} associated to $=\text{CH}$ and $\text{C}=\text{C}$ stretching vibrations of vinyl groups, respectively. Additionally, several signals in the C-H stretching region, below 3000 cm^{-1} , are characteristic of the ethylene bridges in the silica framework and the remaining surfactant into pores. After Diels-Alder reaction, dppz-vPMO showed additional vibrational signals associated to the $\text{C}=\text{N}$ stretching (1560 cm^{-1}) and skeletal vibrational ($1360 - 1600\text{ cm}^{-1}$) of the dipyrindyl-pyridazine units[43].

The solid-state ^{13}C CP/MAS NMR spectrum of vPMO (Fig 4b) showed an intense signal at 5 ppm and signals at 130 and 137 ppm corresponding to the Csp^3 and Csp^2 of the ethane and vinyl groups, respectively[44,45]. Additionally, signals at 21 and 58 ppm could be assigned to non-hydrolysed methoxy ($-\text{OCH}_3$) and ethoxy ($-\text{OCH}_2\text{CH}_3$) groups remaining after the synthesis procedure. Small signals at 71 and 76 ppm are characteristic of P123 surfactant residues, still present in the pores after three successive extractions. After Diels-Alder reaction, new signals appeared in the aromatic region (149 – 125 ppm) corresponding to the aromatic carbons present in the surface adducts[39].

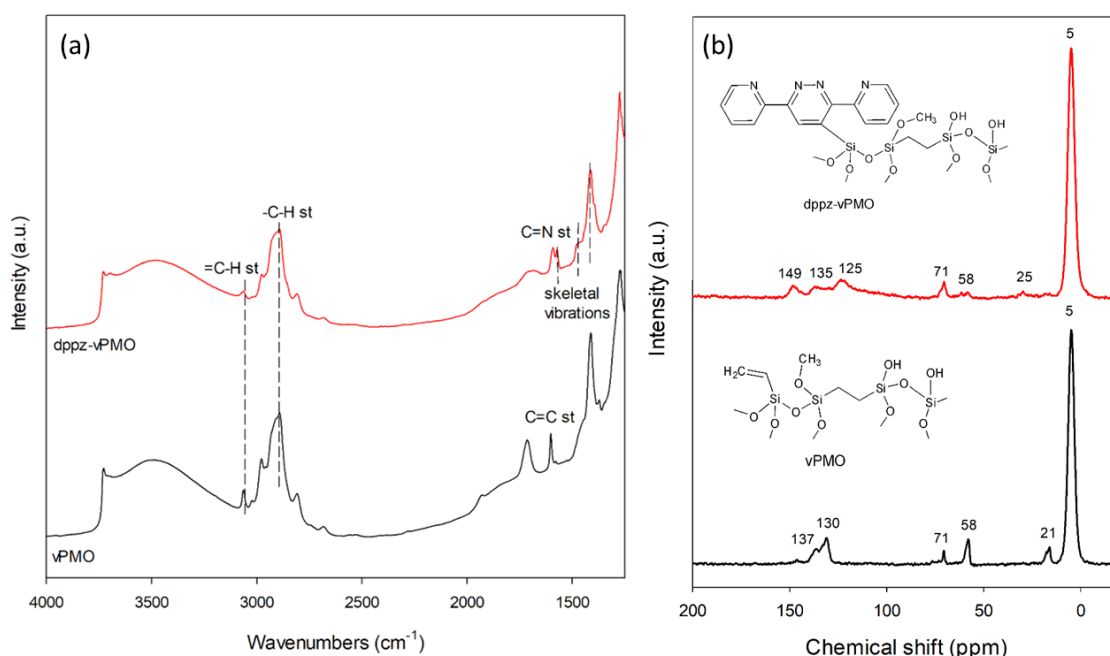


Fig 4. DRIFT spectra (a) and ^{13}C CP/MAS NMR spectra (b) of vPMO and dppz-vPMO.

XPS measurements were performed to obtain surface information of the samples and confirm the incorporation and oxidation state of copper. Survey spectrum of dppz-vPMO (Fig 5a) indicated the presence of Si, C, O and N in the surface analysis of the sample. After copper immobilization on the dipyridyl-pyridazine adducts, additional signals associated to Cu were present for the Cu@dppz-vPMO sample. The N1s XPS spectrum (Fig 5b) for dppz-vPMO only exhibited a component centered at 400.6 eV attributed to

the nitrogen atoms in the pyridine and pyridazine rings[46]. A slight shift (0.3 eV) of the binding energy toward a higher value was observed after copper complexation, in accordance with the electronic interaction between copper and nitrogen atoms in the sample. Furthermore, the Cu2p XPS spectrum (Fig 5c) for Cu@dppz-vPMO showed two characteristic peaks at 934.8 and 954.6 eV, which correspond to Cu2p_{3/2} and Cu2p_{1/2}, respectively. The appearance of shake-up satellite bands at 940-950 eV confirmed the presence of Cu²⁺ [14,47].

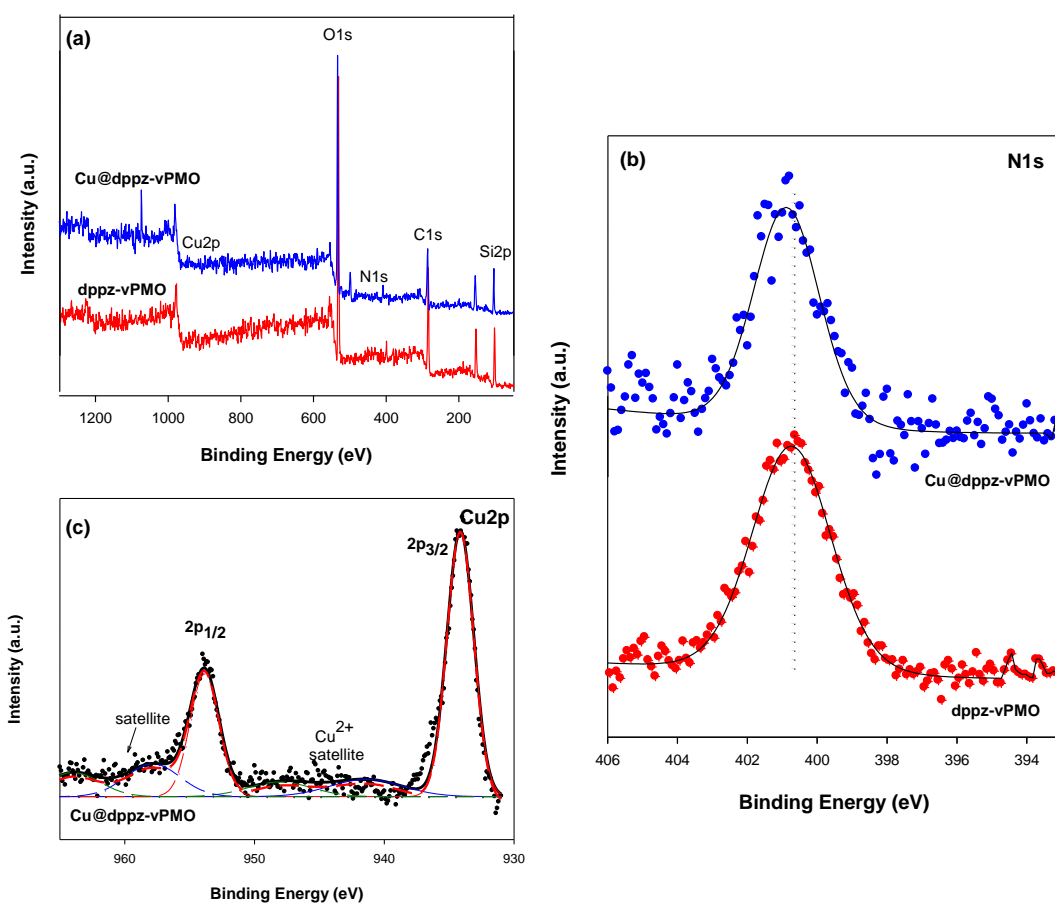


Fig 5. XPS spectra of dppz-vPMO and Cu@dppz-vPMO: (a) survey scan, (b) N1s and (c) Cu2p.

The presence and coordination of the copper complex was further corroborated using UV-vis diffuse reflectance spectroscopy. Fig 6 shows UV-vis diffuse reflectance spectra of

dppz-vPMO and Cu@dppz-vPMO. The material dppz-vPMO exhibited two adsorption bands in the region of 260-320 nm and 500-600 nm which are attributed to the π - π^* and n- π electronic transitions of dipyridyl-pyridazine units[48]. After copper immobilization, the UV-vis diffuse reflectance spectrum of Cu@dppz-vPMO exhibited a wide adsorption ranging from 300-500 nm, with maxima centered at 320 and 380 nm. These bands could be assigned to ligand to metal charge transfer (LMCT). Furthermore, it showed a relatively broad band in the range of 600-800 nm, which may be attributed to the d-d transition at the metal centre. Similar adsorption patterns were observed for Cu^{2+} complexes with N- and O-donor Schiff base ligands anchored on mesoporous silica[29].

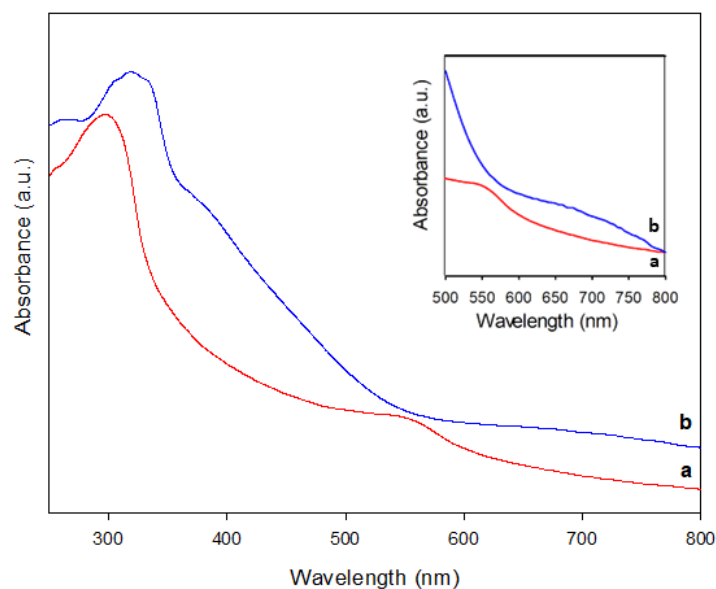


Fig 6. UV-Vis diffuse reflectance spectra of dppz-vPMO (a) and Cu@dppz-vPMO (b) materials.

The nitrogen content in dppz-vPMO determined by elemental analysis was 0.18 mmol g^{-1} . Furthermore, the copper loading for Cu@dppz-vPMO calculated by ICP-MS was 0.13 mmol g^{-1} . Accordingly, the Cu/N ratio on the catalyst was 0.72, slightly higher to the theoretical one (Cu/N = 0.5). This would confirm the coordination of some copper species on the free silanol groups at the pore surfaces of dppz-vPMO[49].

3.2. Catalytic activity in styrene epoxidation

As above-mentioned, the olefins epoxidation is an interesting organic reaction to produce value-added chemicals. In this work, Cu@dppz-vPMO was employed as heterogenous catalyst in the styrene reaction with tert-butyl hydroperoxide (TBHP) as oxidant. The conversion of styrene and the selectivities to different products are displayed in Table 2. Obviously, the blank reaction gave a lower conversion (19.3 %) as resulted from the autoxidation of styrene by TBHP. Without any catalyst, non-formation of styrene oxide (SO) was appreciated. When CuCl₂ was essayed as homogeneous catalyst, the conversion of styrene was 50.5 % but SO was not obtained. Interestingly, our heterogenous catalytic system, Cu@dppz-vPMO, reached a higher conversion (59.1%) and a remarkable SO selectivity of 18.8 %. Other oxidants, such as hydrogen peroxide and oxone, were tested in the styrene oxidation. Under similar conditions, the oxidation reaction did not proceed with oxone as oxidant. Unlike, a styrene conversion of 67.0 % and a high selectivity to BZ (87.6 %) was obtained using H₂O₂ as oxidizing agent.

Table 2. Catalytic activities for selective oxidation of styrene

Entry	Catalyst	Oxidant	Conversion (%)	Selectivity ^d (%)			
				SO	BZ	AP	BO
1	Blank ^a	TBHP	19.3	-	63.9	24.6	11.6
2	CuCl ₂ *2H ₂ O ^a	TBHP	50.5	-	76.7	-	23.4
3	Cu@dppz-vPMO ^a	TBHP	59.1	18.8	58.3	4.3	18.6
5	Cu@dppz-vPMO ^b	H ₂ O ₂	67.0	3.5	87.6	8.6	0.3
6	Cu@dppz-vPMO ^c	Oxone	--	---	---	---	---
7	Cu@dppz-vPMO ^e	TBHP	73.1	36.1	45.9	3.4	14.6

^aReaction conditions: 50 mg of catalyst, 0.5 mmol of styrene, 1 mmol of TBHP, 2 mL of solvent (toluene); reaction temperature, 90 °C; reaction time, 1 h.

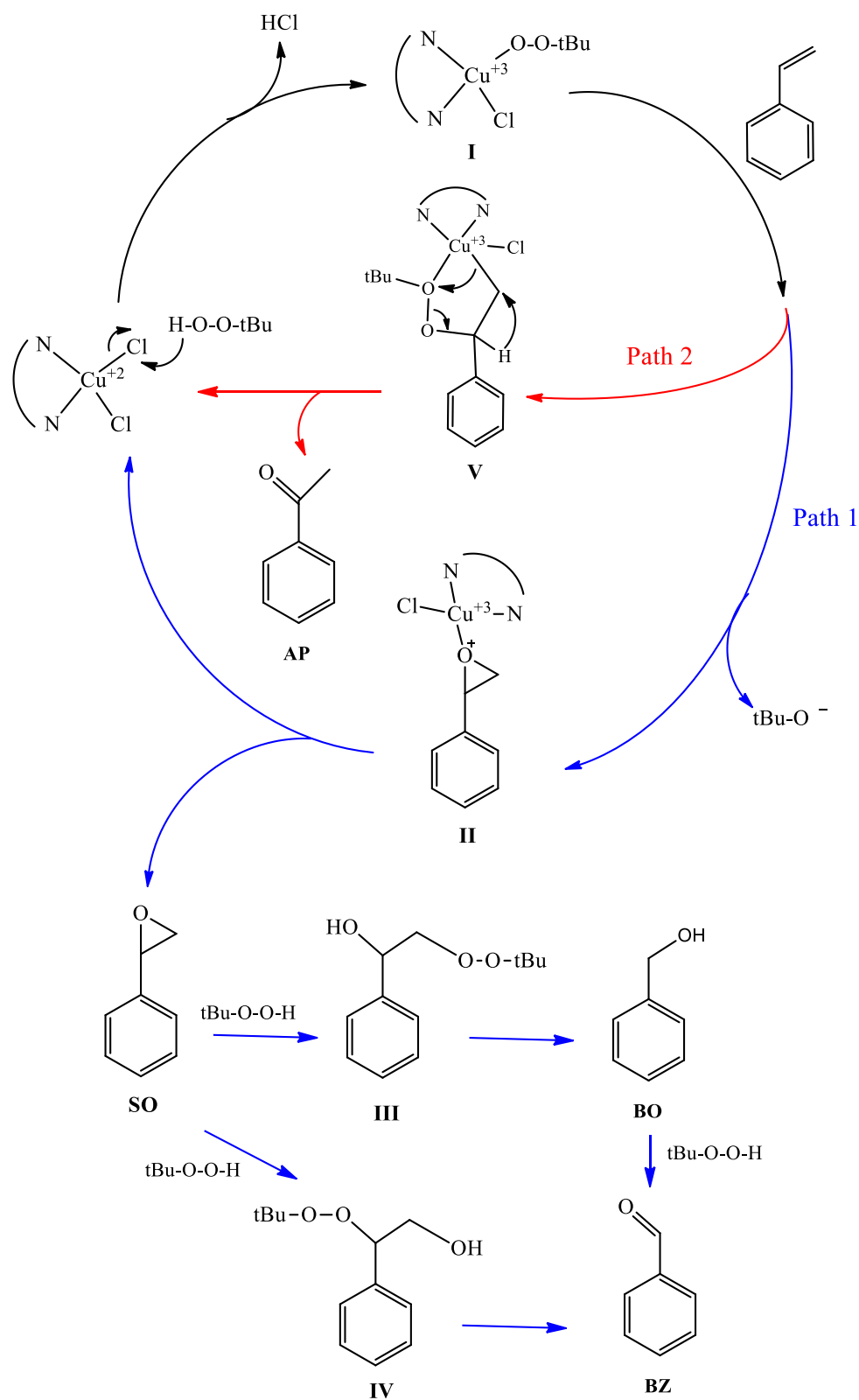
^bReaction conditions: 50 mg of catalyst, 0.5 mmol of styrene, 1 mmol of H₂O₂ (30%), 2 mL of solvent (acetonitrile); reaction temperature, 90 °C; reaction time, 1 h.

^cReaction conditions: 50 mg of catalyst, 0.5 mmol of styrene, 1 mmol of Oxone (dissolved 0.8 ml of water), 2 mL of solvent (toluene); reaction temperature, 90 °C; reaction time, 1 h.

^dSO = styrene oxide, BZ = benzaldehyde, AP = acetophenone, BO = benzyl alcohol

^eOptimized conditions: 50 mg catalyst, 0.5 mmol styrene, 2 mmol TBHP, 2 mL solvent (toluene), reaction temperature 100 °C, reaction time 1h.

Based on the experimental findings of this work and previous literature[15,22,29,50], a plausible reaction mechanism for epoxidation of styrene with TBHP over Cu@dppz-vPMO catalyst has been proposed in Scheme 2. The mechanism begins with the formation of oxygenated intermediary species (*Cu(III)-peroxo*) (**I**) after the coordination of TBHP to the Cu(II) centre. Later, the reaction between the double bonds of styrene and species **I** can occur by two possible reaction pathways according to the observed products. The dominant reaction path (Path 1) consists of a concerted oxygen transfer, giving rise to the cyclic intermediate (**II**) and t-butanol. Subsequently, the cleavage of the Cu-O bond yields styrene oxide (**SO**) together with the simultaneous regeneration of the Cu (II) centre. Additionally, the ring-opening of the epoxide by attack of TBHP can form the peroxide **III** and **IV**, resulting in the formation of benzyl alcohol (**BO**) and benzaldehyde (**BZ**), respectively. This latter could also be formed by direct oxidation of BO with TBHP[51,52]. Furthermore, the oxidation of styrene to acetophenone (**AP**), also detected as reaction product, proceeds via the formation of intermediate peroxo metallocycle species (**IV**) that are formed by the interaction of the peroxo group with the double bonds of styrene molecules (Path 2).



Scheme 2. Proposed mechanism for styrene epoxidation reaction over Cu@dppz-vPMO catalysts using TBHP as oxidant.

The recycling test of Cu@dppz-vPMO catalyst was conducted for five successive cycles under the foresaid reaction conditions. As shown in Fig 7a, the selectivity to all products was kept practically constant during the successive catalytic cycles. Although the styrene conversion remained stable (ca. 60%) during the catalytic cycles, a slight drop of conversion was appreciated in the third cycle. This could be ascribed to the blockage of the active sites by some products molecules that remained adsorbed on the catalyst surface after its filtration and washing. Indeed, the catalytic activity was recovered in the following runs. These results confirmed the high stability of the copper complex on dipyriddy-pyridazine functionalized PMO material in the styrene epoxidation reaction, similar to other copper-supported mesoporous materials reported in literature[36,50]. Furthermore, N₂ adsorption-desorption isotherms (Fig. 7b) and TEM image (Fig. 7c) of Cu@dppz-vPMO after the first and fifth catalytic cycle, corroborated the high mesostructural stability of the material under the oxidative conditions employed.

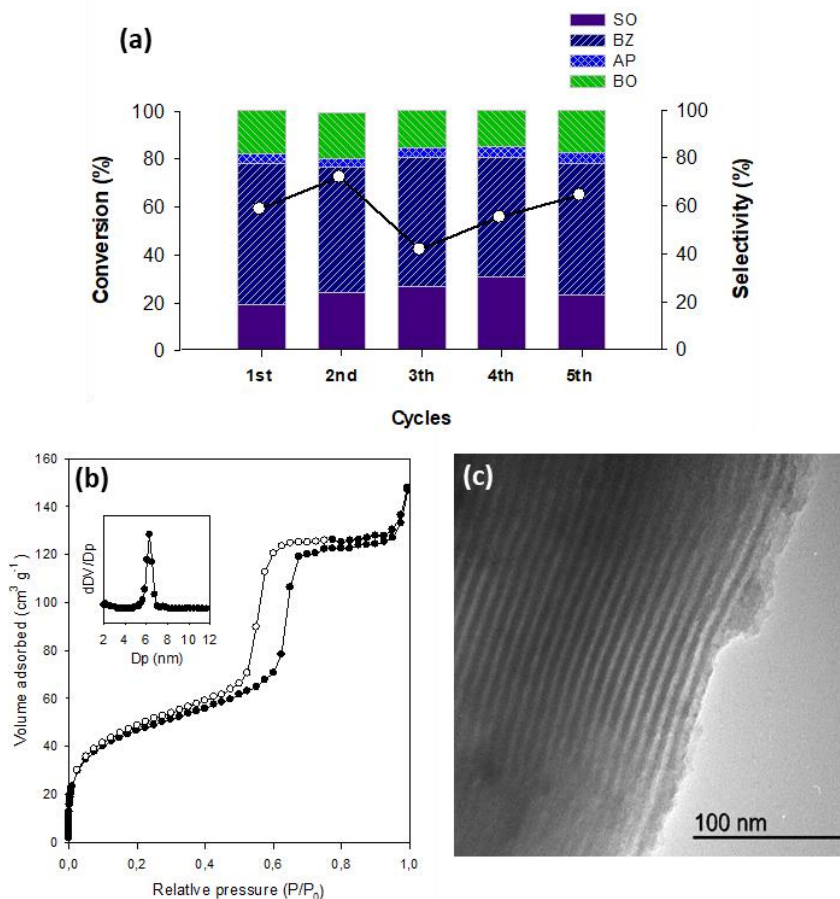


Fig 7. (a) Recycling test of Cu@dppz-vPMO in the styrene epoxidation reaction for five cycles. Reaction conditions: 50 mg of catalyst, 0.5 mmol of styrene, 1 mmol of TBHP, 2 mL of solvent (toluene); reaction temperature, 90 °C; reaction time, 1 h. (b) N₂ adsorption-desorption isotherms of Cu@dppz-vPMO after one reaction cycle. (c) TEM image of Cu@dppz-vPMO after five reaction cycles.

To optimize the reaction conditions, the effect of various reaction parameters - *solvent, temperature and substrate/oxidant molar ratio* - that may affect the conversion and selectivity of the styrene epoxidation was examined (Fig 8). Initially, in order to evaluate the influence of the solvent, the epoxidation reaction was performed with a molar ratio of 1:2 (styrene:TBHP) and different solvents (acetonitrile, benzonitrile, dichloromethane, dimethylformamide and toluene) (Fig 8a). Using acetonitrile and benzonitrile at 80 and

90 °C, respectively, a higher styrene conversion was obtained. Previous studies have reported that nitriles, with a high dielectric constant, are excellent solvents in styrene epoxidation with TBHP due to an increased solubility of the reactants and therefore a better accessibility to the active sites of the catalyst[53,54]. No SO was obtained in acetonitrile, being BZ the major reaction product. The selectivity to SO increased up to 15 % in benzonitrile. Unlike, using dichloromethane and dimethylformamide as solvents at 40 and 120 °C, respectively, the conversion was found to be zero. The highest SO selectivity (18%) was reached in toluene.

To evaluate the influence of the temperature on styrene epoxidation, it was performed at 60, 80, 90 and 100 °C in toluene (Fig 8b). The higher the temperature, the higher the conversion and selectivity to SO. This positive trend in conversion and selectivity with temperature is consistent with previous reports that also found that vinyl C-H bonds of styrene molecules were more active at higher temperatures[28]. Additionally, another reaction parameter widely studied in the epoxidation reaction is the styrene/TBHP molar ratio[50] (Fig 8c). A remarkably improvement on the styrene conversion from 73 % to 86 % was obtained when increasing the styrene/TBHP molar ratio from 1:2 to 1:4. Also, the selectivity towards the epoxide increased to a great extent from 30 to 41.9 %.

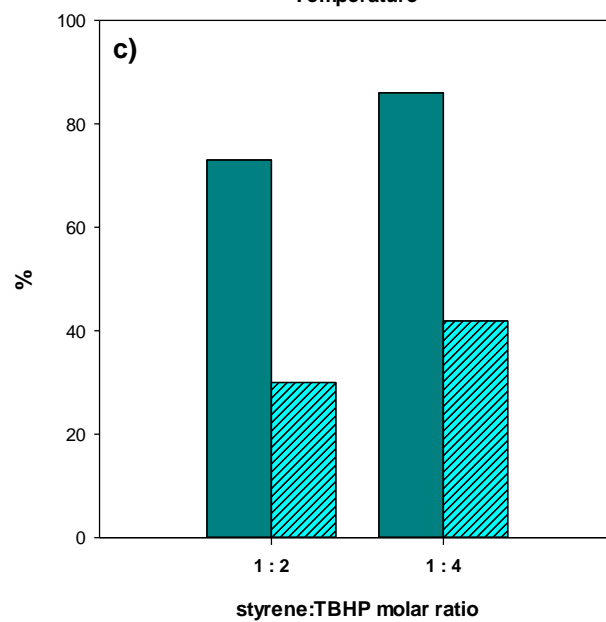
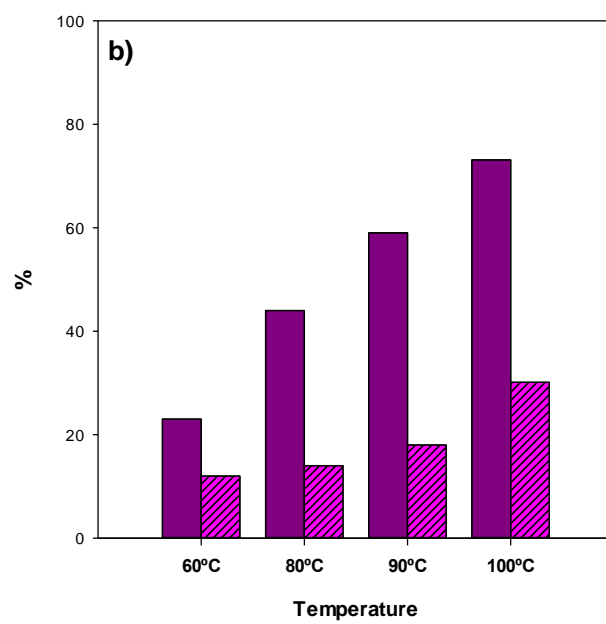
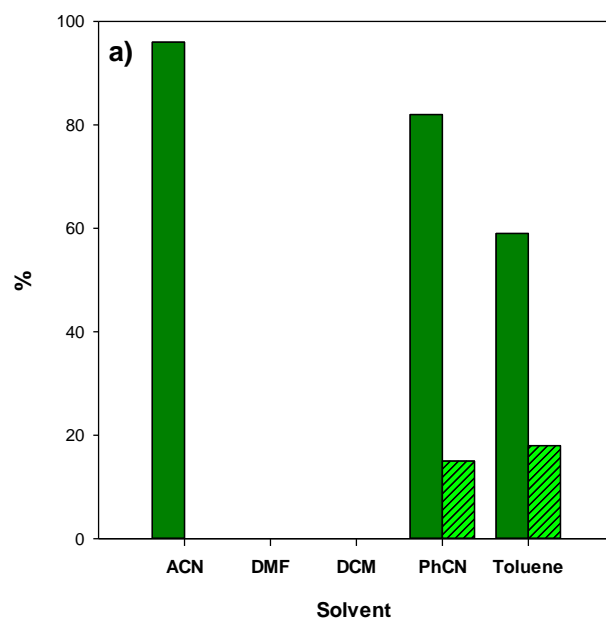


Fig 8. Effect of reaction parameters on the epoxidation of styrene with TBHP (conversion and SO selectivity are indicated in filled and dashed bars, respectively) (a) Effect of solvent (ACN=acetonitrile; DMF=dimethylformamide; DCM=dichloromethane PhCN=benzonitrile;), (b) Effect of reaction temperature and (c) Effect of styrene/TBHP molar ratio. Reaction conditions: (a) styrene, 0.5 mmol; TBHP, 1 mmol; solvent, 2 mL; catalyst, 50 mg; T = 90 °C; t = 1h; (b) styrene, 0.5 mmol; TBHP, 1 mmol; toluene, 2 mL; catalyst, 50 mg; t = 1h (c) styrene, 0.5 mmol; toluene, 2 mL; catalyst, 50 mg; T = 100 °C; t = 1h.

Once the optimal reaction conditions have been established (solvent, toluene; temperature, 100 °C; styrene:TBHP molar ratio, 1:4) for Cu@dppz-vPMO catalyst, it is worth mentioning the excellent yield achieved (86.0 %) and the remarkable epoxide selectivity (41.9 %). Furthermore, copper loading for the recycled catalyst was 0.125 mmol g⁻¹, which indicates that barely exists any leaching of copper species to the solution during epoxidation reaction. We have compared the catalytic performance of our catalyst with previously reported heterogeneous copper-based catalysts in the epoxidation of styrene with TBHP (Table 3). As can be seen, the performance of such catalytic systems depends directly on the active species of Cu (II) present on the support. Compared with those systems where copper is coordinated to nitrogen-chelating heterocyclic compounds comparable to the dppz ligands of our catalyst (i.e. bipyridine groups) (entries 2-3), Cu@dppz-vPMO (entry 1) possesses the highest styrene conversion and epoxide selectivity at shorter reaction times (1 h). By contrast, those systems based on Cu(II) Schiff base complexes anchored onto two- dimensional (entry 5) or three-dimensional (entry 6) mesoporous silicas as well as graphene oxide (entry 7) showed slightly larger styrene conversions and much higher selectivity to epoxide than those over Cu@dppz-

vPMO. It is interesting to note that all of them required around 6-7 h or even longer reaction times to achieve these results for the epoxidation of styrene.

Table 3. Comparison of the catalytic activity of Cu@dppz-vPMO with previously reported heterogeneous copper-based catalysts in the epoxidation of styrene with TBHP.

Entry	Catalyst	Time (h)	Temperature (°C)	Conversion (%)	SO Selectivity (%)	Ref.
1	Cu@dppz-vPMO ^a	1	100	86.0	41.9	This work
2	[Cu(H ₂ btec)(bipy)] _∞ ^b	24	75	23.7	71.0	[22]
3	[Cu ₂ (μ ₂ -O)(4,4'-bpy) ₃ (SiW ₁₂ O ₄₀)(H ₂ O)] ^c	10	70	74.4	44.0	[55]
4	CuY ^d	1	60	20.9	29.5	[56]
5	Cu-AMM ^e	24	60	86.3	95	[29]
6	Cu-NH ₂ -KIT-6 ^f	6	80	98.6	97.8	[50]
7	Cu-NH ₂ -GO ^g	7	80	94.3	99.0	[57]

^aOptimized conditions

^b[Cu(H₂btec)(bipy)]_∞: metal-organic framework [Cu(H₂btec)(bipy)] (H₄btec=1,2,4,5-benzenetetracarboxylic acid; bipy= 2,2'-bipyridine)

^c[Cu₂(μ₂-O)(4,4'-bpy)₃(SiW₁₂O₄₀)(H₂O)]: 3D Keggin-based coordination polymer

^dCuY: copper (II) phthalocyanine encapsulated in zeolite Y.

^eCu-AMM: copper (II) Schiff complex anchored mesoporous material with 2D-hexagonal structure.

^fCu-NH₂-KIT-6: copper (II) Schiff complex onto amine-functionalized KIT-6.

^gCu-NH₂-GO: copper (II) Schiff complex supported onto graphene oxide.

4. Conclusions

In summary, a novel heterogeneous copper-based catalyst was successfully synthesized through the immobilization of a copper complex onto periodic mesoporous organosilica containing surface dipyridyl-pyridazine ligands. XRD, TEM and N₂ adsorption-desorption results revealed that the ordered mesostructure of the parent material remained intact after post-functionalization and complexation. In addition, a detailed study of the surface functionalized materials by different characterization techniques confirmed the presence of N-chelating heterocyclic units in the surface pores resulting from the Diels-Alder reaction as well as the subsequent anchoring of the copper complex. The resulting catalyst showed to be highly active in the epoxidation of styrene with remarkable selectivity to styrene oxide. Furthermore, it has been shown that Cu@dppz-vPMO catalyst exhibits a high stability under the reaction conditions and could be reused at least during five cycles without significant loss of its activity and selectivity.

Acknowledgements

The authors wish to acknowledge the financial support from Ramon Areces Foundation (Spain) and project RTI2018-101611-B-I00, Andalusian Regional Government (FQM-346 group), Feder Funds, the technical staff from the Instituto Universitario de Investigación en Química Fina y Nanoquímica (IUNAN) and Servicio Central de Apoyo a la Investigación (SCAI). J. A. acknowledges the FPU teaching and research fellowship (FPU17/03981).

References

- [1] G. Centi, F. Cavani, F. Trifirò, Trends and Outlook in Selective Oxidation, in: *Sel. Oxid. by Heterog. Catal.*, 2001: pp. 1–24. https://doi.org/10.1007/978-1-4615-4175-2_1.
- [2] H. Adolfsson, Transition Metal-Catalyzed Epoxidation of Alkenes, in: *Mod. Oxid. Methods*, 2005: pp. 21–49. <https://doi.org/10.1002/9783527632039.ch2>.
- [3] B.S. Lane, K. Burgess, Metal-catalyzed epoxidations of alkenes with hydrogen peroxide, *Chem. Rev.* 103 (2003) 2457–2473. <https://doi.org/10.1021/cr020471z>.
- [4] A.S. Sharma, V.S. Sharma, H. Kaur, R.S. Varma, Supported heterogeneous nanocatalysts in sustainable, selective and eco-friendly epoxidation of olefins, *Green Chem.* 22 (2020) 5902–5936. <https://doi.org/10.1039/d0gc01927e>.
- [5] J.M. Judge, Organic peroxides, *J. Polym. Sci. Part B Polym. Lett.* 10 (1972) 230–231. <https://doi.org/10.1002/pol.1972.110100316>.
- [6] G.A. Barf, R.A. Sheldon, Ruthenium catalyzed epoxidations: mechanistic and synthetic aspects, *J. Mol. Catal. A. Chem.* 102 (1995) 23–39. [https://doi.org/10.1016/1381-1169\(95\)00089-5](https://doi.org/10.1016/1381-1169(95)00089-5).
- [7] H. Kwart, D.M. Hoffman, Observations regarding the Mechanism of Olefin Epoxidation with per Acids, *J. Org. Chem.* 31 (1966) 419–425. <https://doi.org/10.1021/jo01340a017>.
- [8] S. Shit, U. Yadava, D. Saha, Roland Fröhlich, 2,2'-Bipyridyl-acetylphenolato mixed ligand copper(II) complexes: Syntheses, characterizations and catalytic activity in styrene epoxidation, *J. Coord. Chem.* 66 (2013) 66–76. <https://doi.org/10.1080/00958972.2012.747088>.
- [9] H.J. Zhan, Q.H. Xia, X.H. Lu, Q. Zhang, H.X. Yuan, K.X. Su, X.T. Ma, Selective epoxidation of styrene with air catalyzed by CoO_x and CoO_x/SiO₂ without any reductant, *Catal. Commun.* 8 (2007) 1472–1478. <https://doi.org/10.1016/j.catcom.2006.12.026>.
- [10] Y. Li, Y. He, J. Feng, D. Li, D. Trans, D.O.I. Cdtf, Synthesis of a highly dispersed CuO catalyst on CoAl-HT for the epoxidation of styrene, *Dalt. Trans.* 46 (2017) 13463–13471. <https://doi.org/10.1039/C7DT02247F>.

- [11] Y. Zhang, F. Yang, R. Gao, W. Dai, Manganese-Doped CeO₂ Nanocubes as Highly Efficient Catalysts for Styrene Epoxidation with TBHP, *Appl. Surf. Sci.* 471 (2019) 767–775. <https://doi.org/10.1016/j.apsusc.2018.11.246>.
- [12] M. Niakan, Z. Asadi, M. Masteri-farahani, Immobilization of salen molybdenum complex on dendrimer functionalized magnetic nanoparticles and its catalytic activity for the epoxidation of olefins, *Appl. Surf. Sci.* 481 (2019) 394–403. <https://doi.org/10.1016/j.apsusc.2019.03.088>.
- [13] G.R. Lucía Rossi-Fernández, Viviana Dorn, A new and efficient methodology for olefin epoxidation catalyzed by supported cobalt nanoparticles, *J. Org. Chem.* 17 (2021) 519–526. <https://doi.org/10.3762/bjoc.17.46>.
- [14] R. Wang, X. Liu, F. Yang, S. Gao, S. Zhou, Y. Kong, Neighboring Cu toward Mn site in confined mesopore to trigger strong interplay for boosting catalytic epoxidation of styrene, *Appl. Surf. Sci.* 537 (2021) 148100. <https://doi.org/10.1016/j.apsusc.2020.148100>.
- [15] M.S. Batra, R. Dwivedi, R. Prasad, Recent Developments in Heterogeneous Catalyzed Epoxidation of Styrene to Styrene Oxide, *ChemistrySelect.* 4 (2019) 11636–11673. <https://doi.org/10.1002/slct.201902396>.
- [16] S. Impeng, T. Roongcharoen, P. Maitarad, H. Wu, C. Chitpakdee, V. Promarak, L. Shi, S. Namuangruk, High Selective Catalyst for Ethylene Epoxidation to Ethylene Oxide: A DFT Investigation, *Appl. Surf. Sci.* 513 (2020) 145799. <https://doi.org/10.1016/j.apsusc.2020.145799>.
- [17] M.A. Andrade, M.D.R.S. Martins, Selective Styrene Oxidation to Benzaldehyde over Recently Developed Heterogeneous Catalysts, *Molecules.* 26 (2021) 1680. <https://doi.org/10.3390/molecules26061680>.
- [18] R. Bera, C. Adhikary, Catalytic potency of zeolite Y immobilized copper - 2, 2' - bipyridine hybrid complex in oxidation of olefins, *J. Porous Mater.* 28 (2021) 695–702. <https://doi.org/10.1007/s10934-020-01023-7>.
- [19] B. Shi, H. Yu, S. Gao, L. Zhang, Y. Liu, K. Huang, Microporous and Mesoporous Materials Copper complex supported on hollow porous nanosphere frameworks with improved catalytic activity for epoxidation of olefins, *Microporous Mesoporous Mater.* 294 (2019) 109890. <https://doi.org/10.1016/j.micromeso.2019.109890>.

- [20] S. Madadi, S. Kaliaguine, Activated Carbon-Supported Ruthenium as a Catalyst for the Solvent- and Initiator-Free Aerobic Epoxidation of Limonene, *ACS Sustain. Chem. Eng.* 9 (2021) 10557–10568. <https://doi.org/10.1021/acssuschemeng.1c02597>.
- [21] C. Chen, P. Shen, M. Wan, N. Ding, X. Shi, X. Wang, N. Zhang, Size-selective epoxidation of olefins in two new metal-organic framework constructed from six-coordinated tetranuclear Cu (II) SBUs, *Microporous Mesoporous Mater.* 232 (2016) 167–173. <https://doi.org/10.1016/j.micromeso.2016.06.013>.
- [22] K. Brown, S. Zolezzi, P. Aguirre, D. Venegas-Yazigi, V. Paredes-García, R. Baggio, M.A. Novak, E. Spodine, [Cu(H₂btec)(bipy)]_∞: A novel metal organic framework (MOF) as heterogeneous catalyst for the oxidation of olefins, *J. Chem. Soc. Dalt. Trans.* (2009) 1422–1427. <https://doi.org/10.1039/b810414j>.
- [23] Y.Y. Liu, K. Leus, T. Bogaerts, K. Hemelsoet, E. Bruneel, V. Van Speybroeck, P. Van Der Voort, Bimetallic-organic framework as a zero-leaching catalyst in the aerobic oxidation of cyclohexene, *ChemCatChem.* 5 (2013) 3657–3664. <https://doi.org/10.1002/cctc.201300529>.
- [24] T. Toyao, K. Miyahara, M. Fujiwaki, T.H. Kim, S. Dohshi, Y. Horiuchi, M. Matsuoka, Immobilization of Cu complex into Zr-based MOF with bipyridine units for heterogeneous selective oxidation, *J. Phys. Chem. C.* 119 (2015) 8131–8137. <https://doi.org/10.1021/jp512749y>.
- [25] P. Karandikar, M. Agashe, K. Vijayamohanan, A.J. Chandwadkar, Cu²⁺-perchlorophthalocyanine immobilized MCM-41: Catalyst for oxidation of alkenes, *Appl. Catal. A Gen.* 257 (2004) 133–143. <https://doi.org/10.1016/j.apcata.2003.07.007>.
- [26] M. Ghadiri, F. Farzaneh, M. Ghandi, M. Alizadeh, Immobilized copper(II) complexes on montmorillonite and MCM-41 as selective catalysts for epoxidation of alkenes, *J. Mol. Catal. A Chem.* 233 (2005) 127–131. <https://doi.org/10.1016/j.molcata.2005.01.046>.
- [27] S. Jana, B. Dutta, R. Bera, S. Koner, Anchoring of copper complex in MCM-41 matrix: A highly efficient catalyst for epoxidation of olefins by tert-BuOOH, *Langmuir.* 23 (2007) 2492–2496. <https://doi.org/10.1021/la062409t>.

- [28] J. Hu, K. Li, W. Li, F. Ma, Y. Guo, Selective oxidation of styrene to benzaldehyde catalyzed by Schiff base-modified ordered mesoporous silica materials impregnated with the transition metal-monosubstituted Keggin-type polyoxometalates, *Appl. Catal. A Gen.* 364 (2009) 211–220. <https://doi.org/10.1016/j.apcata.2009.05.058>.
- [29] M. Nandi, P. Roy, H. Uyama, A. Bhaumik, Functionalized mesoporous silica supported copper(ii) and nickel(ii) catalysts for liquid phase oxidation of olefins, *Dalt. Trans.* 40 (2011) 12510–12518. <https://doi.org/10.1039/c1dt10157a>.
- [30] T. Asefa, M.J. MacLachlan, N. Coombs, G.A. Ozin, Periodic mesoporous organosilicas with organic groups inside the channel walls, *Nature.* 402 (1999) 867–871. <https://doi.org/10.1038/47229>.
- [31] S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, Novel mesoporous materials with a uniform distribution of organic groups and inorganic oxide in their frameworks, *J. Am. Chem. Soc.* 121 (1999) 9611–9614. <https://doi.org/10.1021/ja9916658>.
- [32] B.J. Melde, B.T. Holland, C.F. Blanford, A. Stein, Mesoporous sieves with unified hybrid inorganic/organic frameworks, *Chem. Mater.* 11 (1999) 3302–3308. <https://doi.org/10.1021/cm9903935>.
- [33] P. Van Der Voort, D. Esquivel, E. De Canck, F. Goethals, I. Van Driessche, F.J. Romero-Salguero, Periodic Mesoporous Organosilicas: from simple to complex bridges; a comprehensive overview of functions, morphologies and applications, *Chem. Soc. Rev.* 42 (2013) 3913–3955. <https://doi.org/10.1039/C2CS35222B>.
- [34] M. Gholinejad, B. Karimi, A. Aminianfar, M. Khorasani, One-Pot Preparation of Propargylamines Catalyzed by Heterogeneous Copper Catalyst Supported on Periodic Mesoporous Organosilica with Ionic Liquid Framework, *Chempluschem.* 80 (2015) 1573–1579. <https://doi.org/10.1002/cplu.201500167>.
- [35] D. Elhamifar, H. Ardeshtirfard, Phenyl and ionic liquid based bifunctional periodic mesoporous organosilica supported copper: An efficient nanocatalyst for clean production of polyhydroquinolines, *J. Colloid Interface Sci.* 505 (2017) 1177–1184. <https://doi.org/10.1016/j.jcis.2017.07.010>.

- [36] S. Ishikawa, Y. Maegawa, M. Waki, S. Inagaki, Well-controlled radical-based epoxidation catalyzed by copper complex immobilized on bipyridine-periodic mesoporous organosilica, *Appl. Catal. A Gen.* 575 (2019) 87–92. <https://doi.org/10.1016/j.apcata.2019.02.007>.
- [37] D. Esquivel, E. De Canck, C. Jimenez-Sanchidrian, P. Van Der Voort, F.J. Romero-Salguero, Formation and functionalization of surface Diels–Alder adducts on ethenylene-bridged periodic mesoporous organosilica, *J. Mater. Chem.* 21 (2011) 10990–10998. <https://doi.org/10.1039/c1jm11315a>.
- [38] D. Esquivel, E. De Canck, C. Jiménez-Sanchidrián, F.J. Romero-Salguero, P. Van Der Voort, Pyrrole PMOs, incorporating new N-heterocyclic compounds on an ethene-PMO through Diels-Alder reactions, *Mater. Chem. Phys.* (2014). <https://doi.org/10.1016/j.matchemphys.2014.08.004>.
- [39] D. Esquivel, A.M. Kaczmarek, C. Jiménez-Sanchidrián, R. Van Deun, F.J. Romero-Salguero, P. Van Der Voort, Eu³⁺@PMO: synthesis, characterization and luminescence properties, *J. Mater. Chem. C.* 3 (2015) 2909–2917. <https://doi.org/10.1039/C4TC02553A>.
- [40] A.M. Kaczmarek, D. Esquivel, J. Ouwehand, P. Van Der Voort, F.J. Romero-Salguero, R. Van Deun, Temperature dependent NIR emitting lanthanide-PMO/silica hybrid materials, *Dalt. Trans.* 46 (2017) 7878–7887. <https://doi.org/10.1039/C7DT01620D>.
- [41] A.M. Kaczmarek, D. Esquivel, B. Laforce, L. Vincze, P. Van Der Voort, F.J. Romero-Salguero, R. Van Deun, Luminescent thermometer based on Eu³⁺/Tb³⁺-organic-functionalized mesoporous silica, *Luminescence.* 33 (2018) 567–573. <https://doi.org/10.1002/bio.3447>.
- [42] Q. Yang, J. Liu, J. Yang, L. Zhang, Z. Feng, J. Zhang, C. Li, Acid catalyzed synthesis of ordered bifunctionalized mesoporous organosilicas with large pore, *Microporous Mesoporous Mater.* 77 (2005) 257–264. <https://doi.org/10.1016/j.micromeso.2004.09.009>.

- [43] S. Samanta, S. Das, P. Biswas, Synthesis of 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) capped silver nanoparticles using 3,6-di(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine as reducing agent: Application in naked eye sensing of Cu²⁺, Ni²⁺ and Ag⁺ ions in aqueous solution and paper p, *Sensors Actuators, B Chem.* 202 (2014) 23–30. <https://doi.org/10.1016/j.snb.2014.05.036>.
- [44] T. Asefa, M. Kruk, M.J. MacLachlan, N. Coombs, H. Grondey, M. Jaroniec, G.A. Ozin, V. Uni, S.G. Street, K. State, V. Uni, R. V October, V. Re, M. Recci, V. June, Novel Bifunctional Periodic Mesoporous Organosilicas, BPMOs : Synthesis , Characterization , Properties and in-Situ Selective Hydroboration - Alcoholysis Reactions of Functional Groups, *J. Am. Chem. Soc.* 123 (2001) 8520–8530. <https://doi.org/10.1021/ja0037320>.
- [45] T.T. Igarashi Naoko, Tanaka Yoshinori, Nakata Shin-ichi, Increased Stability of Organically Modified MCM-41 Synthesized by a One-step Procedure, *Chem. Lett.* 28 (1999). <https://doi.org/10.1246/cl.1999.1>.
- [46] J. Amaro-Gahete, A.M. Kaczmarek, D. Esquivel, C. Jiménez-Sanchidrián, P. Van Der Voort, F.J. Romero-Salguero, Luminescent Graphene-Based Materials via Europium Complexation on Dipyridylpyridazine-Functionalized Graphene Sheets, *Chem. - A Eur. J.* 25 (2019) 6823–6830. <https://doi.org/10.1002/chem.201900512>.
- [47] G. Avgouropoulos, T. Ioannides, Selective CO oxidation over CuO-CeO₂ catalysts prepared via the urea – nitrate combustion method, *Appl. Catal. A Gen.* 244 (2003) 155–167. [https://doi.org/10.1016/S0926-860X\(02\)00558-6](https://doi.org/10.1016/S0926-860X(02)00558-6).
- [48] R. Hoogenboom, G. Kickelbick, U.S. Schubert, Synthesis and Characterization of Novel Substituted 3,6-Di(2-pyridyl)pyridazine Metal-Coordinating Ligands, *European J. Org. Chem.* 2003 (2003) 4887–4896. <https://doi.org/10.1002/ejoc.200300505>.
- [49] Y. Naganawa, Y. Maegawa, H. Guo, S.S. Gholap, S. Tanaka, K. Sato, S. Inagaki, Y. Nakajima, Heterogeneous hydrosilylation reaction catalysed by platinum complexes immobilized on bipyridine-periodic mesoporous organosilicas, *Dalt. Trans.* 48 (2019) 5534–5540. <https://doi.org/10.1039/C9DT00078J>.
- [50] J. Sun, Q. Kan, Z. Li, G. Yu, H. Liu, X. Yang, Q. Huo, J. Guan, Different transition metal (Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺ or VO₂⁺) Schiff complexes immobilized onto three-dimensional mesoporous silica KIT-6 for the epoxidation of styrene, *RSC Adv.* 4 (2014) 2310–2317. <https://doi.org/10.1039/c3ra45599h>.

- [51] N. Gogoi, T. Begum, S. Dutta, U. Bora, P.K. Gogoi, Rice husk derived nanosilica supported Cu(II) complex: An efficient heterogeneous catalyst for oxidation of alcohols using TBHP, *RSC Adv.* 5 (2015) 95344–95352. <https://doi.org/10.1039/c5ra21148d>.
- [52] P.H.O. Santiago, C.M. Aiube, J.L. de Macedo, C.C. Gatto, Hydrazone-derived copper(II) coordination polymer as a selective liquid-phase catalyst: Synthesis, crystal structure and performance towards benzyl alcohol oxidation, *Mol. Catal.* 496 (2020) 111177. <https://doi.org/10.1016/j.mcat.2020.111177>.
- [53] C. Saux, L.B. Pierella, *Applied Catalysis A : General Studies on styrene selective oxidation to benzaldehyde catalyzed by Cr-ZSM-5 : Reaction parameters effects and kinetics*, "Applied Catal. A, Gen. 400 (2011) 117–121. <https://doi.org/10.1016/j.apcata.2011.04.021>.
- [54] B. Li, X. Luo, Y. Zhu, X. Wang, Immobilization of Cu(II) in KIT-6 supported Co₃O₄ and catalytic performance for epoxidation of styrene, *Appl. Surf. Sci.* 359 (2015) 609–620. <https://doi.org/10.1016/j.apsusc.2015.10.131>.
- [55] F. Yu, X.J. Kong, Y.Y. Zheng, Y.P. Ren, L.S. Long, R. Bin Huang, L.S. Zheng, pH-dependent assembly of 0D to 3D Keggin-based coordination polymers: Structures and catalytic properties, *J. Chem. Soc. Dalt. Trans.* (2009) 9503–9509. <https://doi.org/10.1039/b911606k>.
- [56] S. Seelan, S. Sinha, D. Srinivas, S. Sivasanker, Spectroscopic investigation and catalytic activity of copper(II) phthalocyanine encapsulated in zeolite Y, *J. Mol. Catal. A Chem.* 157 (2000) 163–171. [https://doi.org/10.1016/S1381-1169\(99\)00432-X](https://doi.org/10.1016/S1381-1169(99)00432-X).
- [57] H. Su, Z. Li, Q. Huo, J. Guan, Q. Kan, Immobilization of transition metal (Fe²⁺, Co²⁺, VO²⁺ or Cu²⁺) Schiff base complexes onto graphene oxide as efficient and recyclable catalysts for epoxidation of styrene, *RSC Adv.* 4 (2014) 9990–9996. <https://doi.org/10.1039/c3ra47732k>.