View Article Online View Journal

CrystEngComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: D. Julião, A. D. S. Barbosa, A. Peixoto, C. Freire, B. de Castro, S. S.Balula and L. Cunha-Silva, *CrystEngComm*, 2017, DOI: 10.1039/C7CE00528H.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/crystengcomm

CrystEngComm

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 06 June 2017. Downloaded by State University of New York at Binghamton on 08/06/2017 15:22:10.

Improved catalytic performance of porous metalorganic frameworks for ring-opening of styrene oxide[†]

Diana Julião[‡], André D. S. Barbosa[‡], Andreia F. Peixoto, Cristina Freire, Baltazar de Castro, Salete S. Balula^{*} and Luís Cunha-Silva^{*}

An emerging strategy to improve the performance of porous metal-organic framework (MOF) materials as heterogeneous catalysts is reported. The incorporation of the iron-substituted polyoxometalate (POM) TBA₄[PW₁₁Fe(H₂O)O₃₉] (PW₁₁Fe) in the porous MOF NH₂-MIL-101(Fe), leading to a novel composite based MOF material, PW₁₁Fe@NH₂-MIL-101(Fe), revealed to be a significant approach to increase the efficiency of the MOF material as regioselective catalyst for ring-opening of styrene oxide with aniline. The conversion after 1 h of reaction using the NH₂-MIL-101(Fe) is 22% and augments to 100% when the PW₁₁Fe@NH₂-MIL-101(Fe) is employed as catalyst. Noteworthy, the catalytic performance of this composite material is also considerably better than that obtained with the respective physical mixture in similar conditions. Furthermore, PW₁₁Fe@NH₂-MIL-101(Fe) revealed to be a remarkable selective heterogeneous catalyst for the studied reaction (100% of selectivity to the 2-phenylamino-2-phenylethanol isomer), with significant robustness and recycle ability.

Introduction

Metal–organic frameworks (MOFs), also known as coordination networks or coordination polymers, are crystalline materials based on metal centers or metallic clusters interconnected by multidentate organic ligands to form uni- (1D), bi- (2D) or three-dimensional (3D) infinite structures.¹⁻⁵ Their synthesis can be judiciously designed and rationalized to obtain porous MOFs with specific structures and topologies, large surface areas and tunable pore features.⁶⁻⁸ These remarkable characteristics confer the porous MOFs a high potential for numerous applications, principally catalysis.⁹⁻¹³, gas adsorption and separation ¹⁴⁻¹⁸, chemical sensing,^{19, 20} luminescence,^{19, 20} drug delivery^{21, 22} and proton conduction^{23, 24}. In particular, porous MOFs have attracted high scientific interest as heterogeneous catalysts in numerous type of chemical reactions, as consequence of the immense possibility of combination of different active sites (active metal centers and / or active functional organic linkers) in the same material.^{10, 11, 25-28} More recently, the porous MOFs have been explored as solid supports of catalytic active species, for example metallic nanoparticles^{29-³¹, metal oxides³²⁻³⁴, organometallic or coordination complexes^{35, 36}, to prepare efficient and sustainable heterogeneous catalysts in distinct reactions.}

In particular, the MIL-101 family of MOF materials reveal a porous 3D framework based in trimeric metal building units, with general formula $[M_3X(H_2O)_2O(L)_3]$ $\cdot n(H_2O)$ (usually M=Cr(III), Fe(III) or Al(III), X⁻ = F⁻ or OH⁻, $n \approx 25$ and L stands for amino- or 1,4-benzene-dicarboxylic acid). These inorganic trimers are formed by three M(III) centres with octahedral coordination environment {MO₆}. Adjacent octahedral moieties interconnect through the μ_3 -O atom to originate the trimeric building unit which are connected by the organic linkers (six ligands bonded at each trimeric cluster), finally leading the porous 3D framework material. This structural arrangement



REQUIMTE - LAQV & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal. e-mails: *sbalula@fc.up.pt* and *l.cunha.silva@fc.up.pt*;

Tel: +351 220402576; Fax: +351 220402659

[†] Electronic Supplementary Information (ESI) available: additional relevant figures, particularly UV-VIS and FTIR spectra, powder XRD patterns, SEM images and ¹H NMR spectrum. See DOI: 10.1039/x0xx00000x

[‡] authors contributed equally as first authors.

ARTICLE

CrystEngComm

establishes a network of microporous channels (apertures of *ca.* 8.6 Å) inter-connecting two different mesoporous cages in a ratio of 2:1, with internal free diameters of *ca.* 29 Å and 34 Å, respectively.³⁷

The epoxide ring-opening reaction by amines is very important since the resulting products, such as β aminoalcohols, possess a considerable interest in the preparation of biologically active compounds and synthetic products in different chemical fields.^{38, 39} The βaminoalcohols are usually synthesized by the direct aminolysis of epoxides. However, this reaction often involves a large excess of amines and high temperatures, so to promote useful modifications in habitual procedures, homogeneous catalysts have been widely applied.40-43, 44 Despite the effort to improve the epoxide ring-opening reaction, most of the homogeneous catalysts used are expensive, not efficient, toxic and instable. Some catalysts showed excellent performance in aminolysis of different kind of epoxides using mild conditions. Particularly, the iron-substituted polyoxometalate (POM) $TBA_4[PW_{11}Fe(H_2O)O_{39}]$ (PW11Fe), revealed high performance as homogeneous catalyst in this reaction;42 nevertheless, its recover and recycle have serious drawbacks. To overcome these limitations new strategies for converting soluble POMs to solid materials that would be stable in the liquid phase have been studied by many research groups.^{33, 45-49} Various types of materials have been used in the heterogenization of catalytically active species resulting in efficient heterogeneous catalyst based materials.50 The incorporation of POMs into porous MOFs have demonstrated to decrease the reaction time, due to concentration effect between the different components from the catalytic reaction, resulting of the large cavities of certain MOFs.33,51

Following the recent investigation of our research group in the design and application of advanced MOF-based materials as catalysts^{32-34, 47, 52-57}, two novel composites were prepared by incorporation of PW11Fe into NH2-MIL-101(Fe) and MIL-101(Cr) (denoted, respectively as and PW₁₁Fe@NH₂-MIL-101(Fe) PW11Fe@MIL-101(Cr), Figure 1), which were employed as heterogeneous catalysts in the ring-opening of cycloalkene oxide. To date there are only a report on the use of POM@MOFs as catalysts in the ring-opening reaction of cycloalkene oxide in the presence of methanol.58 Recently, we demonstrated that iron-based MOFs behave as active and selective catalysts for this type of reaction.57 This work presents a new synthetic strategic to increase easily the catalytic performance of active MOFs by encapsulating a POM guest. Using the POM@MOFs instead of the free MOF structure, in the ring-opening of styrene oxide

in the presence of aniline, 100% yield of 2-phenylamino-2-phenylethanol could be achieved aftep h_0 instead fep 248 needed using the free MOF. Under these conditions, the POM@MOFs showed high robustness and high recycle capacity.



Figure 1. Schematic representation of the composite material PW₁₁Fe@MIL-101(Cr).

Experimental section Materials and methods

All the reagents utilized in the syntheses and preparation of the compounds and materials were used as received: tetrabutylammonium bromide (TBA·Br, $C_{16}H_{36}BrN$, Alfa Aesar, 98%), sodium tungstate dihydrate (Na₂WO₄·2H₂O, Aldrich, \geq 99.0%), sodium phosphate (Na₃PO₄, Aldrich, 96%), iron (III) chloride hexahydrate (FeCl₃·6H₂O, Merck, p.a), chromium(III) nitrate nonahydrate [Cr(NO₃)₃.9H₂O, Aldrich, 99%], terephthalic acid (H₂bdc, $C_8H_6O_2$, Aldrich, 98%), 2-aminoterephthalic acid (NH₂-H₂bdc, $C_8H_8NO_2$, Aldrich, 99%) and dimethylformamide (C₃H₇NO, DMF, Fluka, 99.0%). Furthermore, the chemicals used in the catalytic studies were used as purchased from commercial supplies without any purification: acetonitrile (MeCN, CH₃CN, Panreac, 99.8%), aniline (C₆H₇N, Aldrich, 99%) and styrene oxide (C₈H₈O, Aldrich, 97%), were also used as received.

Powder X-ray diffraction (XRD) patterns were collected at room temperature on a on a Empyrean PANalytical diffractometer (Cu_{Kα1,2} radiation, $\lambda_1 = 1.540598$ Å and $\lambda_2 = 1.544426$ Å), equipped with an PIXcel 1D detector and a flat-plate sample holder in a Bragg–Brentano para-focusing optics configuration (45 kV, 40 mA). Intensity data were obtained by the step-counting method (step 0.02^o), in continuous mode in the approximate range $3.0^o \le 2\theta \le 50^o$.

CrystEngComm

CrystEngComm

Infrared absorption spectra were recorded on a PerkinElmer spectrum BX FTIR spectrometer equipped with a Pike GldiATR device for measurements in attenuated total reflectance (ATR) mode.

W and Fe analysis was carried out by ICP-OES on a Varian 820-MS at "Universidade de Satiago de Compostela".

Scanning electron microscopy (SEM) images were performed in a high resolution scanning electron microscope FEI Quanta 400 FEG ESEM. The energydispersive X-ray spectroscopy (EDX) studies were recorded in the same microscope working at 10 keV and using an EDAX Genesis X4M microanalysis system. SEM and EDX analysis were performed at "Centro de Materiais da Universidade do Porto" (CEMUP, Porto, Portugal).

GC-FID was performed in a Varian V3800 chromatograph to monitor catalytic reactions and a Bruker 430-GC to follow the reactions. In both experiments, hydrogen was the carrier gas (55 cm³ s⁻¹) and fused silica Supelco capillary columns SPB-5 (30 m × 0.25 mm i.d.; 25 μ m film thickness) were used.

Preparation of the materials

Fe-substituted polyoxometalate. TBA salts of ironsubstituted POM, TBA₄[PW₁₁Fe(H₂O)O₃₉] (PW₁₁Fe), was synthesized according to reported procedures.⁵⁹ The compound was characterized by elemental and TGA analysis, FTIR spectroscopy and powder XRD, unequivocally confirming their preparation. Anal. Calcd. (%) for C₆₄H₁₄₆N₄O₄₀PW₁₁Fe (3720,90 gmol⁻¹): C, 21.62; H, 3.72; N, 1.63. Found: C, 20.66; H, 3.95; N, 1.51. FTIR (cm⁻¹): v = 2962(m), 2874 (w), 2360 (s), 2342 (s), 1484 (m), 1064 (s), 960 (s), 884 (s), 800 (vs), 668 (m), 594 (w), 516 (m), 374 (vs).

NH₂-MIL-101(Fe). The porous MOF material NH₂-MIL-101(Fe) was prepared using the reported procedure.⁶⁰ Anal. found (%): Fe, 12.4. FTIR (cm⁻¹): v = 3460 (w), 3324 (w), 1652 (w), 1574 (s), 1496 (m), 1418 (m), 1382 (vs), 1338 (m), 1256 (s), 968 (w), 892 (w), 828 (m), 766 (w), 692 (w), 626 (w), 570 (w), 518 (w), 434 (w), 382 (m).

MIL-101(Cr). The porous MOF MIL-101(Cr) was synthesized employing the original method described by Férey and co-workers.³⁷ FTIR (cm⁻¹): v = 2976 (m), 2902 (m), 2360 (w), 1672 (w), 1632 (s), 1560 (m), 1510 (w), 1434 (vs), 1398 (w), 1076 (s), 1066 (w), 1050 (w), 884 (w), 834 (w), 810 (w), 746 (s), 714 (w), 668 (m), 588 (s), 468 (m).

Composite materials PW₁₁**Fe@MIL-101.** The two composite materials were prepared by adaptation of the method previously reported.⁴⁹ In brief, 0.6 g of the porous support material, NH₂-MIL-101(Fe) or MIL-101(Cr), were added to a solution of PW₁₁Fe in MeCN (10 mM in 13 mL)

Catalytic studies

The ring-opening reactions of styrene oxide (Scheme 1) were carried out in borosilicate 5 mL reaction vessel equipped with a magnetic stirrer and immersed in a thermostated oil bath under air (atmospheric pressure), using acetonitrile (MeCN) as the solvent at 80°C. In a typical procedure the styrene oxide (1 mmol), aniline (0.9 mmol) and the catalyst were dispersed in MeCN (1,5 mL).

As the iron cation is the active catalytic center, all the catalytic reactions were performed using a total of 50 µmol of Fe-amount, what corresponded to use 0,025 g of PW₁₁Fe@NH₂-MIL-101(Fe) and 0,442 g PW₁₁Fe@MIL-101(Cr) of composites. The most efficient heterogeneous catalyst was recycled in consecutive cycles. At the end of each reaction cycle, the composite was washed with MeCN and dried at room temperature overnight. Then, the recovered catalyst was reused in a new catalytic cycle maintaining the previous experimental conditions. The styrene oxide ring-opening reactions were monitored by GC analysis and stopped when a completed conversion of aniline was observed or when the product yields remained constant after two successive GC analyses. An aliquot was taken directly from the reaction mixture with a microsyringe at regular intervals; the heterogeneous catalysts were centrifuged and then the solution was injected into the GC equipment for analysis of the starting material and products. The reaction products were identified ¹HNMR spectroscopy.

CrystEngComm

Page 4 of 11



Scheme 1. Ring-opening of styrene oxide with aniline.

Results and discussion

Catalysts preparation and characterization

The porous MOFs, NH₂-MIL-101(Fe) and MIL-101(Cr), were used as solid support for the incorporation of TBA salt of iron-substituted POM, TBA₄[PW₁₁Fe(H₂O)O₃₉] (PW₁₁Fe), originating two unprecedented composite materials: PW₁₁Fe@NH₂-MIL-101(Fe) and PW₁₁Fe@MIL-101(Cr). These materials were prepared by the impregnation method, which has been largely employed and it is well established in our group. ^{32-34, 47, 52, 55, 56} Initially, the incorporation of the PW₁₁Fe in the MIL-101 frameworks was monitored by UV-Vis spectroscopy (Figure S1 in the Electronic Supplementary Information, ESI). The UV-Vis



Figure 2. FTIR spectra of the PW₁₁Fe, the support NH₂-MIL-101(Fe) and the composite, before (PW₁₁Fe@NH₂-MIL-101(Fe)) and after catalytic use (PW₁₁Fe@NH₂-MIL-101(Fe)_ac, recovered after the 3^{rd} reaction cycle).

spectra of the MeCN solution after 24 hours of react and the MeCN solution after 24 hours of react and the bound of the POM at *ca*. 250 nm (corresponds to the charge transition from the bridging O-atoms to W-atoms) relatively to the spectra of the initial POM solution. This observation confirms the decrease in the amount of the PW₁₁Fe in solution, most probably due to its incorporation into the porous MOFs. The composite materials were further characterized by several techniques including FTIR spectroscopy, powder XRD, metal analysis (ICP), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

The presence of POM in the MIL-101 was initially verified by FTIR spectroscopy, comparing the spectra of the composite materials with the spectra of the POM and respective solid support (Figures 2 and S2 in ESI). The FTIR spectrum of the PW11Fe@NH2-MIL-101(Fe) reveals the characteristic bands of the POM, namely vas(P-O) at 1064 cm⁻¹, v_{as}(W=0) at 966 cm⁻¹ and v_{as}(W-0-W) at 896 cm⁻¹ ¹, as well as the vibrational modes of the MOF, namely the asymmetric and symmetric u(0-C-O) at 1496 cm⁻¹ and 1418 cm⁻¹ respectively (Figure 2). At 3466 cm⁻¹ and 3352 cm⁻¹ the spectra of composite material also exhibits the asymmetric and symmetric stretches associated amine groups and at 766 cm⁻¹ the stretching mode of the aromatic rings δ (C–H) was observed.^{61, 62} The characteristic bands of the PW₁₁Fe in the FTIR spectrum of PW11Fe@MIL-101(Cr) were observed at 1064, 960 and 886 cm⁻¹ and assigned to the P–O, W=O and W-O-W stretching modes, respectively (Figure S2 in ESI). The W and Fe analysis further support the presence of the PW11Fe in the respective composite materials, revealing a PW₁₁Fe loading of 0.046 and 0.113 mmol g⁻¹ in PW₁₁Fe@NH₂-MIL-101(Fe) and PW11Fe@MIL-101(Cr), respectively.





Figure 3. Powder XRD patterns of the $PW_{11}Fe$, the solid support $NH_2\text{-}MIL\text{-}101(Fe)$ and the composite material before $PW_{11}Fe@NH_2\text{-}MIL\text{-}101(Fe)$ and after the 3^{rd} catalytic use $PW_{11}Fe@NH_2\text{-}MIL\text{-}101(Fe)_ac.$

The integrity of the MOF structure in the composite materials was confirmed by powder XRD (Figures 3 and S3 in ESI). The diffraction pattern of the composite material PW11Fe@NH2-MIL-101(Fe) does not reveal extensive changes relatively to that of the "Pree".1969/67/Stopport, indicating that the global crystalline structure of the solid support is maintained after the incorporation of the PW₁₁Fe (Figure 3). The powder XRD pattern of the PW₁₁Fe@MIL-101(Cr) shows significant differences with respect with the difractogram of the MIL-101(Cr) support. Some relevant peaks that do not match with those of PW11Fe emerged between *ca*. 5° and 8° (2 θ) in the diffraction pattern of the composite material. This type of changes were already observed and reported for related composite materials based in MIL-101(Cr).47, 63 Bromberg and co-workers concluded that these emerged peaks are in fact not "new", since the Bragg peak positions are consistent with the unit cell of MIL-101 family. These unmodified MOFs possess those peaks with null or very weak intensity. The incorporation of the POM in porous framework affects the electron density of the crystal structure of MIL-101, creating the observed diffracted intensity at these positions.63 The absence of diffraction peaks corresponding to PW11Fe in the powder XRD pattern of the two composite materials suggests that the POM is incorporated in the solid support in a random dispersed form. In fact, the incorporation of the PW₁₁Fe in the porous framework of the two distinct support materials, NH2-MIL-101(Fe) and MIL-101(Cr), doesn't causes degradation and/or collapse of their structure.



Figure 4. SEM images of solid support NH₂-MIL-101(Fe) (**a**), and the composite material before $PW_{11}Fe@NH_2-MIL-101(Fe)$ (**b**) and after the 3^{rd} catalytic use catalytic use $PW_{11}Fe@NH_2-MIL-101(Fe)_ac$ (**c**).

CrystEngComm

ARTICLE

Published on 06 June 2017. Downloaded by State University of New York at Binghamton on 08/06/2017 15:22:10.



Figure 5. EDX elemental mapping images for the composite material before $PW_{11}Fe@NH_2-MIL-101(Fe)$ (top) and after the 3^{rd} catalytic use $PW_{11}Fe@NH_2-MIL-101(Fe)_ac$ (bottom).

The of the composite SEM images materials PW₁₁Fe@MIL-101 show the same type of particles of the solid supports (Figures 4 and S4 in ESI). The similar morphology showed by the different materials, together with the XRD patterns previously discussed, are a indication that the main features of the crystalline structure of the solid supports are maintained unchanged after the incorporation of the POM. Additionally, the elemental mapping images reveal the presence and a uniform of W, confirming distribution unequivocally the homogeneous incorporation of $\mathsf{PW}_{11}\mathsf{Fe}$ in the composite material (Figure 5).

Catalytic studies

The ring-opening reaction of styrene oxide in the presence of aniline was catalyzed by two different Fe-MOFs based heterogeneous catalysts: $PW_{11}Fe@MIL-101(Cr)$ and $PW_{11}Fe@NH_2-MIL-101(Fe)$. All the reactions were performed using a total amount of 50 µmol of Fe and using MeCN as solvent. A blank reaction was performed without catalyst. In this case the aniline and the styrene oxide were not consumed during 2 h of reaction.

In our previous work, it was demonstrated that the support NH₂-MIL-101(Fe) is an active heterogeneous catalyst for the ring-opening of cyclohexene oxide in the presence of aniline, achieving 87% of conversion after 24 h at 80 °C.57 In this work, the same Fe-MOF support material was used as heterogeneous catalyst for the ring-opening of styrene oxide in the presence of aniline and close complete conversion was also obtained later than 24 h. However, after the first hour only 22% of conversion was achieved, which indicates that the Fe center in the MOF framework presents a small catalytic activity in this type of reaction. In fact the activity of the Fe centers in the MOF structure can be dependent to the presence of surface defects, which originate more active unsaturated Fe metal centers. The catalytic activity of MIL-101(Cr) was also investigated and no reaction occurred during the first 5 h of reaction.

In order to increase the catalytic efficiency of the NH₂-MIL-101(Fe), a strategic method based in the encapsulation of a catalytic active guest (PW₁₁Fe) into its cavities, forming the novel composite PW₁₁Fe@NH₂-MIL-101(Fe) was performed. Also, to evaluate the catalytic participation of the Fe centers from the MOF framework, the same active guest PW₁₁Fe was also encapsulated into the MIL-101(Cr) structure, PW₁₁Fe@MIL-101(Cr).

CrystEngComm

CrystEngComm



Figure 6. Kinetic profile for the ring-opening reaction of styrene oxide with aniline using various Fe-based catalysts (50 μ mol of total Fe) at 80 °C, in MeCN (solvent).

The results displayed in Figure 6 demonstrate that the composite PW11Fe@NH2-MIL-101(Fe) is significantly more active than the support NH₂-MIL-101(Fe), using in both reactions a total of 50 µmol of Fe. In fact, using the heterogeneous PW11Fe@NH2-MIL-101(Fe) catalyst it is possible to achieve complete conversion after 1 h of reaction. The same conversion was obtained by the homogeneous PW11Fe; however, this presents the various disadvantages associated to the homogeneous catalysts, i.e. the impossibility of recovery from the reaction medium and recyclability. Using the PW₁₁Fe@NH₂-MIL-101(Fe) heterogeneous catalyst, after 1 h the catalyst could be isolated from reaction, the solvent could be evaporated and the products could be easily recovered. Comparing the catalytic activity of the PW₁₁Fe@NH₂-MIL-101(Fe) and the PW₁₁Fe@MIL-101(Cr), when in both cases a total of 50 µmol of Fe were used, it is possible to observe the superior catalytic activity of the PW₁₁Fe@NH₂-MIL-101(Fe) composite, demonstrating that the Fe centers in the MOF framework have an important contribution to achieve the complete conversion of the styrene oxide ring-opening reaction in the presence of aniline.

To better understand the contribution of the NH₂-MIL-101(Fe) support to the high catalytic activity of the composite PW₁₁Fe@NH₂-MIL-101(Fe), a comparative study was performed between this composite and the guest compound PW₁₁Fe in equal amounts (1 µmol). As expected, the styrene oxide conversion decreased when a lower amount (1 µmol; Figure 7) of the homogeneous catalyst PW₁₁Fe was used, relatively to the result obtained with higher quantity (50 µmol; Figure 6). Therefore, the 1 µmol of PW₁₁Fe encapsulated into NH₂-MIL-101(Fe) support is much more active than the free PW₁₁Fe (Figure 7). Additionally, when the support NH₂- MIL-101(Fe) (containing 49 µmol of Fe in the framework) is added to 1 µmol $PW_{11}Fe_{35}$ (Figure 7). These activity increased but not as much as the composite $PW_{11}Fe@NH_2$ -MIL-101(Fe) system (Figure 7). These results indicate that the support NH_2 -MIL-101(Fe) has an important influence in the activity of the active $PW_{11}Fe$ guest, in addition to the confinement effect conferred by the MOF cavities.



Figure 7. Kinetic profile for the ring-opening of styrene oxide with aniline in the presence of various Fe-based catalysts, using $1 \mu mol$ of PW₁₁Fe, MeCN as solvent at 80 °C.

The efficiency of the catalyst was also analyzed by its capacity to trail the reaction to produce mostly a single product. An efficient catalyst need to be highly selective. Both composites PW₁₁Fe@NH₂-MIL-101(Fe) and PW11Fe@MIL-101(Cr) presented 96 % of selectivity for the 2-phenylamino-2-phenylethanol (isomer 3 in scheme 1), according to Lewis acid catalyzed SN1 ring opening mechanism at the end of the reaction, i.e. after 1 h (Figures 5 and 7). 64,50 No differences in the selectivity were also found for the active support NH2-MIL-101(Fe) and for the homogeneous catalyst PW11Fe (selectivity of 98 % for isomer 3). The product 2-phenylamino-2-phenylethanol was isolated by column chromatography and identified by ¹H NMR (Figure S5 in ESI). 62, 65

In view of such excellent catalytic performance of the $PW_{11}Fe@NH_2-MIL-101(Fe)$ composite, the recycle capacity and the stability of this composite was investigated. At the end of each reaction cycle, the solid catalyst was recovered from reaction by centrifugation, washed thoroughly with MeCN, dried at room temperature and reused in a new catalytic cycle maintaining the experimental conditions.

CrystEngComm



Figure 8. Kinetic profile for the ring-opening reaction of styrene oxide in the presence of aniline, for three consecutive reaction cycles catalyzed by $PW_{11}Fe@NH_2-MIL-101(Fe)$ (50 µmol of total Fe, 1 µmol of $PW_{11}Fe$).

The recyclability data for PW11Fe@NH2-MIL-101(Fe) is displayed in Figure 8. It is possible to verify a high capacity of recyclability of this composite since complete consume of aniline was achieved for the three consecutive cycles after only 1 h. A slightly increase of activity is observed for the second and the third cycles, what can be associated to some structural reorganization occurred during the first cycle to form a more active catalytic composite. Furthermore, in order to evaluate the stability of the composite and to investigate the possibility of active centers loss, a leaching test was performed. In this experiment, the solid was removed from the reaction mixture after 10 min of its initiation; following the analysis of the filtrate for more 50 min. Figure 8 presents the results obtained from the leaching test, which indicates that the reaction practically stopped after the solid removal. This behavior demonstrates the heterogeneity of the PW₁₁Fe@NH₂-MIL-101(Fe) composite and the absence of loss of active Fe species.

Catalyst material stability

The structural stability of the PW₁₁Fe@NH₂-MIL-101(Fe) catalyst was evaluated through the extensive characterization of the solid recovered after the catalytic use (PW₁₁Fe@NH₂-MIL-101(Fe)-ac). FTIR data of the composite after catalytic use (Figure 2) show that the characteristic bands of the material remain unaltered. In particular, no changes are observed in the bands assigned to the active guest PW₁₁Fe stretching modes (1000-850 cm⁻¹), suggesting that the PW₁₁Fe structure is also preserved after catalytic use. The powder XRD patterns before and after catalytic use (Figure 3) reveal the maintenance of the main diffraction peaks, accompanied with a slight decrease of peak intensity in the 5°-10° range, as well as at 20°, 24° and 29°. This partial loss in crystallinity was expected, as verified in previous literature regarding the Solid 1330 port 2052 and addition, the SEM/EDX techniques were also used to study the morphology and chemical composition of PW11Fe@NH2-MIL-101(Fe)-ac. SEM images (Figure 4) reveal a similar morphology to the as-prepared crystalline composed with no evidence of degradation. EDX mapping images of PW11Fe@NH2-MIL-101(Fe)-ac (Figure 5) also show an identical chemical composition to the sample before catalysis. Thus, the characterization data points out to the PW₁₁Fe@NH₂-MIL-101(Fe) high robustness of the heterogeneous catalyst suggested by the structural preservation of the material after catalytic use.

Concluding remarks

A tactical approach to activate widely the catalytic performance of the MOF structures to form novel heterogeneous catalysts for the ring-opening reaction of styrene oxide in the presence of aniline was reported. The highly active composites were prepared by the simple encapsulation of iron-substituted POM PW11Fe into NH2-MIL-101(Fe) and MIL-101(Cr) large porous cavities. The composites PW11Fe@NH2-MIL-101(Fe) and PW11Fe@MIL-101(Cr) revealed high efficiency and notably selectivity to the 2-phenylamino-2-phenylethanol isomer (isomer 3 in scheme 1) after 1 h of reaction. Both composites PW₁₁Fe@NH₂-MIL-101(Fe) and PW₁₁Fe@MIL-101(Cr) presented 96 % of selectivity for the 2-phenylamino-2phenylethanol, according to Lewis acid catalyzed SN1 ring opening mechanism at the end of the reaction, i.e. after 1 h (Figures 5 and 7). No differences in the selectivity were found for the active support NH2-MIL-101(Fe) and for the homogeneous catalyst PW11Fe (selectivity of 98 % for isomer 3).

The materials PW₁₁Fe@NH₂-MIL-101(Fe) showed higher catalytic performance than the PW₁₁Fe@MIL-101(Cr), what is due to the catalytic activity attributed to the Fe centers of the NH₂-MIL-101(Fe) framework, as well as to the mutual activation occurred between the PW₁₁Fe guest and the NH₂-MIL-101(Fe) support, promoted by the effective interaction of the guest and the MOF framework. Furthermore, when the catalytic activity of the isolated guest PW₁₁Fe and the free support NH₂-MIL-101(Fe) were analyzed separately and also in a physical mixture, their performance was appreciably inferior of the composite material PW₁₁Fe@NH₂-MIL-101(Fe). The high robustness and stability of the composite material was confirmed through characterization after catalytic use.

Following the promising results obtained, further work will be developed using this and other Fe-MOFs based composites as heterogeneous catalysts, to enlarge the success application of these heterogeneous catalysts to the valuable ring-opening reactions. A large number of epoxide compounds and several distinct amines will be evaluated to verify that this procedure based in MOF materials represents a reliable methodology for a broad epoxide aminolysis system.

Acknowledgements

Funding agencies and projects: the work was cofinanced by UE, FEDER - *Fundo Europeu de Desenvolvimento Regional* and COMPETE 2020 – *Programa Operacional Competitividade e Internacionalização* (POCI-01-0145-FEDER-007265) through PT 2020 and by national funds through the FCT / MCTES - *Fundação para a Ciência e a Tecnologia / Ministério da Ciência, Tecnologia e Ensino Superior* for the research centre REQUIMTE - LAQV (UID/QUI/50006/2013).

Individual grants: additional thanks to the FCT / MCTES for the PhD fellowships SFRH/BD/95574/2013 (to ADSB), SFRH/BD/102783/2014 (to DJ), and the Post-doctoral grants SFRH/BPD/72126/2010 (to AFP) and SFRH/BPD/111899/2015 (to LCS).

It is not possible to compare the activity of two different catalysts (PW12 and PW11Fe) in two different reactions (methanolysis and aminolysis of epoxides, respectively).

References

- 1. S. L. James, Chem. Soc. Rev., 2003, 32, 276-288.
- 2. J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mat.*, 2004, **73**, 3-14.
- 3. D. Maspoch, D. Ruiz-Molina and J. Veciana, *Chem. Soc. Rev.*, 2007, **36**, 770-818.
- 4. S. Kitagawa and R. Matsuda, *Coord. Chem. Rev.*, 2007, **251**, 2490-2509.
- D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257-1283.
- O. K. Farha and J. T. Hupp, Accounts Chem. Res., 2010, 43, 1166-1175.

- D. P. Cai, B. Liu, D. D. Wang, L. L. Wang, Y. Liu, B. H. Qu, X.
 C. Duan, Q. H. Li and T. H. Wang, *J. Mater* 101671 (2018) 41, 183-192.
- C. Wang, T. Zhang and W. B. Lin, *Chem. Rev.*, 2012, **112**, 1084-1104.
- 9. D. Farrusseng, S. Aguado and C. Pinel, *Angew. Chem. Int. Edit.*, 2009, **48**, 7502-7513.
- 10. A. Corma, H. Garcia and F. Xamena, *Chem. Rev.*, 2010, **110**, 4606-4655.
- J. W. Liu, L. F. Chen, H. Cui, J. Y. Zhang, L. Zhang and C. Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011-6061.
- 12. E. Gkaniatsou, C. Sicard, R. Ricoux, J. P. Mahy, N. Steunou and C. Serre, *Mater. Horizons*, 2017, **4**, 55-63.
- 13. Y. B. Huang, J. Liang, X. S. Wang and R. Cao, *Chem. Soc. Rev.*, 2017, **46**, 126-157.
- 14. B. Li, H. L. Wang and B. L. Chen, *Chem. Asian J.*, 2014, **9**, 1474-1498.
- 15. J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.
- 16. J. R. Li, Y. G. Ma, M. C. McCarthy, J. Sculley, J. M. Yu, H. K. Jeong, P. B. Balbuena and H. C. Zhou, *Coord. Chem. Rev.*, 2011, **255**, 1791-1823.
- 17. J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869-932.
- 18. J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown and J. Liu, Chem. Soc. Rev., 2012, 41, 2308-2322.
- L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105-1125.
- 20. F. Y. Yi, D. X. Chen, M. K. Wu, L. Han and H. L. Jiang, *ChemPlusChem*, 2016, **81**, 675-690.
- 21. W. Cai, C.-C. Chu, G. Liu and Y.-X. J. Wang, *Small*, 2015, **11**, 4806-4822.
- 22. J. Della Rocca, D. Liu and W. Lin, *Accounts Chem. Res.*, 2011, **44**, 957-968.
- 23. S. Horike, D. Umeyama and S. Kitagawa, *Accounts Chem. Res.*, 2013, **46**, 2376-2384.
- 24. M. Yoon, K. Suh, S. Natarajan and K. Kim, *Angew. Chem. Int. Edit.*, 2013, **52**, 2688-2700.
- 25. A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov and F. Verpoort, *Chem. Soc. Rev.*, 2015, **44**, 6804-6849.
- 26. A. Dhakshinamoorthy, M. Opanasenko, J. Cejka and H. Garcia, *Catal. Sci. Technol.*, 2013, **3**, 2509-2540.

CrystEngComm

- 27. M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, **112**, 1196-1231.
- 28. Y. Liu, W. M. Xuan and Y. Cui, *Adv. Mater.*, 2010, **22**, 4112-4135.
- 29. H. L. Liu, L. N. Chang, C. H. Bai, L. Y. Chen, R. Luque and Y. W. Li, *Angew. Chem. Int. Edit.*, 2016, 55, 5019-5023.
- 30. Q. H. Yang, Q. Xu, S. H. Yu and H. L. Jiang, *Angew. Chem. Int. Edit.*, 2016, **55**, 3685-3689.
- 31. P. Falcaro, R. Ricco, A. Yazdi, I. Imaz, S. Furukawa, D. Maspoch, R. Ameloot, J. D. Evans and C. J. Doonan, *Coord. Chem. Rev.*, 2016, **307**, 237-254.
- 32. C. M. Granadeiro, A. D. S. Barbosa, S. Ribeiro, I. C. M. S. Santos, B. de Castro, L. Cunha-Silva and S. S. Balula, *Catalysis Science & Technology*, 2014, **4**, 1416-1425.
- 33. C. M. Granadeiro, A. D. S. Barbosa, P. Silva, F. A. A. Paz, V. K. Saini, J. Pires, B. de Castro, S. S. Balula and L. Cunha-Silva, *Appl. Catal. A Gen.*, 2013, 453, 316-326.
- 34. C. M. Granadeiro, L. S. Nogueira, D. Juliao, F. Mirante, D. Ananias, S. S. Balula and L. Cunha-Silva, *Catal. Sci. Technol.*, 2016, 6, 1515-1522.
- 35. X. L. Li, R. Van Zeeland, R. V. Maligal-Ganesh, Y. C. Pei, G. Power, L. Stanley and W. Y. Huang, *ACS Catal.*, 2016, **6**, 6324-6328.
- 36. A. B. Redondo, F. L. Morel, M. Ranocchiari and J. A. van Bokhoven, *ACS Catal.*, 2015, **5**, 7099-7103.
- 37. G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040-2042.
- 38. A. V. Narsaiah, D. Sreenu and K. Nagaiah, Synth. Commun., 2006, 36, 3183-3189.
- 39. N. Azizi, B. Mirmashhori and M. R. Saidi, *Catal. Commun.*, 2007, **8**, 2198-2203.
- 40. S. R. Roy, A. Nijamudheen, A. Pariyar, A. Ghosh, P. K. Vardhanapu, P. K. Mandal, A. Datta and S. K. Mandal, *ACS Catal.*, 2014, **4**, 4307-4319.
- 41. N. Aramesh, B. Yadollahi and V. Mirkhani, *Inorg. Chem. Commun.*, 2013, **28**, 37-40.
- 42. H. Danafar and B. Yadollahi, *Catal. Commun.*, 2009, **10**, 842-847.
- 43. S. Tobisch, Chem.-Eur. J., 2015, 21, 6765-6779.
- 44. M. Distaso and E. Quaranta, J. Catal., 2008, 253, 278-288.

- N. V. Maksimchuk, K. A. Kovalenko, S. S. Arzumanov, Y. A. Chesalov, M. S. Melgunov, A. G. Stepanov, W3P. Felth Sand O. A. Kholdeeva, *Inorg. Chem.*, 2010, 49, 2920-2930.
- 46. R. Canioni, C. Roch-Marchal, F. Secheresse, P. Horcajada, C. Serre, M. Hardi-Dan, G. Ferey, J.-M. Greneche, F. Lefebvre, J.-S. Chang, Y.-K. Hwang, O. Lebedev, S. Turner and G. Van Tendeloo, *J. Mater. Chem.*, 2011, **21**, 1226-1233.
- 47. S. Ribeiro, A. D. S. Barbosa, A. C. Gomes, M. Pillinger, I. S. Goncalves, L. Cunha-Silva and S. S. Balula, *Fuel Processing Technology*, 2013, **116**, 350-357.
- J. Juan-Alcaniz, M. G. Goesten, E. V. Ramos-Fernandez, J. Gascon and F. Kapteijn, *New J. Chem.*, 2012, 36, 977-987.
- N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A. N. Shmakov, Y. A. Chesalov, D. N. Dybtsev, V. P. Fedin and O. A. Kholdeeva, *J. Catal.*, 2008, **257**, 315-323.
- 50. C. L. Hill, J. Mol. Catal. A Chem., 2007, 262, 2-6.
- J. Juan-Alcaniz, J. Gascon and F. Kapteijn, J. Mater. Chem., 2012, 22, 10102-10118.
- 52. D. M. Fernandes, A. D. S. Barbosa, J. Pires, S. S. Balula, L. Cunha-Silva and C. Freire, *ACS Appl. Mater. Interfaces*, 2013, **5**, 13382-13390.
- 53. C. M. Granadeiro, M. Karmaoui, E. Correia, D. Juliao, V. S. Amaral, N. J. O. Silva, L. Cunha-Silva and S. S. Balula, *Rsc Advances*, 2015, 5, 4175-4183.
- 54. C. M. Granadeiro, S. O. Ribeiro, M. Karmaoui, R. Valenca, J. C. Ribeiro, B. de Castro, L. Cunha-Silva and S. S. Balula, *Chem. Commun.*, 2015, **51**, 13818-13821.
- C. M. Granadeiro, P. Silva, V. K. Saini, F. A. A. Paz, J. Pires,
 L. Cunha-Silva and S. S. Balula, *Catal. Today*, 2013, 218– 219, 35-42.
- 56. S. Ribeiro, C. M. Granadeiro, P. Silva, F. A. Almeida Paz, F.
 F. de Biani, L. Cunha-Silva and S. S. Balula, *Catalysis Science & Technology*, 2013, 3, 2404-2414.
- A. D. S. Barbosa, D. Julião, D. M. Fernandes, A. F. Peixoto, C. Freire, B. de Castro, C. M. Granadeiro, S. S. Balula and L. Cunha-Silva, *Polyhedron*, 2017, **127**, 464 - 470.
- 58. L. H. Wee, F. Bonino, C. Lamberti, S. Bordiga and J. A. Martens, *Green Chem.*, 2014, **16**, 1351-1357.
- 59. L. I. Kuznetsova, L. G. Detusheva, M. A. Fedotov and V. A. Likholobov, J. Mol. Catal. A Chem., 1996, **111**, 81-90.
- 60. S. Bauer, C. Serre, T. Devic, P. Horcajada, J. Marrot, G. Férey and N. Stock, *Inorg. Chem.*, 2008, **47**, 7568-7576.

Page 11 of 11

CrystEngComm

CrystEngComm

- 61. P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon and F. Kapteijn, *Chem. Mater.*, 2011, **23**, 2565-2572.
- 62. Y. Lin, C. Kong and L. Chen, RSC Adv., 2012, 2, 6417-6419.
- 63. L. Bromberg, Y. Diao, H. Wu, S. A. Speakman and T. A. Hatton, *Chem. Mater.*, 2012, **24**, 1664-1675.
- 64. Shivani, B. Pujala and A. K. Chakraborti, *J. Org. Chem.*, 2007, **72**, 3713-3722.
- 65. F. Ulgheri, G. Orrù, M. Crisma and P. Spanu, *Tetrahedron Letters*, 2004, **45**, 1047-1050.

View Article Online DOI: 10.1039/C7CE00528H