Cr-MIL-101 Encapsulated Keggin Phosphotungstic Acid as Active Nanomaterial for Catalysing Alcoholysis of Styrene Oxide

Lik H. Wee, Francesca Bonino, Carlo Lamberti, Silvia Bordiga, and Johan A. Martensa

Cr-MIL-101 Encapsulated Keggin Phosphotungstic Acid as Active Nanomaterial for Catalysing Alcoholysis of Styrene Oxide

Lik H. Wee,*[a] Francesca Bonino,[b] Carlo Lamberti,[b] Silvia Bordiga,[b] and Johan A. Martens[a]

[a] Centre for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg, 23, B3001, Leuven, Belgium. Fax: +32 (0)163 21498; Tel: +32 (0) 163 76748; E-mail:likhong.wee@biw.kuleuven.be
[b] NIS Centre of Excellence and INSTM Reference Center, Department of Chemistry, University of Turin, Via Quarello 15, 10135, Turin, Italy

Abstract Mesoporous chromium-based terephthalate metal-organic framework (MIL-101) encapsulated Keggin phosphotungstic acid (HPW) [MIL-101(HPW)] was demonstrated to be an active heterogeneous catalyst for selective catalysis of the ring opening reaction of styrene oxide with methanol achieving 99 % yield of 2-methoxy-2-phenylethanol in 20 minutes at 40 °C. Similar MIL-101 samples prepared using one-pot microwave synthesis in the absence of HPW or in the presence of hydrofluoric acid (HF) were less active. The impact of fluoride and HPW polyanions incorporation on the acidity of MIL-101 was investigated by *in situ* Infrared spectroscopy technique using CO as a probe molecule. Additional hydroxyl groups and Lewis acid sites are present in MIL-101(HPW) explaining the observed superior catalytic performance in styrene oxide methanolysis.

1. Introduction

Metal-organic frameworks (MOFs) are a rapidly growing family of organic-inorganic hybrid materials built from organic ligands bridging metal ions.[1] By systematic design and fine-tuning, MOF structures having high accessible porosity and pores with dimensions in the range of several angstroms to nanometres have been achieved.[2] These unique and outstanding features of MOFs imparted for a vast range of promising potential applications such as gas storage,[3] separation,[4] drug release,[5] catalysis[6] and more. The engineering of MOFs with strong Lewis or Brønsted acidity via grafting of functional groups and encapsulation of phorphyrin and nanoparticles makes them excellent candidates as heterogeneous catalysts.[7] In addition, the well-defined pore architecture in MOFs is ideally suited for size- and shape-selective catalysis. A drawback of MOFs is their limited chemical and hydrothermal stability. Therefore, the most successful application area for MOFs in heterogeneous catalysis are reactions running at low temperature under liquid phase conditions.

Chromium terephthalate MIL-101 (Materials of the Institut Lavoisier n°101) is a mesoporous MOF reported by Férey and co-workers.[2a] MIL-101(Cr) was constructed from the linkage of 1,4-benzenedicarboxylate (H$_2$BDC) anions and inorganic trimeric Cr building units leading to a three-dimensional cubic structure of corner-sharing super tetrahedra. MIL-101 has mesosized cages of 2.9 and 3.4 nm, accessible through microporous windows of 1.2 and 1.45 nm giving rise to a high BET surface area of 5900 m^2/g. Several studies on MIL-101 synthesis[8] and its applications for gas storage,[9] separation[10] and catalysis[7,11a,11b] have been reported.

Polyoxometalates (POMs) are excellent homogeneous acid catalysts. However, the recovery and reuse of POM catalyst in liquid reaction media is often hampered by their high

solubility in water and organic solvents.[12] To overcome this limitation, permanent heterogenisation of these homogeneous catalysts into various host supports such as zeolite,[13] silica[14] and activated carbon[15] has been reported. However, these systems tend to have limited POM loading, present some leaching and the supported POMs show a tendency to agglomeration.[16] MIL-101 is an attractive host matrix for the encapsulation of POM taking into account the benefit of its (i) large mesocages for the encapsulation of POM molecules, (ii) good POM dispersion, (iii) high surface area, (iv) simple and efficient one-pot synthesis of the formulation and (v) relatively high framework stability among MOF materials. The encapsulation of POM into the pores of MIL-101 has been achieved via either impregnation[2a,17] or one-pot hydrothermal synthesis approach.[18,19] These MIL-101(POMs) materials show catalytic activity for Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate, esterification reaction of acetic acid with n-butanol, alkene epoxidation, carbohydrate dehydration to 5-hydroxymethylfurfural and Baeyer condensation.[17-20]

Given the promising catalytic activity, we synthesized MIL-101 in the absence of HF, and with encapsulated Keggin HPW ions. The active sites of the MIL-101 catalysts were characterized in detail using *in situ* Infrared spectroscopy and CO as a probe molecule at low temperature. This work adds to the greening of a chemical process considering that (i) an HF free synthesis method for the preparation of MIL-101(HPW) is achieved; (ii) the selective synthesis of 2-methoxy-2-phenylethanol achieving 99% yield under mild reaction conditions represents an energy saving and chemical waste minimisation and (iii) the encapsulation of homogeneous POM into MIL-101 enables facile catalyst recovery and recycling.
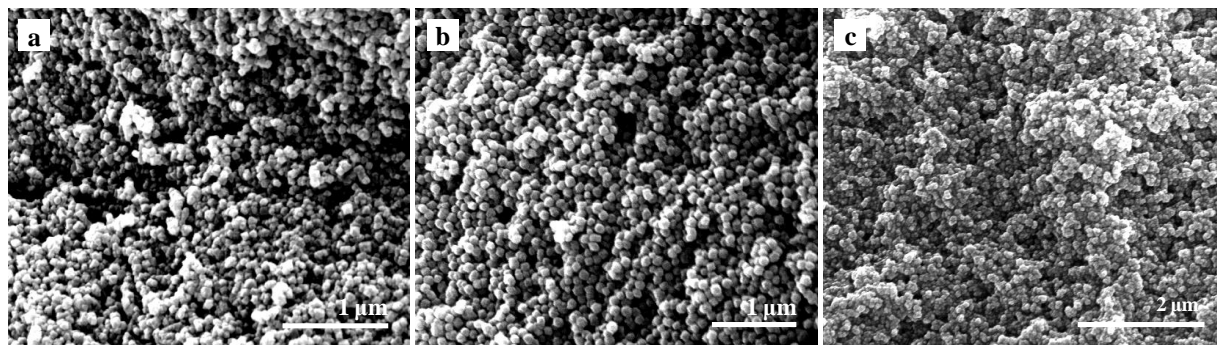
Fig. 1 SEM images of (a) MIL-101(HF), (b) MIL-101(H_2O) and (c) MIL-101(HPW).

2. Experimental section

2.1 Synthesis

MIL-101 samples were prepared according to a previously reported method by Bromberg *et al*.[20] involving microwave heating of a synthesis mixture containing 4 g of $Cr(NO_3)_3 \cdot 9H_2O$ (99%, Sigma-Aldrich), 1.66 g of terephthalic acid (H_2BDC) (98%, Aldrich) in 50 mL of distilled water to produce MIL-101 (H_2O), or with addition of 1.44 g of $H_3PW_{12}O_{40} \cdot nH_2O$ to produce MIL-101(HPW), or with 0.2 mL of hydrofluoric acid to produce MIL-101 (HF). The synthesis mixture was heated to 210 °C in 10 min (microwave heating at 1000 W) and kept at 210 °C for 40 min. The product was washed with DMF (≥99% (GC), Sigma-Aldrich) via a series of centrifugation and redispersion steps in ultrasonic bath. The product was then dried in an air oven at 60 °C overnight and followed by Soxhlet extraction in ethanol (laboratory type, Chem-Lab) for 48 h, and washed with ethanol prior to oven drying. Samples were activated under

vacuum overnight at 140 °C. Elemental analysis (wt%) of: MIL-101(H_2O): C, 37.00; Cr, 6.31; MIL-101(HF): C, 40.93, Cr, 6.40 F, 5.60; MIL-101(HPW): C, 24.84; Cr, 6.40; W, 34.98. Based on the elemental analysis results and molecular weight of hydrated HPW ($H_3PW_{12}O_{40} \cdot nH_2O$), W content, 75.65%; MW, 2916 g/mol), the content of hydrated HPW was calculated according to the formula, HPW (μmol/g) $= 1 \times 10^6$ (W content in the hybrid material,%)/($2916 \times 75.65\%$).[20] The estimated HPW content in MIL-101(HPW) material was 158 μmol/g of dry powder, or 48 wt%.

2.2 Characterization

The synthesized MOFs were characterized by a scanning electron microscope (SEM, Philips XL-30 FEG equipped with a tungsten filament), a powder X-ray diffractometer (XRD, STOE StadiP diffractometer in high-throughput transmission mode; Cu Kα1 radiation), and a N_2 physisorption instrument (Micromeritics Tristar 3000, samples were degassed at 150 °C in N_2 flow overnight prior to analysis). The ^{31}P MAS NMR spectrum was recorded on a Bruker AMX300 spectrometer (7.0 T), using the single-pulse excitation method. 3503 scans were accumulated with a recycle delay of 20 s. The pulse length was 2.0 μs. The sample was packed in 4 mm Zirconia rotors, and the spinning frequency of the rotor was 6 kHz. A solution of 2 ml ortho phosphoric acid (85%, Normapur VWR) in 2 ml water was used as chemical shift reference. FTIR spectra were collected on a Vertex 70 Bruker spectrophotometer equipped with a MCT detector, at 2 cm^{-1} resolution, on a thin self-supported wafer. The sample was activated in a home-made low temperature cell under high vacuum (residual pressure 10^{-4} mbar) at 200 °C for 2 h. CO gas (p_{eq}=50 torr) was dosed on the sample at RT. Successively, the sample in contact with CO is cooled down by means of liquid nitrogen and then, once the temperature equilibrium is reached, it is progressively outgassed.

2.3 Catalysis

Ring opening reactions of styrene oxide with methanol were performed in closed glass vessels inserted into a copper block equipped with temperature control thermocouple set at 40 °C. In a standard experiment, the reaction mixture contained 1.25 mmol of styrene oxide (97+%, ACROS) and 10 mL of methanol (HPLC grade, BDH) and 50 mg MOF catalyst and the content was magnetically stirred at 600 rpm. The reactions were performed for 20 min. Aliquots of the reaction mixture were periodically withdrawn with a microsyringe after 5, 10 and 20 minutes of reaction. Catalyst was removed through centrifugation prior to gas chromatography analysis (GC, Chrompack 8760 WCOT fused silica capillary column, 30 m long). The yields of the product were determined using nonane as an external standard. Leaching test and evidence of heterogeneity in the catalysis of styrene oxide ring opening by methanol was determined by removing the solid catalysts via centrifugation after 5 min of reaction time and analysis of the reaction mixture was continued under similar reaction conditions for another 15 min. The solid was separated by centrifugation, washed with ethanol and dried at 60 °C for subsequent recycling tests.

3. Results and discussions
### 3.1 Synthesis and characterization of MOFs
In this study, MIL-101 samples were prepared in the presence or absence of HF or HPW via microwave heating at 210 °C of a synthesis mixture having a molar composition of 1Cr(NO_2)$_3$:9H_2O:1H_2BDC:280H_2O for 40 min. MIL-101(HF) was first synthesized by Chang

and co-workers[9a] via microwave heating. Therefore, MIL-101(HF) sample is an ideal reference material for direct comparison with MIL-101(H$_2$O) and MIL-101(HPW) samples for phase purity, porosity, pore volume, crystal morphology, acidity and catalytic activity. According to SEM image (Figure 1b), MIL-101(H$_2$O) appears like spherical particles with uniform morphology and particle size around 100 nm. MIL-101(HF) has less defined particle morphology (Figure 1a). MIL-101(HPW) appears like an aggregate of nanocrystallites (Figure 1c). XRD patterns (Figure 2) are characteristic of MIL-101.[2a]
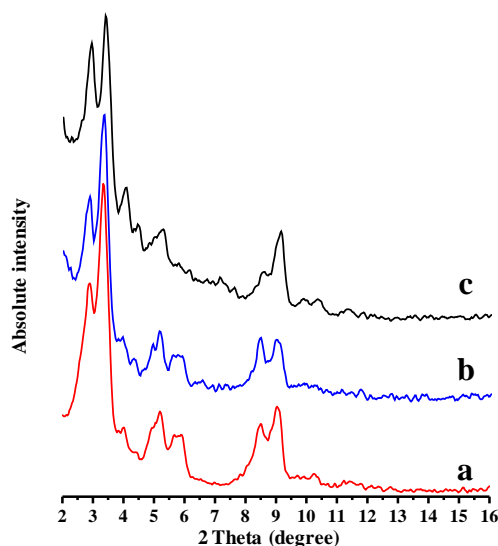
Fig. 2 XRD patterns of (a) MIL-101(HF), (b) MIL-101(H$_2$O) and (c) MIL-101(HPW).

The permanent porosity of MIL-101(H$_2$O) and MIL-101(HPW) was verified by N$_2$ adsorption (Figure 3a). N$_2$ adsorption isotherms show strong uptake at low relative pressure typical of microporous material.[21] MIL-101(H$_2$O) and MIL-101(HF) samples have a similar BET (Brunauer-Emmett-Teller) surface area and pore volume of 2995 m^2/g and 1.31 cm^3/g, respectively. This BET surface area is lower than for micron-sized MIL-101 reported in literature (5900 m^2/g) but similar to the reported nanosized MIL-101 prepared in the presence of HF.[16a] According to the BJH (Barrett-Joyner-Halenda) method based on nitrogen adsorption isotherms, the average pore diameter of MIL-101(HF), MIL-101(H$_2$O) and MIL-101(HPW) was estimated to be in the range of 3.5-3.8 nm. The physiochemical properties of MIL-101 samples are also presented in Table S1 (see Supporting Information). It should be mentioned that MIL-101 with a BET surface area greater than 4500 m^2/g is very difficult to obtain due to the presence of trapped recrystallised H$_2$BDC synthesis residue within the pores of MIL-101.[16] The presence of free dicarboxylic acid impurities in MIL-101 samples was evidenced by IR spectra which showed an absorption band at 1728 cm^{-1} (Figure S1, Supporting Information).[11h] Although many attempts have been made to increase the purity of MIL-101 through various purification steps, the BET surface area of MIL-101 is limited in the range of 2700-4300 m^2/g.[16] Two distinctive secondary uptakes around P/P_o of 0.1 and 0.2 attributed to characteristic micropore window effects.[2e] The shallow hysteresis loops likely are due to capillary condensation of nitrogen in interstitial void volumes between packed nanoparticles revealed by the SEM images (Figure 1).[22]
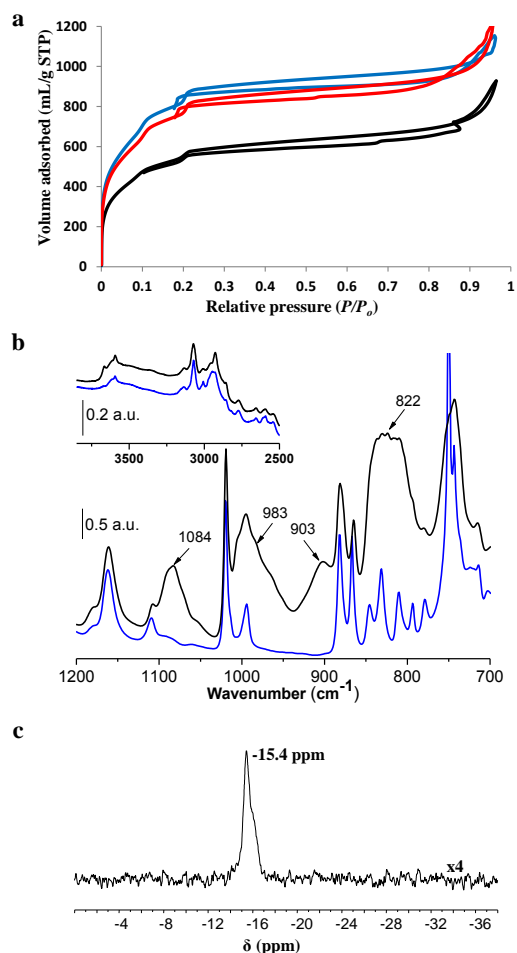
Fig. 3 (a) N_2 adsorption isotherms, (b) IR spectra collected after outgassing at 200 °C and (c) ^{31}P solid-state MAS NMR spectrum. MIL-101(HF) (red), MIL-101(H_2O) (blue) and (b) MIL-101(HPW) (black).

The BET surface area and pore volume of MIL-101(HPW) sample was found to be lower compared to MIL-101 parent material, which is to be expected from the weight of the heavy heteropolyacid molecules and the pore space they occupy. Nevertheless, considerable BET surface area and pore volume of 2124 m^2/g and 0.96 cm^3/g, respectively were preserved. The incorporation of Keggin HPW in MIL-101 was confirmed by IR spectroscopy based on the characteristic bands at 822, 903 v(W-O-W), 983 v(W=O) and 1084 cm^{-1} v(P-O) (Figure 3b, black spectrum).[22,23] The integrity of the Keggin polyoxometal anion within the pores of MIL-101 was further supported by ^{31}P solid-state MAS NMR which revealed a single signal at -15.4 ppm (Figure 3c). Both the IR and ^{31}P solid-state MAS NMR results were in good agreement with the previously reported results.[2a] Keggin polyanion has a relatively large particle size of *ca.* 1.3 nm diameter and 2.25 nm^3 in volume.[2a,11a] Five Keggin ions take up 10.1 nm^3 of volume, which is approximately 50% of the total volume of a large cage (20.6 nm^3) as reported by Férey and co-workers.[2a,11a] Elemental analysis of MIL-101(HPW) revealed HPW represented ca. 48% of weight indicating that each cage is loaded with five Keggin ions, confirming the encapsulation of the Keggin HPW ions in these large cages of MIL-101. Although, it is more likely that only the

large cages can host the HPW.[2a] However, it has been recently claimed by Hatton and co-workers that HPW can reside both in the large and the small cages of MIL-101.[20]

In Figure 3b, all MIL-101 spectroscopic fingerprints in the 1200-700 cm^{-1} range are present. The highest frequency range (3850-2500 cm^{-1}) shown in the inset, shows again many similarities between the MIL-101(H$_2$O) and MIL-101(HPW) samples. These IR spectra were recorded on samples activated at 200 °C to remove all residual solvent and physisorbed water. In this spectral range a lot of bands are due to combination and overtone modes. Nevertheless, some fingerprints are clearly distinguishable: bands at 3070 cm^{-1} and 3592 cm^{-1} due to v(C-H) aromatic linker stretching vibration and to v(O-H) stretching mode, respectively. The presence of an OH group is to compensate the negative default charge per trimer of chromium octahedra. It should be mentioned that similar weak bands were observed by Vimont et al. in the case of Cr-MIL-100[24] and Al-MIL-100,[25] upon treatment in vacuo at moderate temperatures. MIL-101(HPW) shows an additional feature at 3665 cm^{-1}, probably due to the presence of some new hydroxyl groups.

3.2 Ring opening reactions of styrene oxide with methanol

Ring opening reaction of styrene oxide with methanol was selected as acid catalyzed model reaction to compare the catalytic activity of the three types of MIL-101. This reaction also is of practical interest, and especially a heterogeneous catalyst for converting this readily available, inexpensive epoxide to β-alkoxyalcohol, which is a valuable synthetic intermediate for 1,2-diol and 1,2-diol mono-ether organic syntheses is highly desirable.[26] Current processes often suffer from long reaction times, drastic reaction conditions, unsatisfactory conversion and poor regioselectivity.[27]

The catalytic activity of MIL-101, MIL-101(HF) and MIL-101(HPW) in ring opening reaction of styrene oxide with methanol under mild reaction temperature (40 °C) is reported in Figure 4. MIL-101(HPW) catalyst gave an excellent conversion (99.8%) and regioselectivity (≥99%) to 2-methoxy-2-phenylethanol in 20 min of reaction time, higher than MIL-101(HF) (80% conversion) and MIL-101(H$_2$O) (22% conversion) (Figure 4a). Reaction performed without catalyst under these reaction conditions gave less than 1% conversion. The heterogeneity of MIL-101(HPW) catalyst was verified by removing the solids from the reaction mixture after 5 min of reaction time, and heating the filtrate for 15 more minutes. After filtration, a completely clear filtrate was obtained (Figure 4b, insert). No further conversion of styrene oxide was noted, which confirmed that the reaction catalyzed by MIL-101(HPW) is truly heterogeneous (Figure 4b). According to ICP analysis, the detected concentration of W in the supernatant corresponded to less than 0.001 wt% of the nominal amount of HPW in the catalyst. No Cr was detected. MIL-101(HPW) catalyst could be reused and recycled up to 3 times without significant loss of catalytic activity and selectivity (Figure 4c). The crystallinity of MIL-101(HPW) was preserved after catalytic testing as evidenced by XRD (Figure 4d). This is another illustration of the stabilization of MIL-101 by incorporation of HPW reported earlier.[2d,28] However, a gradual loss of surface area and pore volume was noted for the recovered MIL-101(HPW) (cycle 3) sample (BET surface area= 1417 cm^2/g and pore volume= 0.57 cm^3/g) (Figure S2, Supporting Information). This could be reasoned for the observed loss of catalytic activity after recycling test (Figure 4c). Similar observation has also been reported by Kholdeeva and co-workers for MIL-101(HPW) catalysed cyclohexene oxidation reaction.[11g] The stability of MIL-101(HPW) after 10 catalytic cycles was confirmed by XRD (Figure S3, Supporting Information). The 9th reuse MIL-101(HPW) catalyst still gave 30% conversion and high selectivity (>90%). The lower

residual activity is partly due to a loss of the catalyst material in the catalyst recovery operations and partly due to pore blockage by trapped reaction products. Many catalysts have been evaluated for this reaction, such as MOFs (e.g. MIL-100[29a] and HKUST-1[29b]), zeolites,[29c] mesoporous aluminosilicate,[29d] zirconium (IV)-grafted hexagonal MCM-41,[29e] silica supported copper oxide[29f] and polymer supported iron complex.[29g] The catalytic performance of MIL-101(HPW) in ring opening of styrene oxide with methanol appears to be exceptional.
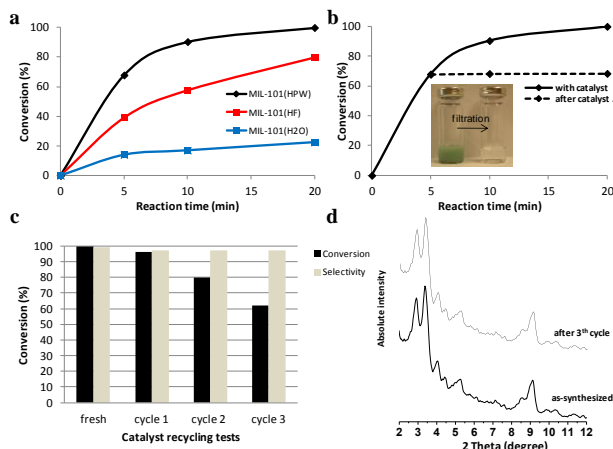

Fig. 4 (a) Ring opening reaction of styrene oxide with methanol catalyzed by MIL-101(H₂O), MIL-101(HF), and MIL-101(HPW), (b) leaching test of MIL-101(HPW), (c) catalyst recycling tests for MIL-101(HPW) and (d) XRD patterns of MIL-101(HPW) before and after three catalytic runs.

3.3 Infrared Spectroscopic Analysis

The catalytic activity of MIL-101 catalysts in opening of styrene oxide in the order of increasing: MIL-101(H₂O)<MIL-101(HF)<MIL-101(HPW). The intriguing difference in catalytic performance of the three different MIL-101 samples invited for further investigation of the catalytic sites by *in situ* IR spectroscopy using CO as a probe molecule known to be a very sensitive probe[19] (see Figure 5). In all the three samples, already at room temperature, a quite intense and sharp band is always present at 2194 cm⁻¹ (light green spectra) showing the presence of strong Cr^{3+} exposed Lewis sites. By lowering the temperature with liquid nitrogen, the band increases in intensity and shifts to 2197 cm⁻¹ (dark green spectra).[24,30] In parallel at lower frequency,

bands due to CO physisorbed (liquid-like) species arise (main feature centered at 2135 cm⁻¹). Besides these features in common with the other two samples, MIL-101(HPW) shows a broadening of the band centered at 2197 cm⁻¹. In particular, when at low temperature CO coverage is decreased, a further component centered at 2202 cm⁻¹ clearly appears. The assignment is not straightforward, but we can hypothesize the presence of other Lewis sites, different from the Cr^{3+} environment present in MIL-101(H₂O) and MIL-101(HF) samples. Two possible new species can be proposed: i) some defects in encapsulated polyanion forming new Lewis sites or ii) Cr^{3+} sites with different acidity because of the presence of HPW.[31] The use of pyridine or ammonia as a probe molecule to monitor the acidity and in particular Brønsted acid of MIL-101(HPW) was not be possible due to the complete overlapping of NH_4^+ or PyH^+ vibrational modes with carboxylate vibrational modes of MIL-101.[32]
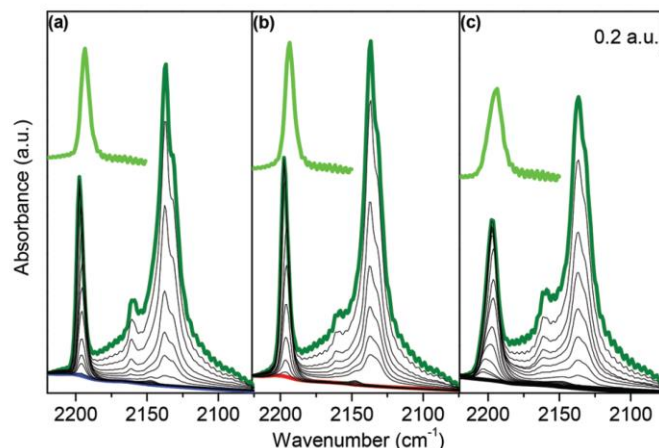
Fig. 5 FTIR spectra of (a) MIL-101(H$_2$O), (b) MIL-101(HF) and (c) MIL-101(HPW) recorded after outgassing at 200 °C for 2 hours (blue, red, black color respectively), after adsorption of CO at room temperature (light green) and low temperature (dark green); black curves show the effect of outgassing in vacuo at low temperature.

The CO probing study revealed that the presence of fluoride ion has no significant Lewis acidity enhancement effect in MIL-101(HF). Interestingly, in styrene oxide methanolysis MIL-101(HF) was more active than MIL-101(H$_2$O) (Figure 4a). According to the chemical composition of MIL-101(HF), the mole ratio of F/Cr is 0.37, which agrees well with the theoretical value of 0.33 for the idealized structure.[2a] It has been previously reported that fluoride ion has a significant influence on the catalytic performance of some solid catalysts such as zeolites[33] and alumina.[34] In MIL-100(Fe) the presence of fluoride acting as electron-withdrawing group significantly strengthens the Lewis acidity in the neighboring unsaturated metal sites has been reported by Serre and co-workers.[35] Another example is the enhancement of Lewis acidity in UiO-66 by introducing electron withdrawing groups such as F, Cl, Br, NO$_2$ on the terephthalate linker.[36] Although in our studies, no significant Lewis acidity enhancement was noted for MIL-101(HF) according to the recorded IR spectra, an additional Lewis acid site was noted for MIL-101(HPW).

4. Conclusions

The catalytic activity of MIL-101 and modified versions with fluoride and Keggin phosphotungstate incorporated during synthesis in styrene oxide methanolysis was investigated. The acid sites were probed using in situ FTIR using CO as a probe molecule. The occluded Keggin polyoxyanions in the pore structure of MIL-101 generates additional hydroxyl groups and Lewis acid sites inferred to be responsible for efficient methanolysis of styrene oxide giving excellent yield of 2-methoxy-2-phenylethanol (99%) in short reaction time at 40 °C. The MIL-101(HPW) catalyst is stable and can be reused without significant loss of activity and selectivity. This is another example of stabilization and catalytic activity enhancement of a MOF through incorporation of heteropolyanion. The presence of HF or HPW in the synthesis mixture results in the formation MIL-101 nanocystallines with less-defined morphology whereas uniform nanospheres of MIL-101 was obtained in absence of these additives. These uniform nanocrystals of MIL-101 though less useful in catalysis could be useful as seed layer for membrane/thin film preparation.

Acknowledgements

Notes and references

1   (*a*) G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191. (*b*) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705.

2   (*a*) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040. (*b*) Y. K. Park, S. B. Choi, H. Kim, K. Kim, B. -H. Won, K. Choi, J. -S. Choi, W. -S. Ahn, N. Won, S. Kim, D. H. Jung, S. -H. Choi, G. -H. Kim, S. -S. Cha, Y. H. Jhon, J. K. Yang and J. Kim, *Angew. Chem. Int. Ed.*, 2007, **119**, 1. (*c*) Y. Yan, S. Yang, A. J. Blake, W. Lewis, E. Poirier, S. A. Barnett, N. R. Champness and M. Schröder, *Chem. Commun.*, 2011, **47**, 9995. (*d*) L. H. Wee, C. Wiktor, S. Turner, W. Vanderlinden, N. Janssens, S. R. Bajpe, K. Houthoofd, G. Van Tendeloo, S. De Feyter, C. E. A. Kirschhock and J. A. Martens, *J. Am. Chem. Soc.*, 2012, **134**, 10911.

3   (*a*) N. Klein, I. Senkovska, K. Gedrich, U. Stoeck, A. Henschel, U. Mueller and S. Kaskel, *Angew. Chem., Int. Ed.*, 2009, **48**, 9954. (*b*) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.

4   D. Britt, H. Furukawa, B. Wang, T. G. Glover and O. M. Yaghi, *Proc. Natl. Acad. Sci.*, 2009, **49**, 20637.

5   P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J. -S. Chang, Y. K. Hwang, V. Marsaud, P. -N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur and R. Gref, *Nature Mater.*, 2010, **9**, 172.

6   (*a*) A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606. (*b*) D. Farrusseng, S. Aguado and C. Pinel, *Angew. Chem.*, *Int. Ed.*, 2009, **48**, 7502. (*c*) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450. (*d*) L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248. (*e*) Y. K. Park, S. B. Choi, H. J. Nam, D. -Y. Jung, H. C. Ahn, K. Choi, H. Furukawa and J. Kim, *Chem. Commun.*, 2010, 3086. (*f*) P. Horcajada, S. Surblé, C. Serre, D. -Y. Hong, Y. -K. Seo, J. -S. Chang, J. -M. Grenèche, I. Margiolaki and G. Férey, *Chem. Commun.*, 2007, 2820.

7   L. H. Wee. L. Alaerts, J. A. Martens and D. De Vos, in *Metal-Organic Frameworks as Catalysts for Organic Reactions*, ed. D. Farrusseng, WILEY-VCH, Weinheim, 2011, ch. 9, pp. 191-212.

8   (*a*) N. A. Khan, I. J. Kang, H. Y. Seok and S. H. Jhung, *Chem. Eng. J.*, 2011, **166**, 1152. (*b*) A. Demessence, P. Horcajada, C. Serre, C. Boissière, D. Grosso, C. Sanchez and G. Férey, *Chem. Commun.*, 2009, 7149. (*c*) D. Jiang, A. D. Burrows and K. J. Edler, *CrystEngComm*, 2011, **13**, 6916.

9   (*a*) S. H. Jhung, J. -H. Lee, J. W. Yoon, C. Serre, G. Férey and J. -S. Chang, *Adv. Mater.*, 2007, **19**, 121. (*b*) J. Yang, Q. Zhao, J. Li and J. Dong, *Micropor. Mesopor. Mater.*, 2010, **130**, 174. (*c*) M. Latroche, S. Surblé, C. Serre, C. Mellot-Draznieks, P. L. Llewellyn, J. -H. Lee, J. -S. Chang, S. H. Jhung and G. Férey, *Angew. Chem., Int. Ed.*, 2006, **118**, 8407.

10   Z. -Y. Gu and X. -P. Yan, *Angew. Chem., Int. Ed.*, 2010, **49**, 1477.

11   (*a*) D. -Y. Hong, Y. K. Hwang, C. Serre, G. Férey and J. -S. Chang, *Adv. Func. Mater.*, 2009, **19**, 1537. (*b*) A. Henschel, K. Gedrich, R. Kraehnert and S. Kaskel, *Chem. Commun.*, 2008, 4192. *(c)* Y. Li and R. T. Yang, *AIChE J.*, 2008, **54**, 269. *(d)* I. Senkovska and S. Kaskel,

Microporous Mesoporous Mater., 2008, **112**, 108. (e) Y. -Y. Liu, J. -L. Zeng, J. Zhang, F. Xu and L. -X. Sun, *Int. J. Hydrogen Energy*, 2007, **32**, 4005. *(f)* S. B. Choi, M. J. Seo, M. Cho, Y. Kim, M. K. Jin, D. -Y. Jung, J. -S. Choi, W. -S. Ahn, J. L. C. Rowsell and J. Kim, *Cryst. Growth Design*, 2007, **7**, 2290. *(g)* N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A. N. Shmakov, Yu, A. Chesalov, D. N. Dybtsev, V. P. Fedin and O. A. Khodeeva, *J. Catal.*, 2008, **257**, 315. *(h)* J. Kim, Y. -R. Lee and W. -S. Ahn, *Chem. Commun.*, 2013, **49**, 7647-7649.

12   *(a)* I. V. Kozhevnikov, *Chem. Rev.*, 1998, **98**, 171. *(b)* H. N. Miras, J. Yan, D.-L. Long and L. Cronin, *Chem. Soc. Rev.*, 2012, **41**, 7403.

13   R. R. Ozer and J. L. Ferry, *J. Phys. Chem. B*, 2002, **106**, 4336.

14   Y. Guo and C. Hu, *J. Mol. Catal. A*, 2007, **262**, 136.

15   B. A. Watson, M. A. Barteau, L. Haggerty, A. M. Lenhoff and R. S. Weber, *Langmuir*, 1992, **8**, 1145.

16   C. -Y. Sun, S. -X. Liu, D. -D. Liang, K. -Z. Shao, Y. -H. Ren and Z. -M. Su, *J. Am. Chem. Soc.*, 2009, **131**, 1883.

17   N. V. Maksimchuk, K. A. Kovalenko, S. S. Arzumanov, Y. A. Chesalov, M. S. Melgunov, A. G. Stepanov, V. P. Fedin and O. A. Kholdeeva, *Inorg. Chem.*, 2010, *49*, 2920.

18   J. Juan-Alcañiz, E. V. Ramos-Fernandez, U. Lafont, J. Gascon and F. Kapteijn, *J. Catal.*, 2010, **269**, 229.

19 Y. Zhang, V. Degirmenci, C. Li and E. J. M. Hensen, *ChemSusChem*, 2010, **4**, 59.

20   L. Bromberg, Y. Diao, H. Wu, S. A. Speakman and T. A. Hatton, *Chem. Mater.*, 2012, **24**, 1664.

21   K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol and T. Siemieniewska, *Pure & Appl. Chem.* 1985, **57**, 603-619.

22   L. H. Wee, S. R. Bajpe, N. Janssens, I. Hermans, K. Houthoofd, C. E. A. Kirschhock and J. A. Martens, *Chem. Commun.*, 2010, **46**, 8186.

23   C. Pazé, S. Bordiga and A. Zecchina, *Langmuir*, 2000, **16**, 8139.

24   A. Vimont, J. -M. Goupil, J. -C. Lavalley, M. Daturi, S. Surblé, C. Serre, F. Millange, G. Férey, N. Audebrand, *J. Am. Chem. Soc.*, 2006, **128**, 3218.

25   C. Volkringer, H. Leclerc, J. -Loiseau, G. Férey, M. Daturi, A. Vimont, *J. Phys. Chem. C*, 2012, **116**, 5710.

26   B. P. Bandgar, A. V. Patil, O. S. Chavan and V. T. Kamble, *Catal. Commun.*, 2007, **8**, 1065.

27   (*a*) M. Tokunaga, J. F. Larrow, F. Kakiuchi and E. N. Jacobsen, *Science*, 1997, **277**, 936. (*b*) C. Schneider, A. R. Sreekanth and E. Mai, *Angew. Chem., Int. Ed.*, 2004, **43**, 5691.

28   (*a*) J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle and C. L. Hill, *J. Am. Chem. Soc.*, 2011, **133**, 16839. (*b*) L. H. Wee, N. Janssens, S. R. Bajpe, C. E. A. Kirschhock, J. A. Martens, *Catal. Today*, 2011, **171**, 275.

29   (*a*) A. Dhakshinamoorthy, M. Alvaro and H. Garcia, *Chem. Eur. J.*, 2010, **16**, 8530. (*b*) L. H. Wee, M. R. Lohe, N. Janssens, S. Kaskel and J. A. Martens, *J. Mater. Chem.,* 2012, **22**, 13742. (*c*) R. Dimitrova, V. Minkov and N. Micheva, *Appl. Catal. A*, 1996, **145**, 49. (*c*) M. W. C. Robinson, R. Buckle, I. Mabbett, G. M. Grant and A. E. Graham, *Tetrahedron Lett.*, 2007, **48**, 4723. (*d*) D. Barreca, M. P. Copley, A. E. Graham, J. D. Holmes, M. A. Morris, R. Seraglia, T. R. Spalding and E. Tondello, *Appl. Catal. A*, 2006, **304**, 14. (*e*) F. Zaccheria, F. Santoro, R. Psaro and N. Ravasio, *Green Chem.*, 2011, **13**, 545. (*f*) S. H. Lee, E. Y. Lee, D. -W. Yoo, S. J. Hong, J. H. Lee, H. Kwak, Y. M. Lee, J. Kim, C. Kim and J. -K, Lee, *New J. Chem.*, 2007, **31**, 1579.

30   P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, Guy De Weireld, J.-S. Chang, D.-Y. Hong, Y. K. Hwang, S. H. Jhung, G. Férey, *Langmuir*, 2008, **24**, 7245.

31   D. Dang, Y. Bai, C. He, J. Wang, C. Duan and J. Niu, *Inorg. Chem.*, 2010, **49**, 1280.

32   *(a)* K. Barbera, F. Bonino, S. Bordiga, T. V. W. Janssens, P. Beato, *J. Catal.*, 2011, **280**, 196. *(b)* A. Zecchina, L. Marchese, S. Bordiga, C. Pazè, E. Gianotti, *J. Phys. Chem. B*, 1997, **101**, 10128.

33   R. B. Borade and A. Clearfield, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 539.

34   A. Corma, V. Fornés and E. Ortega, *J. Catal.*, 1985, **92**, 284.

35   M. Dan-Hardi, H. Chevreau, T. Devic, P. Horcajada, G. Maurin, G. Férey, D. Popov, C. Riekel, S. Wuttke, J. -C. Lavalley, A. Vimont, T. Boudewijns, D. de Vos and C. Serre, *Chem. Mater.*, 2012, **24**, 2486.

36   F. Vermoortele, M. Vandichel, B. Van de Voorde, R. Ameloot, M. Waroquier, V. Van Speybroeck, D. E. De Vos, *Angew. Chem., Int. Ed.*, 2012, **51**, 4887.

Supporting Information

Cr-MIL-101 Encapsulated Keggin Phosphotungstic Acid as Active Nanomaterial for Catalysing Alcoholysis of Styrene Oxide

Lik H. Wee,*[a] Francesca Bonino,[b] Carlo Lamberti,[b] Silvia Bordiga,[b] and Johan A. Martens[a]

[a] *Centre for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg, 23, B3001, Leuven, Belgium. Fax: +32 (0)163 21498; Tel: +32 (0) 163 76748; E-mail:likhong.wee@biw.kuleuven.be*
[b] *NIS Centre of Excellence and INSTM Reference Center, Department of Chemistry, University of Turin, Via Quarello 15, 10135, Turin, Italy*

Table S1. Physiochemical properties of MIL-101 samples

Samples	BET surface area (m^2/g)	Langmuir surface area (m^2/g)	Pore volume[a] (cm^3/g)	Average pore diameter[b] (nm)
MIL-101(HF)	2794	2767	1.20	3.5
MIL-101(H_2O)	2995	2977	1.31	3.8
MIL-101(HPW)	2124	2190	0.96	3.5

[a]Calculated from *t*-plot
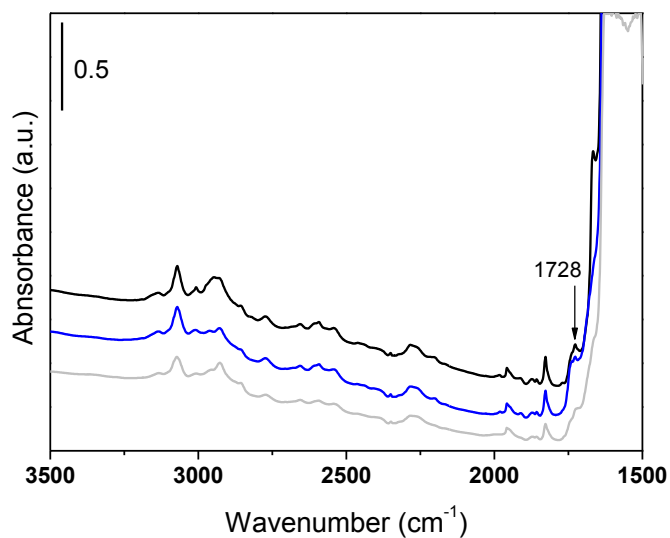[b]Calculated based on BJH (Barrett, Joyner & Halenda) method from nitrogen adsorption isotherms

Figure S1. IR spectra of MIL-101(H$_2$O) (black), MIL-101(HF) (blue) and MIL-101(HPW) (grey) samples collected after outgassing at 200 °C.
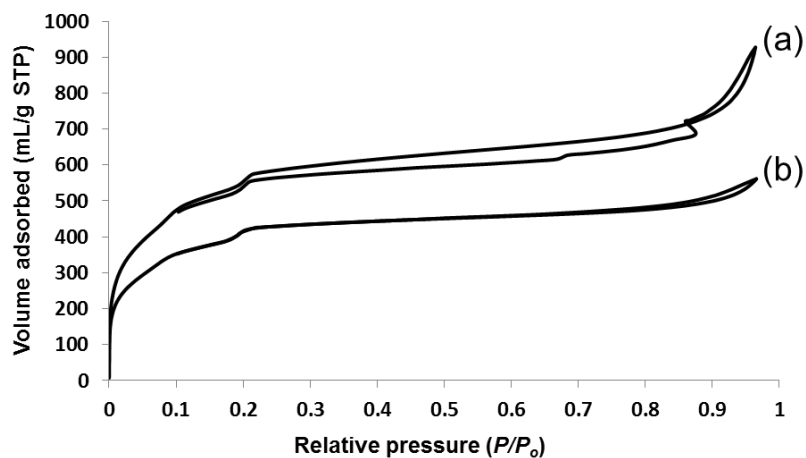

Figure S2. N$_2$ adsorption-desorption isotherms of (a) as-synthesized MIL-101(HPW) and (b) recovered MIL-101(HPW) sample after 4 catalytic runs.
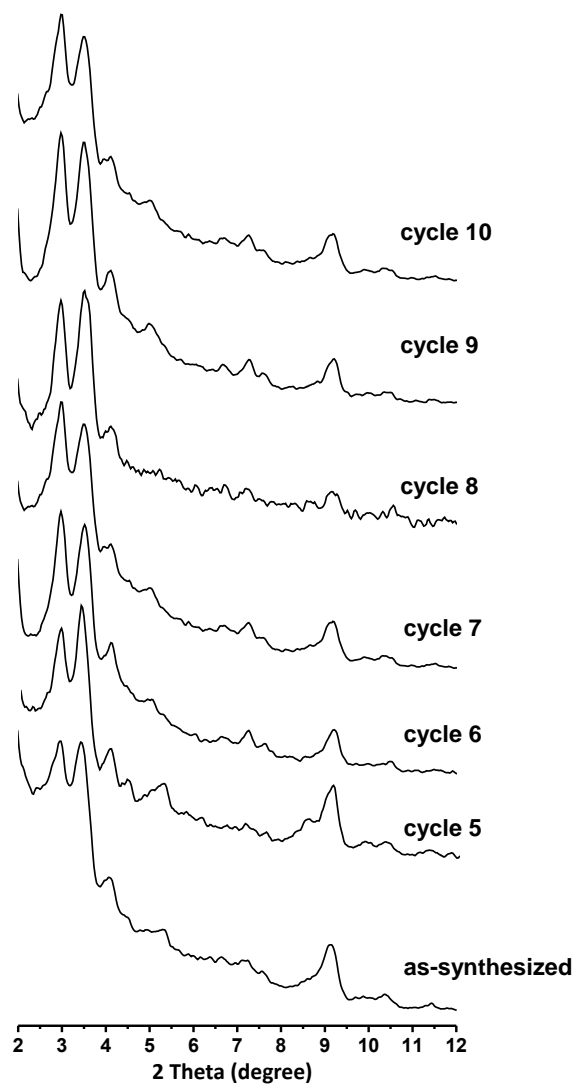
Figure S3. XRD patterns of MIL-101(HPW) before and after 10 catalytic runs.