



# Counteranion effects on the catalytic activity of copper salts immobilized on the 2,2'-bipyridine-functionalized metal–organic framework MOF-253



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## ARTICLE INFO

### Article history:

Received 9 May 2014

Received in revised form 30 July 2014

Accepted 7 August 2014

Available online 30 August 2014

### Keywords:

Metal–organic framework

$\alpha$ -Pinene oxide rearrangement

MOF-253

Copper salt immobilization

Counteranion

EPR

## ABSTRACT

The charge-neutral, aluminium-based metal–organic framework containing accessible 2,2'-bipyridine (bpy) sites, MOF-253, is a suitable host material for the immobilization of various copper catalysts. The catalytic performance of  $\text{CuCl}_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{BF}_4)_2$  and  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$  before and after coordination to the bpy ligands in MOF-253 was studied in the Meinwald rearrangement of  $\alpha$ -pinene oxide to campholenic aldehyde (CA). The coordination environment of  $\text{Cu}^{2+}$  in MOF-253 was further studied via EPR spectroscopy. Although the catalytic activity of the copper salts decreased upon heterogenization through coordination with the bpy linker, the selectivity to campholenic aldehyde markedly increased. Furthermore, the catalytic performance of the MOF loaded with copper salts was shown to vary greatly with the choice of charge compensating anion, allowing for improvement of the heterogeneous catalyst.

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## 1. Introduction

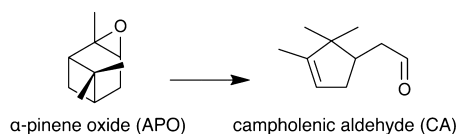
Metal–organic frameworks (MOFs) are microporous crystalline materials consisting of metal ion nodes connected via multi-topic organic linkers. These compounds have attracted significant research attention in recent years because of their high surface areas, functionalizable pores and wide range of potential applications. Although research in this context has been largely devoted to gas storage and separations [1–7], the number of reports on the use of MOFs as heterogeneous catalysts is increasing rapidly [8,9]. As part of a heterogeneous catalyst system, MOFs can fulfil at least two roles [10]: the MOF crystal lattice can possess intrinsic catalytic activity, or a MOF material can serve as a high surface area host for dispersing and immobilizing catalytically active species including metal nanoparticles [11], organometallic complexes [12], and inorganic clusters such as polyoxometallates [13]. In comparison with classical supports such as activated carbons or metal oxides, MOFs allow a more precise design of active sites. Thus, while the coordination environment in many heterogenized catalysts is not uniform, the active sites in MOFs can be improved or

fine-tuned almost as easily as in homogeneous catalysts. For example, MOFs incorporating complex metal-binding motifs such as porphyrin [14] or metallosalen ligands [15], as well as rather simple motifs such as 2,2'-bipyridine (bpy) groups have been synthesized [16,17].

Bipyridine binding sites have been incorporated in the MOF crystal lattice as part of the structural linkers, such as 2,2'-bipyridine-5,5'-dicarboxylic acid. After incorporation in the structure, the free bpy sites are available to coordinate metal complexes, as previously demonstrated with MOF-253 [16] or the zirconium-based framework UiO-67-bpy [17]. In both cases, the hard metal ions  $\text{Al}^{3+}$  or  $\text{Zr}^{4+}$  exclusively coordinate to the carboxylate groups of the organic linker, resulting in a metal–organic framework with open 'soft' bpy sites. These serve as coordination sites during post-synthetic loading with catalytically active metal ions. This has previously been shown with the incorporation of Pt in MOF-253 [18], Ir, Re, and Ru complexes in UiO-67-bpy for use in photocatalysis [17], the use of  $\text{Ru}^{3+}$  incorporated in MOF-253 as a catalyst for the oxidation of alcohols [19] and most recently the use of Ir and Pd immobilized in UiO-67-bpy for borylation and dehydrogenation reactions respectively [20].  $\text{CuI}$  immobilized in MOF-253 was shown to catalyze the coupling of phenols with aryl halides by Wang et al. [21] and Liu et al. [22] studied the use of  $\text{CuCl}_2$  on COMOC-4, the Ga-analogue of MOF-253, in the aerobic oxidation of cyclohexene. In

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Scheme 1.

the former case, CuI immobilized through coordinative interactions with the bpy sites was shown to outperform the homogeneous salt.

To date, for all studies published on the catalytic performance of coordinatively immobilized metal ions, only a single type of charge compensating anion is considered. The present work investigates  $\text{Cu}^{2+}$  with different anions immobilized in MOF-253. The materials are used as catalysts in the Meinwald rearrangement of  $\alpha$ -pinene oxide (APO) to campholenic aldehyde (CA, Scheme 1), an important fragrance compound.

The rearrangement of APO is a reaction sensitive to side product formation. While the use of a suitable Lewis acid catalyst results in a high yield of the preferred CA product, the presence of Brønsted acidity produces a mixture of products in low yield, such as *trans*-carveol, *trans*-sobrerol, *p*-cymene and dimerization products. [23] Lewis acid catalysts classically used for this reaction are metal halides. When these are applied as homogeneous catalysts, their separation and reuse is often troublesome. The development of heterogeneous alternatives is therefore of interest. Examples of performant heterogeneous catalysts include Lewis acids immobilized on oxides, e.g.  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$  or  $\text{H}_3\text{BO}_3$  on  $\text{TiO}_2$  nanoparticles [24] or  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  on hexagonal mesoporous silica (HMS) [23], sulfated alumina, titania or zirconia [25], titanium Beta zeolites [26] or mesoporous aluminosilicates [27]. Several MOFs have also been investigated for this reaction. Our laboratory reported the catalytic activity of  $\text{Cu}_3(\text{BTC})_2$  and acid treated MIL-100(Fe) [28,29]; Garcia et al. [30] investigated a series of Fe-MOFs in solvent-free reaction conditions and, most recently, Timofeeva et al. [31] investigated the use of MIL-100 (Al, Fe and Cr), MIL-110(Al) and MIL-96(Al) as catalysts for this rearrangement. The reaction is therefore well-suited for comparing the activities of various copper salts immobilized on MOF-253, and for evaluating the differences in performance with the homogeneous counterparts.

## 2. Materials and methods

### 2.1. MOF-253 synthesis and copper loading

MOF-253 was synthesized and loaded with  $\text{Cu}^{2+}$  salts according to literature procedures [16]. A solution of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (151 mg, 0.625 mmol) in 10 mL of *N,N'*-dimethylformamide (DMF) was added to a Teflon-capped vial containing 2,2'-bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol). The mixture was heated at  $120^\circ\text{C}$  for 24 h, after which the resulting powder was filtered and washed with DMF. The material was washed further with methanol via soxhlet extraction for 24 h, after which the powder was again collected via filtration and dried under vacuum at  $250^\circ\text{C}$  for 12 h. The material was loaded with e.g.  $\text{Cu}(\text{BF}_4)_2$  by soaking the solid (0.500 g, 1.75 mmol) in a solution of  $\text{Cu}(\text{BF}_4)_2$  (0.455 g, 1.92 mmol) in acetonitrile (15 mL) at  $65^\circ\text{C}$  for 24 h. The loaded material,  $\text{Cu}(\text{BF}_4)_2@$ MOF-253, was then washed repeatedly with acetonitrile, filtered and heated overnight at  $150^\circ\text{C}$  under vacuum prior to catalytic testing. The final  $\text{Cu}^{2+}$  loading of the materials was evaluated via elemental analysis.

### 2.2. Catalysis

Homogeneously catalyzed reactions were performed by adding a mixture of APO (Aldrich, 100 mg, 0.66 mmol) in ethyl acetate (5 mL) to a mixture of copper salt (100 mg) and 2,2'-bipyridine

(varying amount, molar ratio 0 or 1). The reactions were carried out at room temperature for 24 h. The identity of the reaction products was verified by GC–MS (Agilent 6890 gas chromatograph, equipped with a HP-5MS column, coupled to a 5973 MSD mass spectrometer) and the product yields were determined via GC-analysis.

Heterogeneous reactions were performed under identical conditions; however the experimental volume was downscaled by a factor of 5, limiting the amount of catalyst to 20 mg in 1 mL of ethyl acetate.

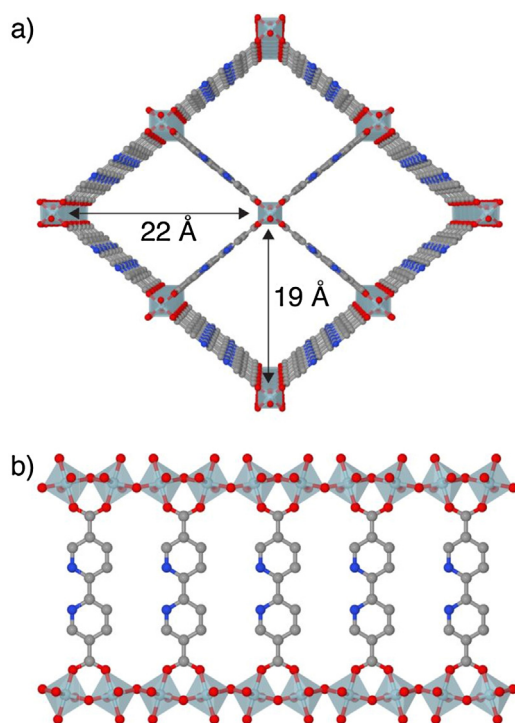
### 2.3. Characterization

Powder X-ray diffraction patterns of the loaded MOF samples were collected using  $\text{CuK}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation on a Bruker D8 Advance diffractometer. The diffraction patterns are depicted in Fig. S1.

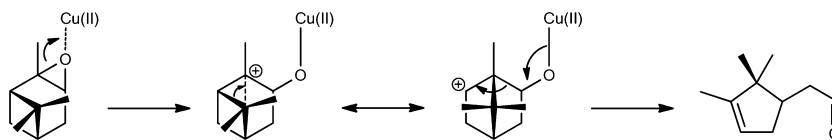
Electron paramagnetic resonance (EPR) spectra of  $\text{Cu}(\text{BF}_4)_2$ ,  $(\text{Cu-bpy})(\text{BF}_4)_2$  and  $\text{Cu}(\text{BF}_4)_2@$ MOF-253 in methanol were recorded using a Bruker 300E continuous wave spectrometer, with the cavity cooled to 115 K. The sample was irradiated with a microwave frequency of 9.59 GHz and the measurement with a sweep width of 200 mT was centred at 320 mT. The data were analyzed and the spectra were simulated using the EasySpin software package [32].

## 3. Results and discussion

The structure of MOF-253 contains rigid diamond-shaped one-dimensional pores, approximately 19 by 22 Å across (Fig. 1) [16]. X-ray powder diffraction data show that the material is of suitable crystallinity, and all major diffraction peaks are preserved after loading with  $\text{CuCl}_2$ ,  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Cu}(\text{BF}_4)_2$  (Fig. S1, supporting information). Nitrogen physisorption confirms that the materials retain their microporosity upon loading with the salts (Fig. S2, Table



**Fig. 1.** View of the pore system of MOF-253 according to the (100) direction (a) and close-up of the pore wall (b). Light blue octahedra represent Al, while grey, red, and dark blue spheres represent C, O and N respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

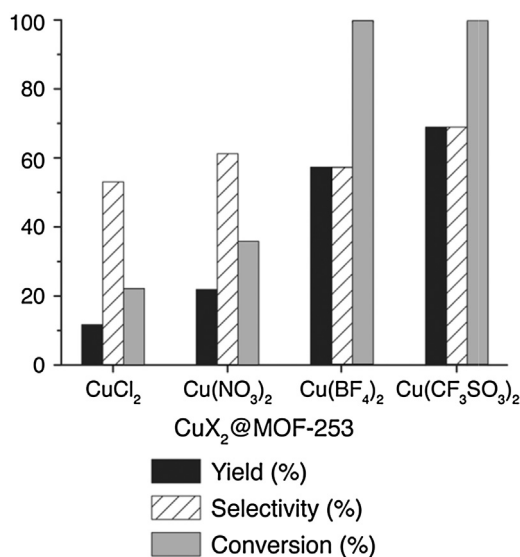


**Scheme 2.** Proposed reaction mechanism for the APO rearrangement reaction.

S1). Rotation of the linker molecules, away from the coplanar configuration depicted in Fig. 1 enables high loadings of  $\text{Cu}^{2+}$  in the material. Elemental analysis of e.g.  $\text{Cu}(\text{BF}_4)_2$  in MOF-253 confirmed loadings of 97% of the available number of coordination sites (Table S2).

As the MOF-253 framework is neutral and as the metal cations are immobilized via coordination, different counteranions can be included for a given metal ion. The catalytic performance of the different copper salts immobilized in MOF-253 (designated  $\text{CuX}_2@MOF-253$ ) in the rearrangement of APO is shown in Fig. 2. No conversion was observed when the reaction was performed in the absence of catalyst.

From the results shown in Fig. 2, it is immediately clear that the counteranion indeed has a large influence on the catalytic performance of divalent copper ions immobilized in MOF-253, most strikingly in terms of conversion in the APO rearrangement reaction. The overall conversion increases strongly as the coordinating ability of the counteranion decreases, with full conversion being reached after 24 h for the materials loaded with  $\text{Cu}(\text{BF}_4)_2$  and  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ . Due to the facile side product formation, the selectivity towards CA is another important parameter. The highest selectivity after 24 h is observed for  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$  (69%) as opposed to 53%, 56% and 61% for  $\text{CuCl}_2@MOF-253$ ,  $\text{Cu}(\text{BF}_4)_2@MOF-253$  and  $\text{Cu}(\text{NO}_3)_2@MOF-253$ , respectively. To better evaluate the selectivity of  $\text{Cu}(\text{BF}_4)_2@MOF-253$  at lower conversions, the progress of the reaction was monitored at regular intervals (Fig. S3, supporting information). This shows that the selectivity drops slightly as the reaction progresses, and after 2 h, at 40% conversion, which is a similar conversion level as with  $\text{Cu}(\text{NO}_3)_2@MOF-253$  after 24 h, the selectivity towards CA was also 61%. Hence, with both activity and selectivity in mind,  $\text{CF}_3\text{SO}_3^-$  appears to be the anion of choice for this reaction, followed by  $\text{BF}_4^-$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ .



**Fig. 2.** Yield, selectivity and conversion after 24 h in the APO rearrangement catalyzed by different copper salts immobilized on MOF-253. Reactions were performed at room temperatures using 0.1 g of APO in 5 mL ethyl acetate added to 0.1 g of catalyst.

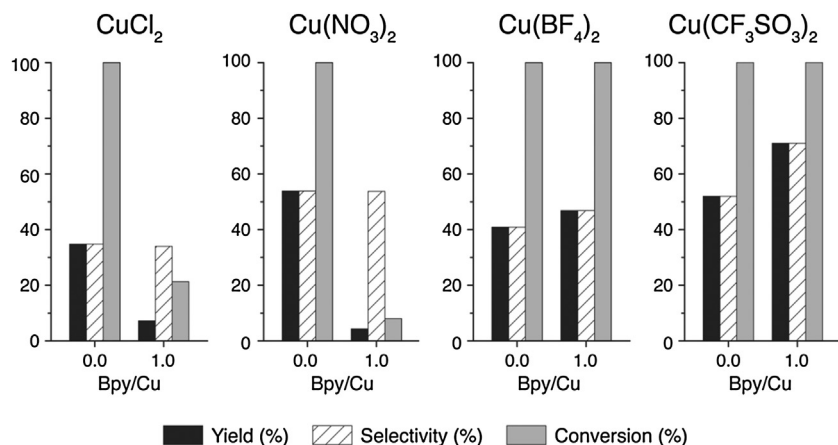
The origin of the observed counteranion effect is likely related to the coordinating nature of the anion. The APO rearrangement on copper presumably follows a mechanism as illustrated in Scheme 2. As APO coordination to the copper ion is essential for the catalytic cycle to proceed, the accessibility of the copper ion is a determining factor in the catalytic activity, especially with the presence of a 2,2'-bipyridine ligand in the coordination sphere of copper. Indeed, the highest conversions are observed for weakly coordinating anions,  $\text{CF}_3\text{SO}_3^-$  and  $\text{BF}_4^-$ . Similarly, the catalytic activity in the cyclopropanation of styrene, of bis(oxazoline)-copper complexes immobilized by electrostatic interactions was found to be dependent on the nature of the anionic support [33]. In this case, weakly coordinating anionic groups, such as the perfluorosulfonic groups of Nafion, were determined to be the best option.

Although no conclusive rationalization for the observed differences in selectivity towards campholenic aldehyde can be given at this time, these differences are likely due to differences in the coordination environment of the copper ion as a result of the different anions.

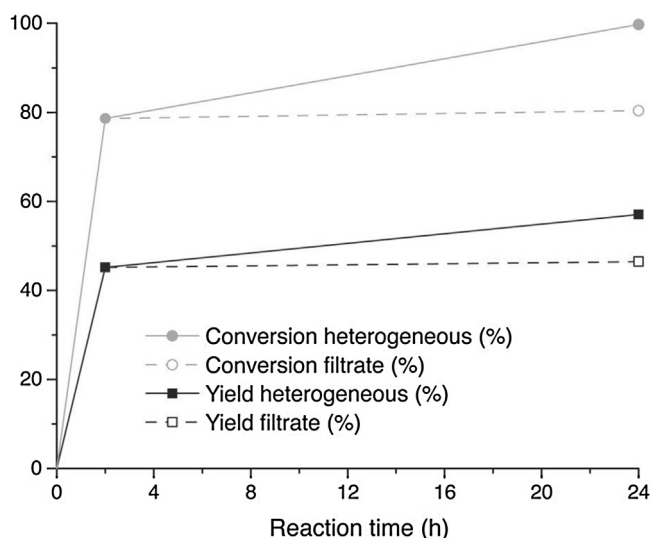
The catalytic activity of the copper salts in homogeneous solution was studied in the absence of added bipyridine to evaluate whether the trends in catalytic performance are similar as after immobilization in MOF-253 (Fig. 3). After 24 h, all copper salts show full conversion. At this equal, complete conversion, the selectivity increases in the series of counteranions  $\text{Cl}^-$  (35%) <  $\text{BF}_4^-$  (41%) <  $\text{CF}_3\text{SO}_3^-$  (52%) <  $\text{NO}_3^-$  (54%), similar to what is observed with the immobilized salts in the MOF. Clearly, the conversions are lower for the heterogenized systems, as would be expected because of mass transfer effects related to the porous framework of the MOF; however, upon heterogenization, the selectivity of the Cu compounds is at least maintained or even improved. This effect of the MOF is remarkable, since more often than not the selectivity of homogeneous complexes decreases after immobilization [34].

To better understand the influence of bpy on the catalytic performance of the salts, 1 equivalent of bpy was added to the homogeneous solutions of Cu compounds (i.e.,  $\text{bpy}/\text{Cu} = 1.0$ ). Generally, the addition of bpy resulted in the formation of poorly soluble copper bipyridine complexes which precipitated under reaction conditions. Only for the adducts of  $\text{Cu}(\text{BF}_4)_2$  and  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$  with 2,2'-bipyridine, the combined catalytic activity of the resulting precipitate and the  $\text{Cu}^{2+}$  ions remaining in solution was still sufficiently high to attain full conversion within 24 h, and in fact even after 30 min. As for  $\text{Cu}(\text{BF}_4)_2$  and  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$  immobilized in MOF-253, the addition of bpy results in an increase in the selectivity towards CA (47% as opposed to 41% for  $\text{Cu}(\text{BF}_4)_2$  and 71% compared to 52% for  $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ ), yet the selectivity increase observed for the  $(\text{Cu-bpy})(\text{BF}_4)_2$ -adduct is less pronounced than for  $\text{Cu}(\text{BF}_4)_2@MOF-253$  (56%). For  $\text{CuCl}_2$  and  $\text{Cu}(\text{NO}_3)_2$ , the precipitation of the copper compound led to a major loss of catalytic activity. Interestingly, the conversions observed after 24 h were higher for  $\text{CuCl}_2$  and  $\text{Cu}(\text{NO}_3)_2$  immobilized in MOF-253 than for the same compounds in combination with 1 equivalent of bpy. This shows that in these cases, the beneficial effect of the optimal dispersion of the catalytic sites in MOF-253, more than compensates for the possibly unfavourable accessibility of the  $\text{Cu}^{2+}$  centres inside the one-dimensional pores of the framework.

To assess the stability and heterogeneity of the catalyst under reaction conditions, a filtration test was performed using the most



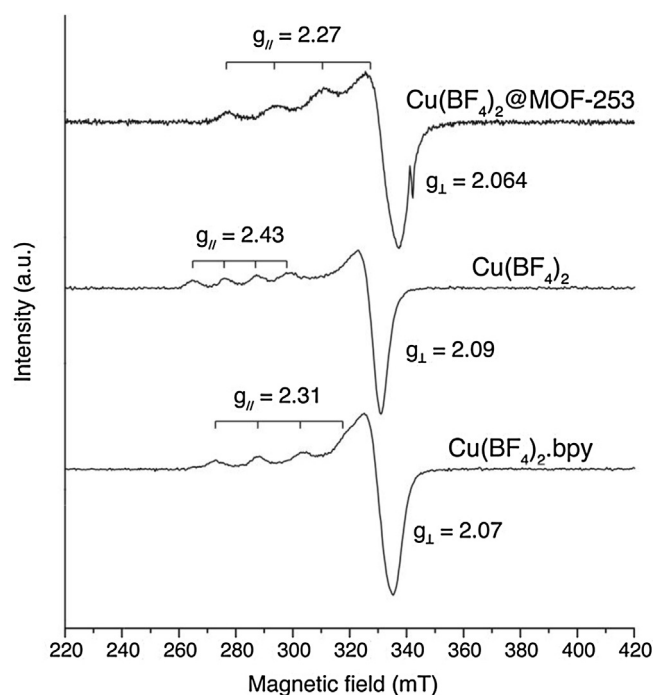
**Fig. 3.** Yield, selectivity and conversion after 24 h in the APO rearrangement catalyzed by different copper salts and their adducts with one equivalent of bpy. Reactions were performed at room temperatures using 0.1 g of APO in 5 mL ethyl acetate added to 0.1 g of catalyst.



**Fig. 4.** Filtration test for Cu(BF<sub>4</sub>)<sub>2</sub>@MOF-253 in the APO rearrangement reaction.

active material, i.e. Cu(BF<sub>4</sub>)<sub>2</sub>@MOF-253 (Fig. 4). The absence of further conversion after removal of the catalyst via filtration confirms that the catalytic copper ions do not leach from the MOF support. Furthermore, the catalyst could be reused without loss in catalytic activity or selectivity.

Electron paramagnetic resonance (EPR) spectroscopy was employed to probe the Cu<sup>2+</sup> environment in MOF-253 (Fig. 5). The introduction of a nitrogen-containing ligand in the coordination sphere of copper results in a shift of the *g*-parameters to lower values, e.g. *g*<sub>||</sub> = 2.43 and *g*<sub>⊥</sub> = 2.09 for Cu(BF<sub>4</sub>)<sub>2</sub> in methanol as opposed to *g*<sub>||</sub> = 2.31 and *g*<sub>⊥</sub> = 2.07 for the mono-bipyridine complex (Cu-bpy)(BF<sub>4</sub>)<sub>2</sub>. In order to avoid excessive peak broadening due to dipolar interactions, the amount of Cu(BF<sub>4</sub>)<sub>2</sub> loaded in the MOF was lowered to 16.8 μmol of Cu(BF<sub>4</sub>)<sub>2</sub> per g of MOF, covering approximately 0.5% of the available bpy sites in the MOF. Even though it might be theoretically feasible for the copper ion to simultaneously coordinate to two adjacent bpy linkers, the spectrum of the diluted copper ions on the MOF closely resembles that of the homogeneous (Cu-bpy)(BF<sub>4</sub>)<sub>2</sub> compound, strongly suggesting that the copper ions are indeed immobilized via the formation of a complex with a single bpy linker in a 1:1 bpy/Cu-ratio. This spectroscopic result corresponds nicely with the trends observed in catalysis, in which the catalytic performance of the Cu@MOF-253 catalysts most closely



**Fig. 5.** EPR spectra of Cu(BF<sub>4</sub>)<sub>2</sub>@MOF-253, Cu(BF<sub>4</sub>)<sub>2</sub> and (Cu-bpy)(BF<sub>4</sub>)<sub>2</sub> in methanol at 115 K.

resembles that of the bpy/Cu = 1.0-complexes, as well as with the high loading of Cu(BF<sub>4</sub>)<sub>2</sub> in MOF-253.

#### 4. Conclusion

MOF-253 is a suitable matrix for the immobilization of copper salts via coordination to the bipyridine motif incorporated in the linker molecule. As such, a large number of optimally dispersed catalytic sites can be introduced into the framework. Although the catalytic activity of the copper ions decreased upon coordination with the bpy linker, the selectivity in the Meinwald rearrangement of α-pinene oxide to campholenic aldehyde markedly increased. Furthermore, the catalytic performance of the MOF loaded with copper salts was shown to depend greatly upon the choice of charge-compensating anion. Hence the non-ionic interaction of the MOF with guest species offers an additional advantage over traditional supports such as ion exchange resins, as it allows for

the optimization of the immobilized catalyst by variation of the counteranions.

### Acknowledgements

The authors are grateful to the Belgian Federal Government for support in the IAP project 07/05 Functional Supramolecular Systems, D.V. and P.V. are grateful to K. U. Leuven for the Methusalem CASAS grant, and to FWO Vlaanderen for research project funding G.0453.09 and G.0486.12. P.V. and R.A. are grateful for a fellowship from FWO Vlaanderen. Efforts in Berkeley were supported by the Laboratory Directed Research and Development Programme of Lawrence Berkeley National Laboratory (Contract No. DE-AC02-05CH11231). We gratefully acknowledge Gerald K. Branch and Arkema for fellowship support of E.D.B.

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cattod.2014.08.006>.

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