

# Synergistic effects of encapsulated phthalocyanine complexes in MIL-101 for the selective aerobic oxidation of tetralin†

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**Metal phthalocyanine complexes encapsulated in MIL-101, and used as “ship-in-a-bottle” catalysts, show outstanding TONs in the aerobic oxidation of tetralin.**

Over the last decade, metal–organic frameworks (MOFs) have been introduced as a new class of heterogeneous catalyst systems.<sup>1–7</sup> Rapid progress is being made in developing MOF-based catalysts for selective oxidation of hydrocarbons. One approach consists in designing MOFs that possess metallic clusters with catalytic centers.<sup>8–11</sup> Corma *et al.* have investigated Cu-pymo and Co-ZIF-9, in which the clusters are responsible for the selective oxidation of tetralin in air.<sup>12</sup> Another approach resides in using MOFs as a host matrix to support the catalyst, as in the case of zeolites.<sup>13</sup> Thanks to their cage-type structures, faujasite (FAU) zeolites in particular can encapsulate “nano” catalysts, but the small size of the FAU cavities (0.74 nm) prevents the hosting of large catalytic systems. The use of activated carbons or mesoporous silica can permit the insertion of large systems, but leaching can easily take place, posing a problem for the retention of guest species. In contrast, MIL-101, which exhibits a 3D pore system with calibrated cavities of 2.9 nm and 3.4 nm,<sup>14,15</sup> presents a very promising pore structure for the development of supported metallic or oxide complexes as “ship-in-a-bottle” catalysts. Such an approach has recently been undertaken to encapsulate inorganic clusters such as polyoxometalates,<sup>14,16–18</sup> metallic nanoparticles<sup>13,19,20</sup> and molecular catalysts.<sup>21–23</sup>

Metal phthalocyanine complexes (MPc) exhibit outstanding performance as oxidation catalysts.<sup>24,25</sup> Recently, our group showed that a bulky N-bridged diiron phthalocyanine complex, (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N, allows the selective oxidation of methane, benzene and alkylaromatics.<sup>26–28</sup> The EXAFS structural determination indicates a linear Fe<sup>+3.5</sup>(μ-N)Fe<sup>+3.5</sup> unit with equivalent Fe–N distances (1.65 Å) and a 3.33 Å distance between parallel Pc planes.<sup>29</sup> Unfortunately, MPc usually self-assemble to oligomer structures in solution through π stacking, which strongly limits their catalytic applications in homogeneous processes.<sup>30</sup> To overcome this issue, silica- and zeolite-supported MPc have therefore been developed.<sup>31–35</sup>

The objective of this work is to encapsulate large MPc in cavities of MIL-101 for the selective oxidation of tetralin into 1-tetralone, a diesel fuel additive and an intermediate for the synthesis of agricultural chemicals.<sup>12</sup> To the best of our knowledge, this is the first report on the synergistic effect of the confinement of molecular catalysts in porous MOFs.

A catalytic screening of different unsupported metal phthalocyanine catalysts in aerobic tetralin oxidation (Table S1, ESI†) has enabled the identification of two different perfluorinated complexes (MPcF<sub>16</sub>, M = Fe, Ru) and the bulky dimer, (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N, which were selected for encapsulation. The activities and selectivities are presented in Table 1. This reaction was performed in parallel batch reactors at 8 bar of O<sub>2</sub> at 90 °C with a substrate-to-MPc molar ratio of 36 000 : 1. The products were analyzed by GC and GC-MS. The TONs of the molecular catalysts follow the order (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N > RuPcF<sub>16</sub> > FePcF<sub>16</sub>. Interestingly, similar selectivities toward 1-tetralone were obtained for the three molecular complexes.

The MPc–MOF composite materials were prepared by wet infiltration of the deep blue-colored MPc solutions into Cr–MIL-101 with a maximal theoretical complex loading inside the MOF of 9 wt%. After slow evaporation of the solvent (acetone for MPcF<sub>16</sub> and CH<sub>2</sub>Cl<sub>2</sub> for (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N), any complexes not strongly bound to the host MOFs were removed by intensive washing until the filtrate remained colorless. The actual complex loading for the perfluorinated complexes inside the MIL-101 was determined by ICP-OES measurements to be 2.1 wt% and 3.6 wt% for FePcF<sub>16</sub> and RuPcF<sub>16</sub>, corresponding to approximately 0.8 and 1.2 complexes per large pore respectively. Considering also the access to the smaller pores, the total pore filling would correspond to an average of app. 0.3 (FePcF<sub>16</sub>) and 0.4 (RuPcF<sub>16</sub>). A higher loading of 5.2 wt% is obtained for the (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N dimeric complex. This last result was also confirmed by diffuse reflectance UV-VIS spectra of pristine

**Table 1** Catalytic activity, selectivity and turnover numbers after 6 h for the applied phthalocyanine complexes used as homogeneous catalysts in tetralin oxidation

	Complexes		
	(FePc <sup>t</sup> Bu <sub>4</sub> ) <sub>2</sub> N	FePcF <sub>16</sub>	RuPcF <sub>16</sub>
X <sup>a</sup> [%]	25	21	38
S <sub>one</sub> <sup>b</sup> [%]	69	68	70
TON <sup>c</sup>	7400	3400	5200

<sup>a</sup> Conversion of tetralin. <sup>b</sup> Selectivity toward 1-tetralone. <sup>c</sup> Turnover number after 6 h for 1-tetralol and 1-tetralone.

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and complex loaded MOFs (Fig. S1, ESI†). In agreement with the literature, two adsorption maxima at 446 nm and 600 nm can be identified for the non-loaded MIL-101.<sup>36</sup> For the loaded materials, a shift of the peak maximum to around 615 nm was observed due to the presence of the Pc complexes.<sup>32</sup>

X-Ray powder diffraction and N<sub>2</sub> physisorption measurements demonstrate the stability of MIL-101 host materials after the encapsulation process, since similar diffraction patterns and isotherm shapes were obtained (Fig. S2 and S3, ESI†). As expected, the specific surface area and pore volume decrease for complex-containing MOF systems (Table 2).

For RuPcF<sub>16</sub>@MIL-101, the total pore volume decreases by 16 % with respect to pure MIL-101, which is more than the weight loading of 3.6 wt%. This clearly shows that the complexes are incorporated into the porous structure and thus reduce the pore volume by preventing the N<sub>2</sub> from entering the cavities. Similar decreases in specific surface area and pore volume were also reported for nanoparticle and polyoxometalate functionalized MIL-101 materials.<sup>16,20</sup> For the bulky (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N@MIL-101, the total pore volume decreases by only 5%, which corresponds to the weight gain of 5.2 wt% after loading. This indicates that the voluminous (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N complex is not incorporated into the mesoporous structure of the MIL-101. Indeed, the dimer (~2.0 × 2.0 nm) is too large to enter the hexagonal pore windows of the MIL-101 (1.47 × 1.6 nm).<sup>14</sup> It would appear that (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N complexes are strongly adsorbed at the outer surfaces of the crystallites and/or in macroporous cavities formed by MOF particle agglomeration.

The homogeneous distribution of different iron and ruthenium complexes inside the MIL-101 support was verified by EDS analysis (Fig. S4, ESI†).

The encapsulated perfluorinated complexes were tested in similar conditions with a tetralin-to-complex molar ratio of 147 000 : 1 for FePcF<sub>16</sub>@MIL-101 and 92 000 : 1 for RuPcF<sub>16</sub>@MIL-101, respectively. Note that pure MIL-101 shows no catalytic activity (Table 2). FePcF<sub>16</sub>@MIL-101 and RuPcF<sub>16</sub>@MIL-101 catalysts show very high TONs. The turnover number of FePcF<sub>16</sub>@MIL-101 was 48 200 after 24 h, almost eight times higher than for the homogeneous FePcF<sub>16</sub> catalyst (TON = 6300). Significantly, the FePcF<sub>16</sub>@MIL-101 catalyst provided a higher selectivity (up to 80 %) toward the desired 1-tetralone compared to the homogeneous FePcF<sub>16</sub> (68 %) at similar conversion. An

**Table 2** N<sub>2</sub> physisorption results and catalytic performance of incorporated MPC@MIL-101 after 6 h and 24 h

Pc@MIL-101	MIL-101	N(FePc <sup>t</sup> Bu <sub>4</sub> ) <sub>2</sub> @MIL-101	FePcF <sub>16</sub> @MIL-101 <sup>c</sup>	RuPcF <sub>16</sub> @MIL-101
S <sub>BET</sub> <sup>a</sup> [m <sup>2</sup> g <sup>-1</sup> ]	2500	2450	2220	2120
V <sub>p</sub> <sup>b</sup> [cm <sup>3</sup> g <sup>-1</sup> ]	1.22	1.16	1.08	1.03
X [%]	0/—	4/—	17/33	34/48
S <sub>one</sub> <sup>d</sup> [%]	—/—	79/—	80/80	62/74
TON <sup>e</sup>	0/—	5100/—	24 200/ 48 200	30 900/ 46 300
Size [nm × nm]	1.47 × 1.6 <sup>f</sup>	~2.0 × 2.0 <sup>g</sup>	~1.3 × 1.3 <sup>g</sup>	~1.3 × 1.3 <sup>g</sup>

<sup>a</sup> S<sub>BET</sub> at  $p/p_0 = 0.05-0.2$ . <sup>b</sup> Total volume at  $p/p_0 = 0.95$ . <sup>c</sup> Conversion of tetralin. <sup>d</sup> Selectivity toward 1-tetralone. <sup>e</sup> Turnover number after 6 h/24 h. <sup>f</sup> Hexagonal pore window of MIL-101. <sup>g</sup> Sizes of Pc complexes.

analogous rise and change in selectivity was already reported for the hydroperoxide-mediated cyclohexane oxidation of zeolite-supported Ru complexes.<sup>32</sup>

The higher activity for encapsulated complexes has previously been explained by the preclusion of the dimerization process by  $\pi$  stacking that is typically observed for homogeneous catalysts.<sup>32</sup> Previously published activities of up to 3000 TON d<sup>-1</sup> are, however, significantly lower than those determined in the present study. To the best of our knowledge, this is the highest catalytic activity ever reported for homo- and heterogeneous tetralin oxidations. Note that the terminology of TON may be generally misused for metal-initiated free-radical oxidations. It expresses the activity in terms of the product (mol)/catalyst (mol) ratio, which is the indicator commonly used by the community.

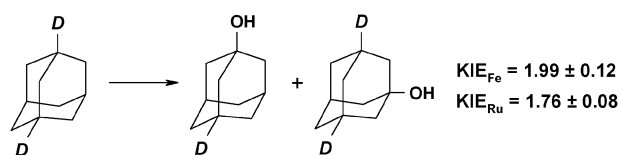
In contrast, a limited conversion of up to 4 % was obtained for the (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N@MIL-101 catalyst. In this case, the synergistic effects arising from the confinement in the pore do not take place. This is consistent with the hypothesis that (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N is not encapsulated within the mesoporous structure of the MIL-101. The observed residual conversion (4 %) may arise from the (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N complexes that are on or close to the external surface of the MIL crystallites and that are easily accessible for the tetralin.<sup>14,37</sup> This hypothesis is confirmed by similar TONs obtained for (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N (7400) and (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N@MIL-101 (5100).

Compared to the homogeneous perfluorinated catalysts, an induction period of up to three hours was observed for the encapsulated systems (Fig. 1). A similar phenomenon was also obtained for Co-MOF catalyzed aerobic cyclohexene (MFU-1) and tetralin oxidations (Co-ZIF-9), respectively.<sup>10,12</sup>

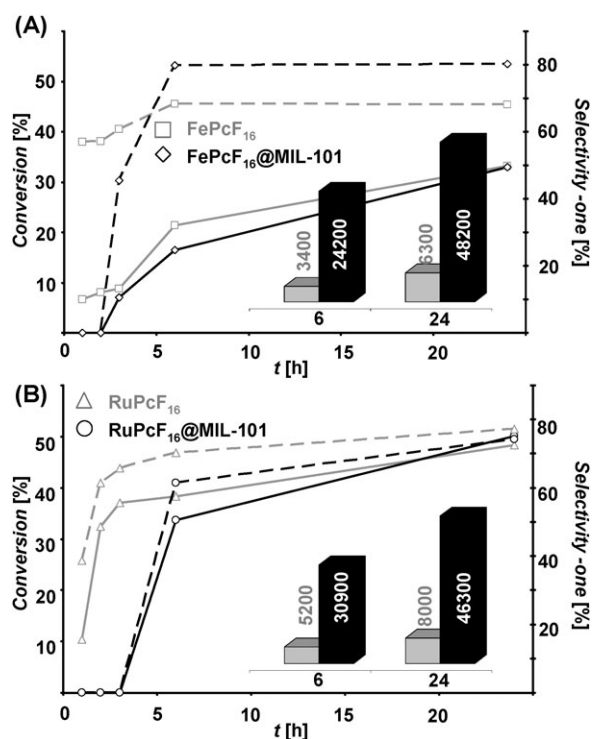
A release of the complexes by progressive degradation of the host structure in the reaction medium could have led to an induction period, as found for drug delivery mechanisms.<sup>38</sup>

No leaching of the complexes was detected by UV-VIS as the reaction proceeded, however (pure phthalocyanine structures are soluble in the reaction medium). This further demonstrates the robustness of the host matrix and the strong adsorption of the complexes into the MOF porous structure.

In order to gain insight into the mechanism of this oxidation, we studied the kinetic isotope effect (KIE) on the oxidation of adamantane-1,3-d<sub>2</sub>. This substrate is a useful probe to determine an *intra*-molecular KIE since it contains two equal tertiary C-H and two C-D bonds in the same molecule.<sup>39</sup> It should be noted that the reactivity of adamantane was much lower compared to tetralin. The analysis of the isotopic composition of the adamantanol-1 product directly provides an intrinsic KIE:



The KIE values were determined to be  $1.99 \pm 0.12$  and  $1.76 \pm 0.08$  for FePcF<sub>16</sub>@MIL-101 and RuPcF<sub>16</sub>@MIL-101, respectively. The KIE measured using FePcF<sub>16</sub> and RuPcF<sub>16</sub> in homogeneous solutions are similar:  $1.94 \pm 0.10$  and  $1.68 \pm 0.11$ , respectively, suggesting that the same mechanism



**Fig. 1** Tetralin conversion (solid line) and selectivity toward 1-tetralone (dashed line) of homogeneous FePcF<sub>16</sub> and RuPcF<sub>16</sub> complexes (grey) and FePcF<sub>16</sub>@MIL-101 (A) and RuPcF<sub>16</sub>@MIL-101 (B) (black) with significantly lower catalyst contents ( $n(\text{tetralin}) : n(\text{MPCF16}) = 147\,000 : 1$  (Fe) and  $92\,000 : 1$  (Ru)) compared to the non-incorporated complexes ( $36\,000 : 1$ ) explaining the clear difference in turnover numbers (TONs) after 6 h and 24 h (inset), respectively.

should be operating in homogeneous and heterogeneous systems. These low KIE values indicate the involvement of a radical mechanism in this reaction. The occurrence of an induction period and the detection of a small concentration of tetralinhydroperoxide by GC-MS over the course of tetralin oxidation are also consistent with a free radical mechanism of oxidation, as previously suggested elsewhere.<sup>12</sup>

In summary, this study demonstrates that the encapsulation of MPC in MIL-101 allows an activity increase of approximately one order of magnitude. This increase in activity may arise from the dispersion of the molecular complexes as isolated monomers in the nanopore cavities and/or from the confinement effects provided by the host porous structure. In contrast, the (FePc<sup>t</sup>Bu<sub>4</sub>)<sub>2</sub>N dimer, which is too large to penetrate into the porous structure, does not show this synergistic effect.

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