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Metal organic frameworks (MOFs) as catalysts: A combination of Cu^{2+} and Co^{2+} MOFs as an efficient catalyst for tetralin oxidation

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Abstract

Two metal–organic frameworks, $[Cu(2\text{-pymo})_2]$ and $[Co(PhIM)_2]$ (2-pymo = 2-hydroxypyrimidinolate; PhIM = phenylimidazolate), containing respectively Cu^{2+} and Co^{2+} ions and anionic diazaheterocyclic ligands (pyrimidinolate and phenylimidazolate) as organic linkers, have been successfully used for the aerobic oxidation of tetralin, yielding α-tetralone (T=O) as the main product. Both materials are stable and recyclable under the reaction conditions. Kinetic studies revealed significant differences between the two MOFs, as a consequence of the different catalytic behavior of their central metal ions. $[Cu(2\text{-pymo})_2]$ is highly active for the activation of tetralin to produce tetralinhydroperoxide (T–OOH), and less efficient in reacting the peroxide. Meanwhile, the use of the cobalt catalyst involves a long induction period for the reaction. However, once T–OOH is formed, Co^{2+} rapidly and efficiently transforms this into T=O, with high tetralone-to-tetralol ratio (T=O/T–OH of *ca.* 7). The combination of both materials has revealed as a convenient strategy for preparing a highly efficient, selective and reusable catalyst for the liquid phase aerobic oxidation of tetralin.

Keywords: Metal–organic framework; Coordination polymer; Tetralin aerobic oxidation

1. Introduction

Selective oxidation of cycloalkanes is an industrially relevant process for converting petrochemical raw materials into more valuable chemical products [1–3]. Among them, oxidation of cyclohexane and tetralin (1,2,3,4-tetrahydronaphthalene) are widely operated, while oxidation of naphtheno-aromatic compounds can be of interest for the production of oxygenated diesel molecules that help to reduce emissions [4], and to prepare ketone derivatives for fine chemicals. In particular, oxidation of tetralin to α-tetralone is interesting, since α-tetralone is used as starting material for preparing a number of chemicals, including insecticides, agricultural chemicals and drugs. This process is generally performed industrially in liquid phase using air (or oxygen) as oxidant, and with homogeneous or heterogeneous catalysts based on transition metals or metal complexes. For this purpose, a number of metal ions including Cu, Co, Cr, Pd, Ni, Mn and Fe have been successfully used in homogeneous processes, especially when complexed with N-containing ligands, such as porphyrins. It is generally recognized that the catalytic activity of the metal ion depends on the redox potential of the metal centre, and consequently on the nature of the ligands [5,6]. In the absence of a catalyst, oxidation of paraffins can proceed via radical intermediates through an autooxidation process [7]. When metal ions are present in the medium, they can catalyze the oxidation reaction, through the homolytic decomposition of the intermediate hydroperoxide via a Haber–Weiss cycle [8].

Development of selective and stable heterogeneous catalysts that can be efficiently and easily recovered from the reaction medium and reused in consecutive cycles, is an active research area [9]. Among the different heterogeneous systems studied, polymer-bound-metal catalysts such as Cu^{2+} in poly-(4-vinylpyridine) (Cu/PVP) have been tested for several organic reactions [10–20]. These supports can be functionalized to provide suitable ligands for incorporating transition metal ions (or metal complexes) through coordination bonds, thus mimicking

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the properties of homogeneous complexes while introducing the advantages of the heterogeneous systems.

An alternative approach to obtain heterogeneous catalysts that emulate the catalytic properties of homogeneous complexes consists in the preparation of metal–organic framework materials (MOFs), also known as coordination polymers. These crystalline materials are formed by a 3D extended network of metal ions connected through multidentate organic molecules, leading in most cases to a regular system of channels and cavities of molecular dimensions [21,22]. In the structure of MOFs, the metal ions are locally connected to the organic molecules through coordination bonds, thus resembling a spatially ordered three-dimensional array of metal coordination complexes. On these bases, the potential of MOFs for catalysis can be foreseen since, in principle, the adequate design and selection of organic linkers allows the preparation of MOFs with a local structure similar to any given metal coordination complex with the required catalytic activity. This strategy has actually shown to be effective in a number of different reactions and with different metal ions and complexes, and a comprehensive overview on the use of MOFs in catalysis can be found in the review by Kitagawa et al. [23].

There are however a series of drawbacks that preclude the extended use of MOFs in catalysis. One of them is their low thermal and chemical stability (as compared to inorganic counterparts, such as zeolites [24]), that limits their use to reactions performed under mild conditions. A second problem is that in most known MOF structures, the coordination sphere of the metal ion is completely blocked by the organic linkers, so that they have no free positions to interact with the substrates. These two main limitations are responsible for the scarce number of catalytic studies [23,25–27] with respect to the large number of reports describing preparation and structure of MOFs.

We have recently shown [28] the catalytic performance of a MOF composed of palladium and 2-hydroxypyrimidinolate as organic linker, $[Pd(2\text{-pymo})_2]\cdot 3H_2O$ (2-pymo = 2-hydroxypyrimidinolate). This material is topologically related to a 3D cubic sodalite-type framework, with accessible Pd(II) ions in a square planar coordination [29]. The Pd-MOF was found to be active in a series of reactions, such as alcohol oxidations, Suzuki–Miyaura C–C bond formation reactions and hydrogenation of olefins, for which several homogeneous Pd complexes are known to perform well. Moreover, the regular pore system of the material (accessible through two different hexagonal windows with free openings of 4.8 and 8.8 Å) conferred potential shape-selective properties to the material, that was demonstrated for the hydrogenation of olefins with different steric hindrance [28]. The structure of Pd-MOF was found to remain intact under the reaction conditions tested, allowing recovering and reuse for successive catalytic cycles.

The structure of the Pd-containing MOF is analogous to that of a Cu-containing MOF of composition $[Cu(2\text{-pymo})_2]\cdot 2.25H_2O$ [30], in where copper ions are in square planar coordination and linked to 4 nitrogen atoms of the pyrimidine ring. The chemical environment around the central copper ions in this Cu-MOF resembles that present in Cu/PVP, in the sense that in both cases copper ions are bound to nitrogen-containing heterocycles (a pyrimidine in Cu-MOF and a pyridine in Cu/PVP). In general, azaheterocycles are known to be good ligands for copper ions when catalytic oxidation of paraffins is to be carried out [5,6].

Therefore, given the chemical similarities between Cu-MOF and Cu/PVP, as well as our previous success with the topologically analogous Pd-MOF, it was expected the former to have potential as oxidation catalyst.

We have also tested the catalytic activity of a cobalt-containing MOF for tetralin oxidation, since cobalt catalysts are known to be active and selective for the oxidation of cycloalkanes. However, we could not use the analogous $[Co(2\text{-pymo})_2]$ material [31], since it lacks structural porosity. Instead, we have prepared ZIF-9 [32]. This MOF (hereafter Co-MOF) contains phenylimidazolate as the organic component, and it is also topologically related to a 3D sodalite-type framework, with tetrahedrically coordinated cobalt ions. Although Cu-MOF and Co-MOF are chemically different, they still have important similarities: both materials have anionic diazaheterocyclic ligands (pyrimidinolate and imidazolate) and they both are topologically related to the same SOD structure type (and thus diffusivity of products within the pores in both materials should be similar).

In the present work, we will show the results obtained for the aerobic oxidation of tetralin using both Cu-MOF and Co-MOF separately, as well as combinations of them. We have chosen this reaction as a test to evaluate the potential of the materials because of the given fundamental and economic interest in converting low cost petrochemical raw materials such as tetralin into more value-added chemicals, such as α-tetralone. Analysis of the kinetic data obtained for this reaction has allowed us to draw some general insights on the catalytic roles of Cu^{2+} and Co^{2+} ions separately, and to rationalize the collaborative effects observed when the two materials are simultaneously used as catalysts. Special attention has also been paid to their stability and reusability under reaction conditions.

2. Experimentals and methods

2.1. Preparation of Cu-MOF and Co-MOF

The materials $[Cu(2\text{-pymo})_2]$ (Cu-MOF) and $[Co(PhIM)_2]$ (Co-MOF) where prepared according to the procedure described elsewhere [30,32]. Their structure and crystallinity where confirmed by X-ray powder diffraction (Phillips X'Pert diffractometer), by comparison with the data reported in literature [30,32].

2.2. Catalytic tests and product analysis

7.0 g of tetralin (0.052 mol) were loaded in a three-necked flask with the corresponding amount of catalyst to obtain a tetralin/metal molar ratio of 2000. The system was heated at 90 °C and then the reaction started by feeding air into the reaction mixture at a constant flowrate (0.5 mL/s) by means of an adjustable valve. A reflux system with PEG at 0 °C was installed, so that vapours were condensed, being the total mass

Table 1
Recycling of Cu-MOF for the oxidation of tetralin[a]

	Cu-MOF		
	USE 1	USE 2	USE 3
Conversion (mol%)	51.5	53.8	45.6
Yield (mol%)[b]			
T–OOH	1.2	0.6	1.7
T–OH	13.6	12.4	9.9
T=O	36.7	40.8	33.8
By-products	0.0	0.0	0.1
T=O/T–OH ratio	2.7	3.3	3.4

[a] Reaction conditions: 7.0 g T–H (0.053 mol) at 90 °C, 0.1 MPa bubbled air pressure at 0.50 mL/s flowrate. Molar ratio T–H/Cu was kept constant throughout all catalytic tests and equal to 2000.

[b] Calculated as: mol product × 100/mol of initial T–H at 48 h, when conversion reached a plateau. (T–H: tetralin, T–OOH: tetralynhydroperoxide, T–OH: tetralol, T=O: tetralone.)

balances 99 ± 1%. After each catalytic test, the solid catalyst was recovered by filtration and thoroughly washed with acetone and dried in an oven at 60 °C overnight. At this point the material was ready for reuse. Tetralin, tetralol and tetralone concentrations were determined by GC analysis of the samples using *n*-hexadecane as external standard. The reaction intermediate tetralinhydroperoxide (T–OOH) was quantitatively determined by means of an indirect method using triphenylphosphine (TPP) [33].

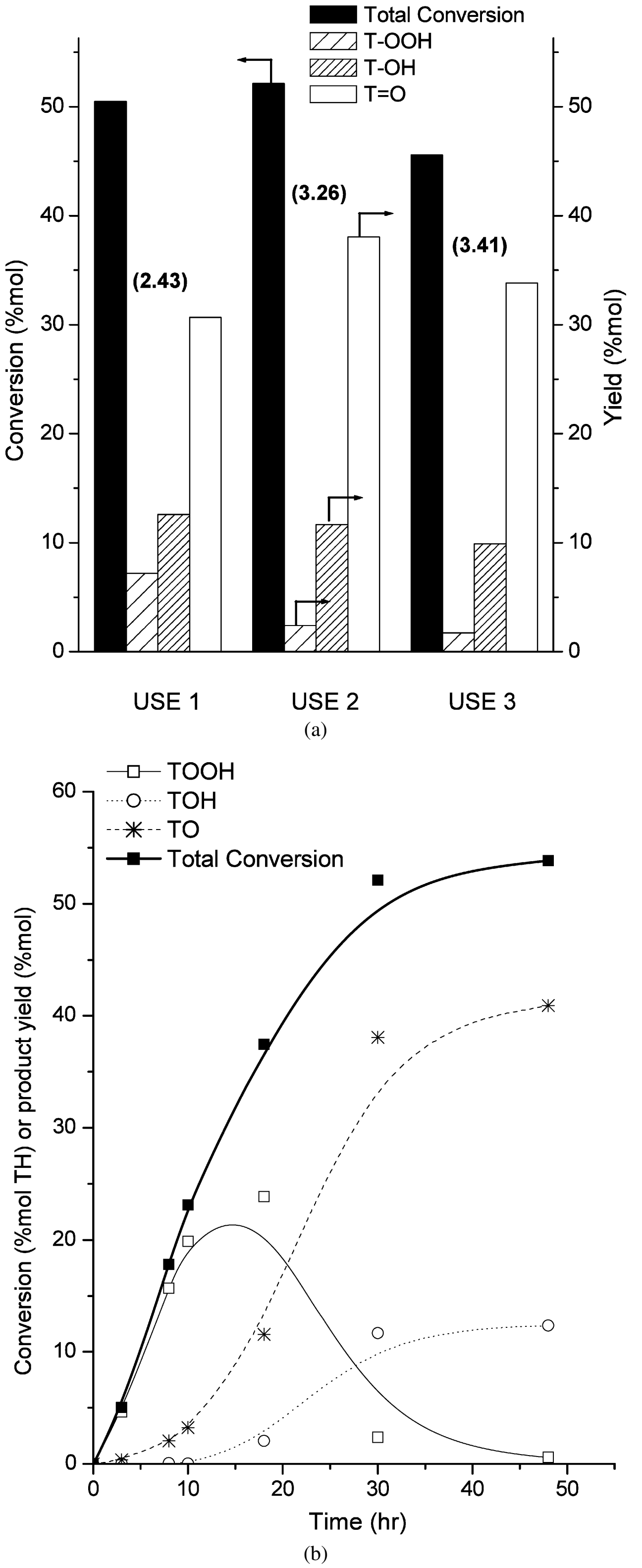
3. Results and discussion

3.1. Liquid phase oxidation of tetralin with Cu-MOF: Activity, selectivity and reusability

The results obtained for the liquid phase oxidation of tetralin with Cu-MOF are summarized in Table 1 and Fig. 1, for the fresh catalyst and for successive catalyst reuses. The data contained in Table 1 include the values of maximum conversion for each catalyst, as well as product distribution and tetralone/tetralol ratio obtained at maximum conversion.

After successive runs, we observed that the time needed for reaching maximum conversion increased; *i.e.*, the catalytic activity of the catalyst decreased progressively, while the maximum conversion finally reached was practically the same in all cases (only a slight decrease is observed after 2 reuses), and close to *ca.* 50% (see Fig. 1a, black columns).

As far as product distribution is concerned, the conversion of tetralin and the evolution of T–OOH, T–OH and T=O with time was found to be virtually identical in all cases. To illustrate this, the product evolution for the second use of the catalyst is shown in Fig. 1b. In all three runs, a rapid conversion of tetralin to T–OOH was initially observed, with small formation of T–OH and T=O. At this initial stage, T–OOH was practically the only observed product of tetralin conversion. After the first *ca.* 15 h of reaction, the concentration of T–OOH reached a maximum of around 25% yield and then starts to decrease until almost complete disappearance. The decrease in T–OOH yield was accompanied by the concomitant increase of T–OH



(a)

(b)

Fig. 1. (a) Conversion of tetralin over Cu-MOF for the fresh catalyst (USE 1) and for two successive reuses (USE 2 and USE 3). Black columns refer to total T–H conversion, while the other columns refer to product yield as indicated in the text box. The numbers in parentheses correspond to the T=O/T–OH ratio. (b) Time conversion of T–H and kinetic evolution of products obtained in the first reuse of Cu-MOF (USE 2). The lines between points are only indicative, to help following the evolution of the experimental points. Symbols as indicated in the text box.

and T=O, being always T=O the main product. After *ca.* 30 h, and coinciding with the disappearance of T–OOH, tetralin conversion (together with T=O and T–OH formation) reached a plateau, that corresponds to the maximum conversion and product distribution presented in Table 1. Besides the decrease in catalyst activity observed after successive uses, the only significant difference among the three runs is the final T=O/T–OH ratio obtained, which progressively increases from 2.7 for the fresh catalyst to 3.4 after three reuses. This ratio is a relevant indicator of the performance of the catalyst, as it measures the selectivity for the oxidation of tetralin to tetralone.

We have compared the IR spectra of fresh and used Cu-MOF catalyst, and the results are shown in Fig. S1 in supplementary material. We can observe that the used catalyst shows a series of bands in the 1800–1600 cm^{-1} region that are absent on the fresh catalyst. These bands can be attributed to adsorbed T=O that has not completely been removed after washing with acetone. The relatively low intensity of these bands indicates that the amount of adsorbed T=O is in any case low, which is in agreement with the fairly good mass balance obtained by GC. The results indicate however that the catalyst is deactivated to some minor extend by product adsorption, and that the initial activity can not be completely recovered after exhaustive washing. This in turn explains: (a) the decrease of the initial activity of the catalyst after successive runs; (b) the deactivation of the catalyst and the lower T=O/T–OH ratio at higher T–H conversions; and (c) the increment in the T=O/T–OH ratio after successive runs (as the catalytic activity diminishes, the relative importance of the autooxidation contribution increases, which produces a progressive increment of the T=O/T–OH ratio).

3.2. Stability and leaching tests of Cu-MOF

In heterogeneous catalysis it is always important to check for the possible occurrence of any leaching. Otherwise, in certain cases, we might wrongly conclude that the metal centers in the solid catalyst are responsible for the observed catalytic transformation, when this should be rather attributed to soluble metal species leached from the solid.

Chemical analysis of the reaction medium after hot filtration of the catalyst [34] can provide information on catalyst leaching during reaction. Nevertheless, the absence of any metal traces in the filtrate does not discard that some metal release from the catalyst has occurred [35,36]. In these cases where no metal traces are detected in the reaction medium after hot filtration of the catalysts, additional tests are usually needed to completely rule out metal leaching [37].

In the case of tetralin oxidation by Cu-MOF, extensive leaching of Cu under the reaction conditions could be ruled out, not only because no traces of copper were detected in the reaction medium after hot filtration, but also by comparing the X-ray diffractograms of the fresh and used catalysts, recovered by filtration after each catalytic run. As it is shown in Fig. 2, no significant differences are observed between the diffractograms, which indicates that the crystalline structure of the material is preserved. Notice that in the case of Cu-MOF, leaching of Cu necessarily would cause a collapse of the MOF structure. Therefore, releasing of copper from the catalyst can be excluded within the detection limits of XRD.

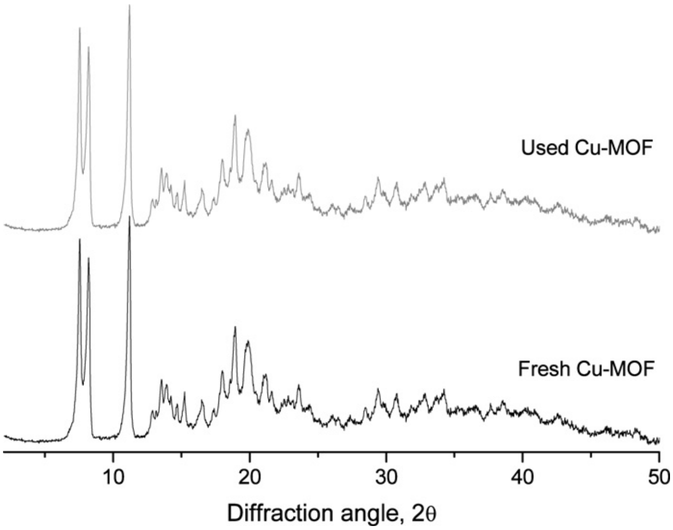


Fig. 2. X-ray diffraction patterns (Cu$K\alpha$) of fresh and used Cu-MOF.

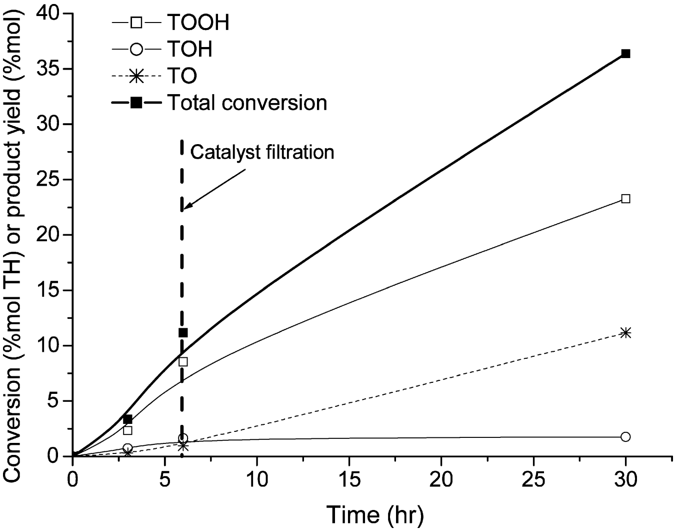


Fig. 3. Hot filtration experiment. After the first 6 h of T–H conversion over Cu-MOF (dashed line), the solid catalyst was filtered off.

However, it might still be possible that a small amount of Cu could pass to the solution, being responsible for the catalytic activity, while the corresponding small decrease in crystallinity would not be detected by XRD. If this occurs, we could not rule out the possibility that a homogeneous oxidation mechanism could also be operative. In order to check this possibility, we have conducted a series of additional experiments. The first of them consists in repeating the reaction under the same conditions as before when using fresh catalyst, but after 6 h reaction time the solid catalyst was separated by filtration. At this point we followed the time evolution of the products in the filtrate. The results obtained are given in Fig. 3, and show that after 6 h and with the solid catalyst no longer present in the filtrate, the product distribution follows a completely different pattern from that observed when in the presence of solid catalyst (see Fig. 1b). Indeed, it is observed a gradual and parallel increase

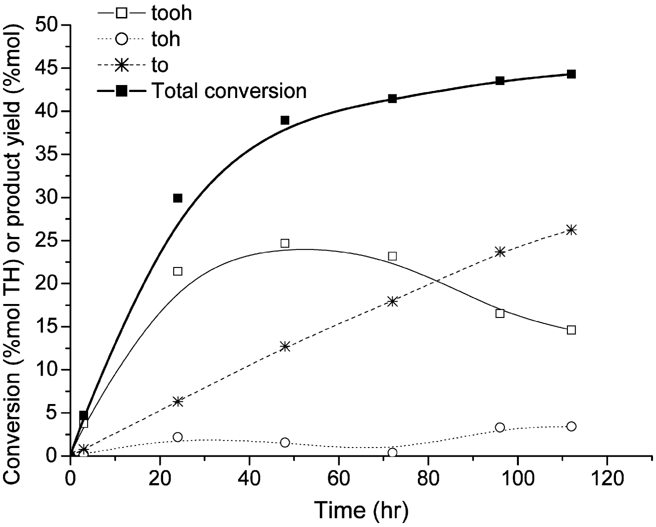


Fig. 4. Tetralin oxidation with copper acetate.

Table 2
Recycling of Co-MOF for the oxidation of tetralin[a]

	Co-MOF		
	USE 1 24 h	USE 2 24 h	USE 3 34 h
Conversion (mol%)	23.2	22.8	22.2
Yield (mol%)[b]			
T–OOH	0.2	1.1	0.6
T–OH	2.9	1.8	1.8
T=O	19.8	19.9	19.8
By-products	0.3	0.1	0.1
T=O/T–OH ratio	6.8	11.2	11.3

[a] Reaction conditions: 7.0 g T–H (0.053 mol) at 90 °C, 0.1 MPa bubbled air pressure at 0.50 mL/s flowrate. Molar ratio T–H/Co was kept constant throughout all catalytic tests and equal to 2000.

[b] Calculated as: mol product × 100/mol of initial T–H at the reaction time as indicated, when conversion was maximal. (T–H: tetralin, T–OOH: tetralynhydroperoxide, T–OH: tetralol, T=O: tetralone.)

of T–OOH and T=O concentrations, without any appreciable change in the amount of T–OH, which remains at a very low level. In our opinion, these data indicate that when the catalyst is no longer present, but when a high concentration of hydroperoxides has already been reached, the reaction taking place is a thermal autooxidation, which produces mainly T–OOH and T=O from tetralin molecules (T–H), in agreement with what observed with other paraffins [38]. Indeed, in a parallel run we have observed that when enough T–OOH is initially formed (or intentionally added to the reaction medium, see Fig. S2 in supplementary material), this reaction actually takes place thermically without the aid of a catalyst, and the product distribution is analogous to that observed in Fig. 3.

Therefore, by comparing the results of these two experiments, we can conclude that when Cu-MOF was hot filtered after 6 h of reaction, enough T–OOH was already present in the filtrate (*ca.* 10% of the initial tetralin concentration) that can initiate the thermal conversion of T–H into T–OOH and T=O, independently of the presence of the catalyst.

As a final test to reveal the possibility of copper leaching, we have studied the oxidation of tetralin with a soluble copper salt (copper acetate) as catalyst. Although the catalytic activity of the soluble copper species is highly dependent on the nature of the ligands, this experiment with copper acetate still provides an appropriate insight on the behavior of homogeneous copper species. The experiment was done with a copper concentration in solution that corresponds to 10% of the total copper content in Cu-MOF. These conditions would be equivalent to assume that a 10% copper leaching occurred from Cu-MOF, something that certainly would be detected by a loss of crystallinity. As it can be seen in Fig. 4 even with this large excess of Cu^{2+} species in solution, tetralin conversion is very slow as compared to the results obtained with Cu-MOF. Moreover, the product distribution with copper acetate is completely different, since soluble Cu^{2+} species are not able to decompose T–OOH even after 120 h. For comparison purposes, it can be seen that the level of T–OOH decreases below 2% after *ca.* 30 h when Cu-MOF was used (see Fig. 1b).

In summary, with all the above experiments we can say that leaching of copper from Cu-MOF is not occurring (as far as we could directly or indirectly detect), and that in no case the eventual copper species in solution are responsible for the observed catalytic activity of Cu-MOF. Nevertheless, a decrease in conversion is observed when the catalyst is reused that may be better related with a catalyst deactivation.

3.3. *Oxidation of tetralin with Co-MOF*

The next set of experiments was conducted with Co-MOF as catalyst, while maintaining all other experimental conditions as with Cu-MOF. The results obtained for the fresh catalyst and two successive reuses are presented in Table 2 and Fig. 5. The results show clear differences between Cu-MOF and Co-MOF. In Co-MOF, a clear induction period of about 10 h exists (see Fig. 5b), in which no tetralin conversion is observed. This induction period was practically absent, or was very short, in Cu-MOF. Also the values of maximum tetralin conversion are significantly lower for Co-MOF than for Cu-MOF (51.5 *versus* 23.2 mol% for fresh Cu-MOF and Co-MOF, respectively, see Figs. 1 and 5). However, the most significant differences between the two catalysts concern the product distribution (T=O/T–OH ratio) and the kinetic pathway. The T=O/T–OH ratio is found to be remarkably higher for Co-MOF than for Cu-MOF, with values as high as *ca.* 7 (as compared to 2.7 observed for Cu-MOF, see Tables 1 and 2, and Figs. 1 and 5). This ratio is even higher with the recycled Co-MOF catalyst, going from 6.8 for the fresh catalyst to 11.3 for the third reuse at practically the same level of conversion (see Table 2). Concerning the temporal evolution of products shown in Fig. 5b, the most outstanding feature of Co-MOF is that, contrary to Cu-MOF, the level of T–OOH accumulated throughout the whole reaction is very low. These results indicate that the Co^{2+} centers in Co-MOF are not very effective to generate T–OOH species (as evidenced by the marked induction period), but once T–OOH is generated, this is rapidly converted with a good selectivity towards T=O.

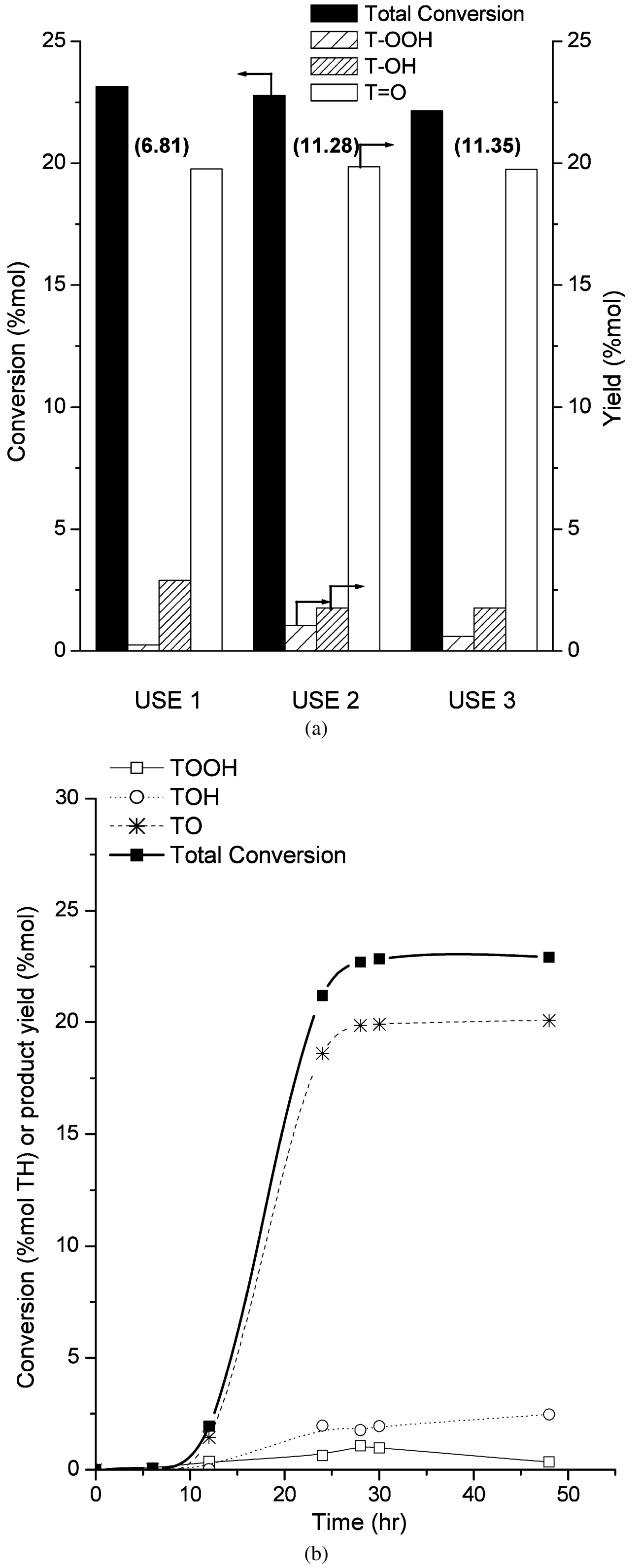


Fig. 5. (a) Conversion of tetralin over Co-MOF for the fresh catalyst (USE 1) and for two successive reuses (USE 2 and USE 3). Black columns refer to total T–H conversion, while the other columns refer to product yield as indicated in the text box. The numbers in parentheses correspond to the T=O/T–OH ratio. (b) Time conversion of T–H and kinetic evolution of products obtained in the first reuse of Co-MOF (USE 2). The lines between points are only indicative, to help following the evolution of the experimental points. Symbols as indicated in the text box.

By comparing the reactivity observed with Cu-MOF and Co-MOF, we assume that the suppression of the induction period in Cu-MOF and not in Co-MOF could involve a direct participation of the metal in the generation and reaction of hydroperoxides, and not only on the ensuing Haber–Weiss cycle.

Regarding reusability of Co-MOF, the data in Table 2 indicate that the material can be recycled, without appreciable decrease of the maximum T–H conversion. Similar leaching experiments as those performed for Cu-MOF allowed us to conclude that Co leaching can be ruled out for Co-MOF, at least within the limits of experimental detection.

In summary, Co-MOF showed a better performance with respect to Cu-MOF concerning selectivity (T=O/T–OH ratio) and low accumulation of T–OOH, but it has the drawback of the large induction period required to form the T–OOH intermediate species. Cu-MOF on the contrary, showed almost no induction period, but gives a lower selectivity to T=O and a high level of T–OOH.

Taking into account the above conclusions it appears that an optimum catalyst could be achieved by combining the catalytic advantages of Cu-MOF and Co-MOF, *i.e.* minimum induction period, low levels of peroxides in solution, and high maximum conversion and T=O/T–OH ratio. Then, Cu-MOF would be responsible for a rapid generation of the T–OOH intermediate, while Co-MOF will rapidly react the hydroperoxide to yield T=O effectively. In order to test this hypothesis, we have prepared several physical mixtures of the two catalysts while maintaining the same metal-to-tetralin ratio as in the previous tests.

3.4. *Tetralin oxidation with a combination of Co-MOF and Cu-MOF*

The results obtained with different catalyst compositions are summarized in Table 3 and Fig. 6, including also the values obtained for the pure catalysts as a reference.

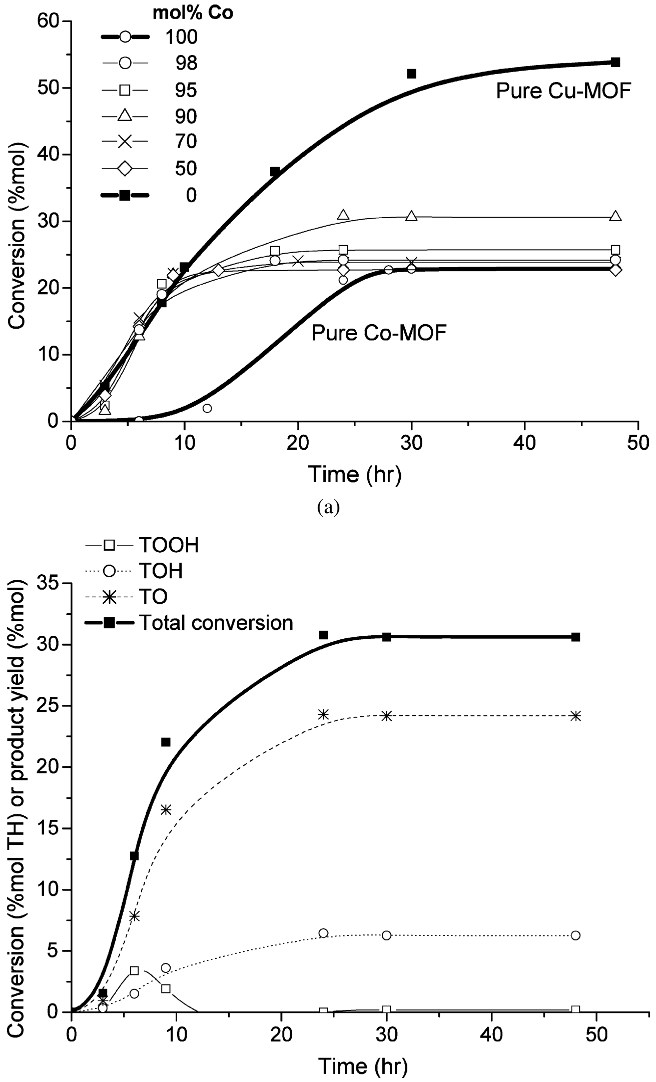
From the results in Table 3 and Fig. 6a, we can see that the addition of a small amount (2 mol%) of Cu-MOF to Co-MOF has already a dramatic effect on the induction period observed for the pure cobalt catalyst, which is now almost completely suppressed. The activity of all the mixtures, measured from the slope of the conversion curves at short reaction times, is very similar and comparable to that of pure Cu-MOF, but significantly higher than for pure Co-MOF. However, introduction of Cu-MOF has just a slightly beneficial effect on maximum conversion with respect to pure Co-MOF. An optimal value of about 31% total T–H conversion is obtained for the 90 Co/10 Cu mixture, which lies between the values obtained for pure Cu-MOF (∼52%) and Co-MOF (∼23% conversion). Finally, the composite catalyst gives values of T=O/T–OH ratio which are intermediate between the two pure catalysts separately (see Table 3). With respect to product distribution, the most noticeable result is that all the mixtures tested are characterized by low levels of T–OOH in the reaction media which, in neither case, increased beyond 3–4% yield. However, we have observed that these values of T–OOH concentration started to become important if the fraction of Cu-MOF in the mixture was

Table 3
Catalytic oxidation of T–H with Co-MOF/Cu-MOF mixtures of different composition[a]

	Co-MOF/Cu-MOF mixtures (mol% Co/mol% Cu)							
	100/0	98/2	95/5	90/10	70/30	50/50	30/70	0/100
Conversion (mol%)	23.2	24.2	25.6	30.8	23.8	22.7	30.7	51.5
Yield (mol%)[b]								
T–OOH	0.2	0.0	0.0	0.0	0.0	0.3	0.2	1.2
T–OH	2.9	4.7	5.0	6.5	6.3	6.6	8.2	13.6
T=O	19.8	19.5	20.5	24.3	17.4	15.9	20.4	36.7
By-products	0.3	0.0	0.0	0.0	0.0	0.0	0.5	0.0
T=O/T–OH ratio	6.8	4.2	4.1	3.8	2.8	2.4	2.5	2.7

[a] Reaction conditions: 7.0 g T–H (0.053 mol) at 90 °C, 0.1 MPa bubbled air pressure at 0.50 mL/s flowrate. Molar ratio T–H/(Co + Cu) was kept constant throughout all catalytic tests and equal to 2000.

[b] Calculated as: mol product × 100/mol of initial T–H at the reaction time as indicated, when conversion was maximal. (T–H: tetralin, T–OOH: tetralinhydroperoxide, T–OH: tetralol, T=O: tetralone.)



(a)

(b)

Fig. 6. (a) Conversion of T–H over pure Co-MOF and Cu-MOF (bold lines) and mixtures of the two catalysts of different composition, as indicated in the text box. (b) Time conversion of T–H and kinetic evolution of products obtained with the 90 Co/10 Cu mixture. The lines between points are only indicative, to help following the evolution of the experimental points. Symbols as indicated in the text box.

Table 4
Catalytic oxidation of T–H with 90 Co/10 Cu MOF mixtures and the pure copper and cobalt acetate homogeneous counterparts. The values are given at partial conversion, just before reaching the plateau[a]

	Catalyst		
	90 Co/10 Cu	$Cu(AcO)_2$	$Co(AcO)_2$
T–H conversion (mol%)	23	20	21
Yield (mol%)[b]			
T=O	18	12	12
T–OH	4	5	4
T–OOH	1	3	5
T=O/T–OH ratio	4.5	2.4	3.0
(T=O + T–OH)/T–OOH ratio	22	5.7	3.2

[a] Reaction conditions: 7.0 g T–H (0.053 mol) at 90 °C, 0.1 MPa bubbled air pressure at 0.50 mL/s flowrate. Tetralin-to-metal ratio was kept constant throughout all catalytic tests and equal to 2000.

[b] Calculated as: mol product × 100/mol of initial T–H after 10 h reaction time. (T–H: tetralin, T–OOH: tetralinhydroperoxide, T–OH: tetralol, T=O: tetralone.)

further increased. This fact imposed that the maximum admissible amount of Cu-MOF in the mixture should be below 50%. Thus, in the 30 Co/70 Cu mixture, the yield of T–OOH reached a maximum value of about 10 mol%.

A typical product distribution plot is shown in Fig. 6b, for the 90 Co/10 Cu mixture, where all the characteristics mentioned above can be clearly observed: (i) absence of appreciable induction period; (ii) good selectivity towards T=O formation (high T=O/T–OH ratio); and (iii) low levels of T–OOH. This catalyst composition combines the best advantages of Cu-MOF (high activity) and Co-MOF (low level of hydroperoxide and good selectivity towards T=O), while overcoming the drawbacks of the two pure catalysts separately.

The 90 Co/10 Cu mixture was also found to perform better than the homogeneous counterparts, both in terms of activity and selectivity. To illustrate this, we performed the oxidation of tetralin using copper and cobalt acetate, with the same metal-to-tetralin molar ratio, and the results are presented in Table 4.

At 10 h reaction time (at partial T–H conversion, just before reaching the plateau, and with T–OOH still present in the reaction medium), the 90 Co/10 Cu mixture yielded a T–H conversion of 23 mol%, as compared to values of 20% and 21 mol% obtained with copper and cobalt acetates, respectively. The selectivity expressed as T=O/T–OH ratio was found to be also better for the solid mixture (4.5 versus 2.4 and 3.0), as well as the selectivity expressed as total product formation (conversion to non-peroxidic products, (T=O + T–OH)/T–OOH ratio): 22 for 90 Co/10 Cu and 5.7 for $Cu(AcO)_2$ and 3.2 for $Co(AcO)_2$.

The last point to be assessed is whether the good performance obtained for the 90 Co/10 Cu catalyst is preserved after successive reuses. The results obtained after three reuses indicate that the induction period remains negligible, although a small loss of the overall conversion occurred (from 31 to 25 mol%), together with a considerable increase in the T=O/T–OH ratio (from 3.8 to 6.0), when compared with the fresh 90 Co/10 Cu catalyst. The concentration of T–OOH was always low, as in the fresh mixture.

4. Conclusions

We have presented the results obtained for the liquid phase aerobic oxidation of tetralin using two metal–organic frameworks containing Cu^{2+} and Co^{2+} as the metallic component, and anionic diazaheterocyclic ligands (pyrimidinolate and imidazolate, respectively) as the organic linkers. In both cases we have observed high performances of the materials for the above reaction, with good reusability, especially in the case of Co-MOF. However, the two pure materials separately present some disadvantages that can be overcome by preparing combinations of the two catalysts. As a result of this, a compromise between the two effects has been reached with a mixture containing 10 wt% Cu-MOF and 90 wt% Co-MOF, that yields the best performance in terms of activity, selectivity and low level of hydroperoxides.

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Supplementary material

The online version of this article contains additional supplementary material.

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