Nanocrystalline M–MOF-74 as Heterogeneous Catalysts in the Oxidation of Cyclohexene: Correlation of the Activity and Redox Potential

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In some aspects, the potential of metal-organic framework (MOF) materials as heterogeneous catalysts has been realized, at least in an academic context. However, one of their most promising catalytic properties, that is, the presence of open metal sites, is far from understood properly. In this work, a series of M-MOF-74 (M=Mn, Co, Ni, Cu, Zn) materials, prepared under sustainable conditions, was tested systematically in the oxidation of cyclohexene, which can proceed by either radical or epoxidation routes. Under the optimized reaction

Introduction

Metal-organic framework (MOF) materials with permanent porosity^[1] notably extend the properties, versatility, and, importantly, potential applications of such microporous materials.^[2] Together with the extreme flexibility^[3] and catenation^[4] of some MOF networks, the presence of exposed and unsaturated metal sites in the framework^[5] was probably the most remarkable aspect of MOFs compared with other microporous materials. These open metal sites are particularly attractive in two direct applications. On one hand, the highly demanded adsorption and separation of gases with high energetic and/or environmental interest, such as $H_{2'}^{[5b,6]} CO_{2'}^{[7]}$ or light hydrocarbons,^[7b] found in these unprecedented centers is an incentive with respect to common adsorbents (zeolites, carbons, etc.),^[8] which normally act as inert storage systems. The highest heats of adsorption for these gases and some of their most efficient separations were achieved with MOFs that contain open metal sites.^[9] On the other hand, in a heterogeneous catalysis context, MOF materials not only cover the lack of zeolites and zeotypes for the incorporation of certain metal ions but also introduce exposed metal centers, which allows their direct interaction with reactants/adsorbates. Although tens of academic studies have focused on the application of these MOF materials in different catalytic reactions,^[10] their generally unsystematic character led rarely to consolidated knowledge. It is particularly strange if we consider the existence of families of isostructural MOFs that contain open metal sites that can be prepared with different metal ions. For instance, M–MOF-74 materials,^[11]

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conditions, the radical route is spontaneous to some extent and it is enhanced in the presence of any M–MOF-74 that has a metal with a redox character but not Zn. However, the epoxidation of cyclohexene is also promoted by a redox catalyst in such a way that the conversion correlates qualitatively with the redox potential of the metal. Thus, for the first time, a chemical property of M is correlated with the catalytic activity of the M–MOF-74 family.

also known as CPO-27M,^[12] M₂(dobdc),^[13] or M₂(dhtp)^[14] (dobdc = 2,5-dioxido-1,4-benzenedicarboxylate, dhtp = 2,5-dihydroxyterephthalate), can be prepared with Mg, Mn, Fe, Co, Ni, Cu, Zn, and Cd divalent ions^[11-15] or their mixtures.^[16] The reported catalytic studies of this family of MOFs have normally investigated a particular M–MOF-74 material^[17] rather than the effect of the nature of the different metal ions.

This work focuses on the catalytic activity of the nanocrystalline M-MOF-74 materials prepared at room temperature^[18] in the oxidation of cyclohexene. As this catalytic reaction requires redox centers, Mn, Co, Ni, and Cu were selected as the redoxactive M of the M-MOF-74 materials over, for instance, Mg and Cd ions. Zn-MOF-74 was selected as a non-redox-active material because of the chemical similarity of Zn with the other chosen metal ions. The spontaneous oxidation of cyclohexene with tert-butylhydroperoxide was accelerated significantly by the presence of any redox-active M-MOF-74 material, whereas it was inhibited by Zn-MOF-74. However, the epoxidation of cyclohexene occurs necessarily in the presence of redox-active MOF-based catalysts, the activity of which was correlated to the redox potential of M. Moreover, these nanocrystalline samples were more active than their micrometer-sized homologues. The stability of the catalysts and metal leaching to the reaction media were studied and explained in terms of the possible reaction mechanism.

Results and Discussion

MOF-74 materials

The synthesis and characterization of four of the five tested catalysts in this paper are described elsewhere.^[18] The main characteristic of these samples is their nanocrystalline nature,

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M	Crystal size ^[a] [nm]	BET area [m ² g ⁻¹]	External BET area ^(b) [m ² g ⁻¹]	PSD ^[c] [nm]
Zn	16.7	948	235	29.5
Cu	14.0	1103	286	39.8
Mn	13.6	791	273	24.4
Co	5.0	693	416	2.3
Ni	2.9	514	65	-
[a] Estimated by the Scherrer equation. ^[18] [b] Estimated by the t-plot method. [c] Maximum pore size distribution of the N ₂ adsorption branch.				

which covers a crystal size range from 16.7 (Zn-MOF-74) to 2.9 nm (Ni-MOF-74) (Table 1). As a result of the small crystal size, they have strong tendency to be agglomerated/aggregated. The crystalline units above approximately 10 nm are simply agglomerated and they are isolable by a mild sonication treatment. Conversely, the crystalline units below 10 nm are domains rather than crystals, and they are aggregated in hardly isolable particles. In both cases, the agglomeration/aggregation is relatively ordered, and the particles contain certain intercrystalline mesoporosity.^[18] Therefore, these materials are expected to reduce diffusion problems compared to their homologous micrometer-sized MOF-74 materials prepared under solvothermal conditions.

The most promising first-period transition metal ion as a catalytic center in oxidation reactions is probably Cu,^[19] particularly in Cu-MOF materials.^[20] This is why a particular effort has been made to prepare a nanocrystalline Cu-based MOF-74 material at room temperature.^[18,21] The preparation of a Cu-based MOF-74-like material has been described for the first time recently under solvothermal conditions.^[17a] Therefore, the roomtemperature synthesis and characterization of Cu-MOF-74 deserve some attention. A detailed description of the synthesis and characterization of Cu-MOF-74 is given in the Supporting Information, and the powder XRD pattern is presented in Figure 1. The crystal size of Cu-MOF-74 is guite similar to that of Zn- and Mn-MOF-74 (Table 1) and significantly higher than that of Ni- and Co-MOF-74. If we apply the Scherrer equation with the same criteria described elsewhere,^[18] the crystalline units have an average size of 14.0 nm, which is only exceeded by that of the Zn sample (16.7 nm). The other characterization results (Supporting Information) indicate that the Cu-dhtp sample is nanocrystalline and has a MOF-74-like structure.

In addition to the crystal size estimation by the Scherrer equation, some textural properties of the series of M–MOF-74 are given in Table 1, which are extracted from the isotherms shown in the Supporting Information. The textural properties of our samples were slightly better than those published,^[18] which is probably because the N₂ adsorption–desorption isotherms were measured immediately after preparation and washing. Cu-MOF-74 has the best textural properties of the series, which confirms the successful preparation of this sample. Nevertheless, the pore size distribution (PSD) is slightly higher than expected (Table 1).^[18] As described previously,^[18]



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Figure 1. Powder XRD patterns of the nanocrystalline M–MOF-74 materials tested in the oxidation of cyclohexene. The intensity of the patterns of Niand Co-MOF-74 have been multiplied by a factor of 5. At the top, a powder XRD pattern of a conventional micrometer-sized Zn-MOF-74 is shown for comparison. The powder XRD patterns of the samples based on Cu, Mn, Co, and Zn have a significant background caused by a fluorescence phenomenon.^[18]

and the maximum PSD decreases as the average crystal size decreases. Ni-MOF-74 is not considered in this trend because its intercrystalline pore diameter, if any, should be in the microporous range.^[18]

Optimizing the reaction conditions: Choice of oxidant

The choice of cyclohexene oxidation as the catalytic test in this work was based on the high versatility of this reaction. The versatility covers a large number of solvents,^[22] all M of the series of M–MOF-74 (except Zn, taken as reference) already tested in the reaction,^[17b,23] two different oxidation routes^[24] (Scheme 1), and different oxidizing agents.^[25] Acetonitrile was selected as the solvent because it is one of the most widely used in cyclohexene oxidation and it is able to dissolve all reactants in a unique liquid phase even if 30 wt% H_2O_2 in aqueous solution was used as the oxidant.^[24b]



Scheme 1. Products generated from the oxidation of cyclohexene through either the radical (top) or epoxidation (bottom) routes.

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Previous studies of MOF-based catalysts in this reaction^[17b,23b,26] do not clarify anything about the influence of the nature of the oxidant. In our opinion, the oxidant deserves to be studied, not only because of its oxidizing potential but also because the solvent in which it is stabilized (water in the case of H₂O₂ and *n*-decane for *tert*-butylhydroperoxide; TBHP) could play a key role in both the global catalytic activity and the MOF stability.

The yield of the products from the oxidation of cyclohexene with either H_2O_2 or TBHP as the oxidant in the presence of the nanocrystalline Ni-MOF-74 catalyst are plotted as a function of reaction time in Figure 2. Surprisingly, no conversion of cyclo-



Figure 2. Sum of the yields of the products that result from the oxidation of cyclohexene in the presence of Ni-MOF-74 with H_2O_2 30 wt% or TBHP as oxidizing agents.

hexene was detected during 26 h reaction if the oxidant was 30 wt % H_2O_2 . In contrast, the use of TBHP led to an acceptable conversion of 40% of cyclohexene after a similar reaction time. Moreover, almost the whole oxidation took place through the allylic mechanism (95.5%). (Yields of the different products at the end of the reaction are given in the Supporting Information). The preference for the radical route was further confirmed by the dramatic decrease of the activity in the presence of a radical inhibitor (Supporting Information).

The ultimate reason for this spectacular difference, which depends on the nature of the peroxide-based oxidant, is not completely clear, as some features of the system could disfavor the catalytic conversion in the presence of H₂O₂. Firstly, the unsaturated metal sites must have an asymmetric charge distribution,^[27] so it is expected that water rather than acetonitrile, H₂O₂, or cyclohexene is coordinated to the catalytically active sites M, which causes the deactivation of these centers. In addition, H₂O is present in excess of the other very polar chemical species H_2O_2 in the 30 wt% oxidant source (H_2O/H_2O_2 molar ratio of \approx 4.4). Conversely, TBHP, although less polar than H_2O_2 , has to compete with highly hydrophobic *n*-decane instead of water. In this sense, the activity of Ti-MCM-41 catalysts in the epoxidation of alkanes is weakened if anhydrous TBHP becomes hydrated.^[28] As a second possible reason, water acts as an inhibitor in the oxidation of cyclohexene through the radical route,^[24a,b] which dominates over the epoxidation route under the tested conditions. Finally, this radical route requires the homolytic rupture of the O–O bond of the peroxide, which has been calculated to be more unfavorable for H_2O_2 than for TBHP in the presence of a Ni-based catalyst.^[29]

As a result of the questioned stability of MOF-based catalysts in the reaction media, the comparison between TBHP and H_2O_2 should not be limited to cyclohexene conversion and structural stability should be also considered. The powder XRD patterns of Ni-MOF-74 before and after the reaction with both oxidizing agents are shown in Figure 3. After the oxidation of



Figure 3. Powder XRD patterns of the Ni-MOF-74 samples before (top) and after reaction using TBHP (middle) and H_2O_2 (bottom) as oxidizing agents. The intensity of the two top patterns was multiplied by 2 for an easier comparison. The background in all patterns is caused by a fluorescence phenomenon.^[18]

cyclohexene with TBHP that gave an acceptable cyclohexene conversion, the catalyst basically conserved its MOF-74 structure. The slight difference in the patterns of the catalyst before and after the reaction can be attributed to the chemicals that occupy the MOF-74 pores because the XRD pattern of the former was measured as-reacted without any extra washing or treatment. Conversely, the structure of the same sample after the reaction in the presence of H_2O_2 underwent a complete transformation although no cyclohexene was oxidized. Although it is not completely clear what causes the transformation of the Ni-MOF-74 catalyst, it must be related to the presence of H_2O_2 and/or H_2O under the reaction conditions.

As a result of both the cyclohexene conversion and the structural stability of Ni-MOF-74, TBHP (5.5 M in *n*-decane) was selected as the oxidizing agent for further catalytic investigations in this work.

Influence of the nature of M on the oxidation of cyclohexene catalyzed by M-MOF-74

As mentioned in the Introduction, the M–MOF-74 family offers a unique opportunity for systematic comparisons of the catalytic activity of different exposed and unsaturated M centers. In addition, the catalysts tested here were prepared at room temperature, which provides two extra important advantages: (i) one in a sustainable aspect, which contrasts with the MOF



materials prepared under conventional solvothermal conditions, and (ii) the other one in a catalytic aspect as this preparation method implies the formation of nanocrystalline M–MOF-74^[18] (Table 1), which should minimize diffusion problems. The improvement in reactants/products diffusion associated with the "nano" nature of the M–MOF-74 catalysts prepared at room temperature is evidenced clearly for Cu- and Co-MOF-74 (Supporting Information).

Plots of the kinetics of the total yield of the products oxidized from cyclohexene using the five M–MOF-74 catalysts and in the absence of any catalyst (blank experiment) are shown in Figure 4. Detailed data for the catalysts at the end of the reac-



Figure 4. Sum of the yields of the products that result from the oxidation of cyclohexene in the presence of M-MOF-74 and without catalyst (blank) with TBHP as a function of the reaction time.

tion (after ≈ 24 h) are shown in Table 2. All M–MOF-74 that have a redox-active M gave cyclohexene conversions that were significantly higher than that of the blank reaction. However, the conversion in the presence of Zn-MOF-74 was lower than that of the catalyst-free reaction. This result corroborates that the redox character of M is essential to make the M–MOF-74 material a viable catalyst for cyclohexene oxidation. Further-

Table 2. Sum of the yields of the different products generated by the oxidation of cyclohexene with TBHP at 70 °C after \approx 24 h of reaction catalyzed by M–MOF-74. Detailed yield data for the identified products are given in the Supporting Information.						
Catalyst	Total yield [%]	Radical yield [%]	Epoxidation yield [%]	TC [h ⁻¹)F ¹] ^[a]	
				2 h	24 h	
Cu-MOF-74	90.0	35.7	54.3	6.70	0.59	
Co-MOF-74	71.5	43.1	28.4	4.98	0.49	
Mn-MOF-74	68.2	29.0	39.2	4.27	0.46	
Ni-MOF-74	40.0	38.2	1.8	60.57	0.30	
Zn-MOF-74	5.0	5.0	0	0.05	0.04	
Blank	18.8	18.8	0	-	-	
[a] Total (radical+epoxidation) TOF after 2 and 24 h of reaction.						

more, the presence of M–MOF-74 with a non-redox-active M, far from enhancing the conversion, seems to act as an inhibitor, which gives extra relevance to the intrinsic catalytic activity of redox-active M.

The order of the catalytic activity at any time of the reaction is: Cu > Co > Mn > Ni > blank > Zn. Notably, a very high cyclohexene conversion is achieved by Cu-MOF-74 (90%, Table 2), which is practically reached after the first 2 h of reaction (Figure 4). Similarly, Co- and Mn-based samples also reach a kind of plateau after relatively short reaction times (around 5 h). Conversely, the blank reaction and the reactions catalyzed by the Ni- and Zn-MOF materials gave very low conversions in short reaction times, and their conversions did not reach a plateau after 24 h of reaction. The lower activity of Ni-MOF-74 compared with the other M–MOF-74 materials with a redoxactive M is in good agreement with the only published work in which two M–MOF-74 materials (M=Co and Ni) were tested in this reaction.^[23b]

A detailed comparison of the cyclohexene conversion with the physical properties of the MOF-74-based redox catalysts suggests that the conversion correlates linearly with the surface area of the catalyst (Figure 5) irrespective of the nature of



Figure 5. Total yield of products generated by the oxidation of cyclohexene after \approx 24 h vs. the BET area of the M–MOF-74 catalysts with a redox-active M. The black line corresponds to the least-squares adjustment of the four plotted points.

M. In other words, the redox-active ions are equally active, if accessible. The only slight alteration of the otherwise perfect linear correlation is found for the Mn and Co samples, which are quite different to each other (very different crystal size, external/microporous surface area ratio, presence of impurities in the Mn-based sample,^[18] etc.). The other possible analysis of the deviation from linearity shown in Figure 5 implies that only the Co-based catalyst is slightly away, probably because its huge external surface area ($\approx 60\%$ of the whole surface area; Table 1) reduces the diffusional limitations, which suggests that even the metal centers on the external surface could be catalytically active.^[30]

As the oxidation of cyclohexene can be catalyzed by at least two different routes that give different chemical products (Scheme 1),^[31] an analysis of the yields of the products generat-

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Time / h

Figure 6. Sum of the yields of the products generated by either the radical oxidation (top) or epoxidation (bottom) of cyclohexene as a function of reaction time for M–MOF-74 and for the blank experiment.

ed by these pathways can provide additional information. The selectivity to either allylic oxidation or epoxidation of cyclohexene for all tested catalysts is shown in Figure 6 top and bottom, respectively. The complete distribution of the products at the end of the reaction is given in the Supporting Information. The cyclohexene oxidation in the absence of a catalyst (blank) and with the non-redox-active Zn-MOF-74 catalyst takes place through the radical route. In other words, the allylic oxidation of cyclohexene is somehow spontaneous under the tested reaction conditions. Nevertheless, it is evident that any redox-active M enhances the conversion through that route in the order Co > Ni \sim Cu > Mn, whereas Zn-MOF-74 hinders the radical-based oxidation.

If we take into account the spontaneity of the allylic oxidation of cyclohexene, it is not easy to extract any information on the catalytic role of the redox center M. In addition, this aim is even more complicated if we consider that the M–MOF-74 materials have quite different crystal sizes and surface areas, that is, different degrees of accessibility to the metal centers. However, the presence of an MOF-74 catalyst that contains a redox-active M is compulsory to oxidize cyclohexene through the epoxidation pathway (Table 2 and Figure 6 bottom). Indeed, the blank and the Zn-MOF-74-catalyzed reactions did not yield any product from the cyclohexene epoxide. Therefore, the yield of the epoxidation route a priori emerges as a promising variable to shed light on the catalytic role of the open metal sites. As the crystal size and/or textural properties influence the catalytic activity (Figure 5), the ratio between the yields of the redox-required epoxidation and the spontaneous radical pathways (E/R ratio, Table 3) is analyzed instead of

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Table 3. E/R ratio of the different M–MOF-74 materials and reduction po-
tential (E ⁰) for the most probable redox pair of each metal ion. Data for
samples that have positive and negative E^0 values are written in green
and black, respectively, to underline the effect of the sign of the E^0 in the
E/R ratio.

М	E/R ratio	Reduction potential E ⁰ [V] ^[a]	
Cu	1.52	+0.15	
Mn	1.36	+1.54	
Со	0.66	+1.92	
Ni	0.05	-0.25	
Zn	0	-0.76	
[a] E^0 values correspond to the redox pairs Cu ²⁺ /Cu ⁺ , Mn ³⁺ /Mn ²⁺ , Co^{3+}/Co^{2+} Ni ²⁺ /Ni ⁰ and Zn ²⁺ /Zn ⁰ in aqueous solution ^[32]			

the yield of the products formed by the epoxidation mechanism. Thus, diffusional problems, which are unique to each catalyst, should be cancelled, and then the intrinsic catalytic capability of the metal centers should emerge. Therefore, it seems reasonable to try to relate the E/R ratio to the redox capability of M, that is, to its redox potential (Table 3). Although the redox potential values used in Table 3 are taken from the tabulated reduction potential in aqueous solution,[32] they are adequate to understand the catalytic behavior of metal oxides^[33] and some other properties of MOFs.^[34] In any case, these values will be discussed in qualitative terms in this work. Facilitated by the color code, the first message from the data shown in Table 3 is that only the catalysts based on M with oxidizing power, that is, those with reduction potentials $E^0 > 0$, are able to catalyze the cyclohexene epoxidation to a significant extent. Conversely, M-MOF-74 with the most reductant metal ion, Zn, was unable to catalyze the epoxidation of cyclohexene in a detectable level.

Following this reasoning, it could seem surprising that the E/R ratio decreases as the positive reduction potential of M increases (Table 3). However, it must be taken into account that M is not the oxidizing species but the catalytic center, which must complete the redox cycle (oxidation and subsequent reduction half reactions) to become ready to catalyze the oxidation of another cyclohexene molecule.[35] This means that a metal ion with a high oxidizing power such as Co will be reduced easily from Co³⁺ to Co²⁺ but the recovery the oxidation state Co³⁺ from Co²⁺ will be kinetically difficult. However, the cycle in the case of the Cu²⁺/Cu⁺ redox pair will not have such a high barrier to overcome, so both the oxidation and reduction half reactions will be kinetically favored in comparison to that of the Co^{3+}/Co^{2+} redox pair. The need to complete the redox cycle is evident from the turnover frequency (TOF) values given in Table 1, which is 23.5 h⁻¹ for Cu-MOF-74 after 0.5 h of reaction. A similar correlation between the catalytic



behavior and the reduction potential of the metal ions has been described for metal oxides in the literature. $^{\left[33\right] }$

Catalyst stability and metal leaching

The structural and compositional versatility of MOFs allows them to potentially close the gap between selective homogeneous catalysts and more sustainable but less active/selective heterogeneous catalysts. However, to be strictly considered as heterogeneous, a catalyst must necessarily obey some guidelines, which includes no significant leaching of the active centers (metal ions in this case) and maintaining an intact structure. The study of these two points is particularly interesting in this work because (i) the thermal and chemical stabilities of MOFs are always under suspicion and (ii) metal leaching and/or stability of the systematic series of M–MOF-74 catalysts could provide some important information to help understand their catalytic behavior.

The most relevant results of the total X-ray fluorescence (TXRF) analysis of the filtered reaction mixtures as well as the XRD characterization (Figure 7) of the M–MOF-74 catalysts



Figure 7. Powder XRD patterns of the M–MOF-74 materials before (left) and after (right) use as catalysts in the oxidation of cyclohexene.

after reaction are summarized in Table 4. Although metal leaching could seem random at first glance, detailed analyses led us to relate these values to different systematic tendencies in both the catalytic behavior and the physicochemical properties of these materials. Generally, metal leaching increases with the catalytic activity (Figure 4) and with the E/R ratio (Tables 2 and 3) of the M–MOF-74. For instance, high leaching values (above 20 ppm) were found in the reaction mixtures catalyzed by Cuand Mn-MOF-74, which gave high catalytic conversions (90 and 68 %, respectively; Table 2) and the highest E/R ratios (1.52 and 1.36; Table 3). Similarly, the almost inactive Zn-MOF-74 catalyst releases three times less metal ions to the solution than the other materials. However, the metal leaching generated by Co- and Ni-MOF-74 is markedly lower than expected according to the trend, although Co leaching is much higher than that of **Table 4.** Metal leaching of the filtered mixtures after reaction measuredby TXRF and nature of the phase in the resultant solid according topowder XRD (Figure 7).

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Μ	Metal leaching $[mg L^{-1}]$	Phase identification
Cu	20	No crystalline phase
Mn	23	MOF-74
Со	6	MOF-74
Ni	0.16	MOF-74
Zn	7	MOF-74

Ni as predicted from the much higher catalytic activity (and E/ R ratio) of the former. Notably, these two materials consist of large particles formed by fused nanodomains rather than by isolable crystals unlike Zn-, Cu-, and Mn-MOF-74. It is even possible that some disaggregated nanocrystals (< 20 nm) of the latter materials are able to cross the filtration system (the pore diameter of the filter is 0.45 μ m) so that the metal leaching is overestimated by TXRF analysis. In any case, the detected metal leaching seems to be the sum of two contributions: (i) the catalytic activity of M (mainly through the epoxidation pathway) and (ii) the presence of the disaggregated nanounits in M–MOF-74.

The powder XRD patterns of the five M-MOF-74 materials tested in the cyclohexene oxidation are shown both before and after reaction in Figure 7. The reacted samples were simply collected by filtration before the patterns were measured. Moreover, the quality of the patterns of the samples measured after reaction could show the effects of: (i) nanocrystallinity, such as before the reaction, (ii) the presence of chemical species (reactants, solvent, products, etc.) within the pores, and/or (iii) the scarce amount of the recovered sample, which makes it difficult to measure a reliable quantitative diffractogram. In any case, they indicate clearly that, except for the Cubased sample, all catalysts keep the MOF-74 structure to some extent. Despite the temptation to attribute the structural transformation of Cu-MOF-74 to its high catalytic conversion of cyclohexene, particularly by the epoxidation route, the fact that other quite active M-MOF-74 catalysts maintain the MOF-74 structure leads us to think that it is related to another feature of this sample.

The low chemical stability of Cu-MOF-74 in reaction media has been made clear in the sole reported catalytic study with this material.^[15c] Cu-MOF-74 was transformed to copper(I) chloride under conventional conditions, although Cu was present as Cu^{II} in the MOF-74 material and the tested reaction (acylation of anisole with acetyl chloride) does not require redox centers. However, the tested reaction in the current work requires redox centers. Unlike the other two most active catalysts of the series, Mn- and Co-MOF-74, the redox cycle of Cu is presumably between the oxidation states 2+ and 1+. It is quite probable that the MOF-74 structure undergoes an irreversible structural transformation as Cu^{II} is reduced to Cu^I. That reduction would imply the need to compensate a negative framework charge in a region in which an exposed and unsaturated metal center that has a positive electronic density



charge is present. In this sense, it is remarkable that the thermogravimetric (TG) profile of Cu-MOF-74 registered under an air flow (Figure S4) shows the very low thermal stability of this sample in comparison with its homologues (i.e., it is \approx 150 °C less stable than Zn-MOF-74 and almost 300 °C less stable than nanocrystalline Mg-MOF-74). Therefore, in both oxidant media (reaction and TG analysis under air flow), Cu-MOF-74 has a much lower stability than its homologues. However, the intrinsic stability of Cu-MOF-74 is not much lower, which is demonstrated if TG analysis is performed under an inert flow.^[15c] Co^{III} (or Mn^{III}) is stabilized easily within the MOF-74 framework, for instance, by linking an OH⁻ group to the open metal site. These OH⁻ groups are generated in the initiation step of the radical pathway.^[36] Therefore, Mn- and Co-MOF-74, but not Cu-MOF-74, could work as real catalysts that are able to recover their structure and metal environment after a catalytic cycle.

Conclusions

A series of nanocrystalline M-MOF-74 (M=Mn, Co, Ni, Cu, or Zn) materials prepared at room temperature has been tested systematically in the catalytic oxidation of cyclohexene using peroxides as oxidizing agents. *tert*-Butylhydroperoxide (TBHP) was a more efficient oxidizing agent than H_2O_2 (30 wt% in water), which, at least in the presence of the Ni-MOF-74 catalyst, was absolutely inactive. The oxidation of cyclohexene with TBHP takes place even in the absence of a catalyst. The nanocrystalline M-MOF-74 materials were much more active than their micrometer-sized homologues. M-MOF-74 with a redoxactive metal accelerates the spontaneous reaction, whereas Zn-MOF-74 inhibits it partially. Any accessible redox center can catalyze the cyclohexene oxidation to a similar extent in such a way that the textural properties of the material rather than the nature of M govern the total catalytic activity of M-MOF-74. However, the route of cyclohexene oxidation (either through a radical or epoxidation route) depends strongly on the nature of M. In particular, the proportion of epoxidation with respect to the total oxidation is notable for oxidant M and negligible for reductant M. The maximum epoxidation proportion is reached by M-MOF-74 with a slightly positive reduction potential (Cu), as it can complete its catalytic cycle easily. Metal leaching increases with both the activity of the catalyst and the ease of their particles to be disintegrated into their nanocrystals/nanodomains. Amongst the most redoxactive M-MOF-74 (M = Cu, Co, or Mn), the Cu-based material is unique in that it loses its MOF-74 structure during the reaction, presumably because its reduced form Cu¹ cannot be accommodated in the M-MOF-74 structure with divalent M.

The results of this work provide a significant contribution to the general knowledge of the catalytic behavior of MOF materials that contain open metal sites.

Experimental Section

The five M–MOF-74 materials were prepared at RT according to the method described in the literature.^[18] In the preparation of Cu-MOF-74, which has not been described expressly at RT, copper(II)

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acetate monohydrate was used as the Cu source. 2,5-Dihydroxyterephthalic acid (dhtp) and the corresponding divalent metal acetate (with different degrees of hydration) were dissolved individually in DMF. A metal acetate/dhtp molar ratio of 2.6 was used. The linker solution was added dropwise to the metal solution at RT under stirring. The addition produces the immediate appearance of a precipitate. The resultant suspension was stirred at 23 °C for 18 h. The solid was recovered by centrifugation and then washed with DMF several times and subsequently with methanol three times. The solid was kept submerged in methanol until the isotherms were measured or until it was tested in the catalytic reaction.

The catalysts were studied by powder XRD before and after the reaction to follow any possible structural modification. The PXRD patterns were recorded by using a Philips X'PERT diffractometer using CuK_a radiation. ($\lambda = 1.54$ Å) in the 2 θ range of 4–90°. The step size was 0.2°, and the accumulation time was 50 s per step with variable slit. The textural properties of the catalysts were studied by N₂ adsorption–desorption at –196 °C. Surface areas were estimated by applying the BET method, whereas the t-plot method was used to estimate both the microporous and external surface areas. The samples were evacuated at 100 °C for at least 16 h before the isotherms were measured.

As a pretreatment step before the catalytic test, M-MOF-74 samples were placed in a round-bottomed flask submerged in a silicone bath at 150 °C overnight under a constant N₂ flow. The oxidation of cyclohexene was performed at 70°C under atmospheric pressure with stirring (400 rpm). The system was refrigerated with water at 5°C (the reactant evaporation was below 3 wt% after 48 h of reaction). The substrate cyclohexene (10 times the weight of the evacuated catalyst), the solvent acetonitrile (cyclohexene/ acetonitrile molar ratio of 30), and the internal standard toluene (the same weight as the catalyst) for GC were added to the catalyst. Once this mixture reached 70 °C (the temperature was controlled with a thermometer in contact with the mixture), the oxidizing agent (either H₂O₂ or TBHP) was added, and the moment of this addition was taken as reaction time zero. Aliquots at different reaction times (0-25 h) were taken under stirring to follow the kinetics. These aliquots were analyzed by GC (Varian 430 GC; capillary column of 15 m length, 0.25 mm diameter, 1 µm stationary phase thickness; flame ionization detection; FID) and TXRF after filtration (filter paper with pores of 0.45 μm). Identification of the noncommercial 2-cyclohexenyl peroxide product was performed as described elsewhere.^[24a] As a result of the high volatility of cyclohexene, its conversion was calculated indirectly through the sum of the detected products. The mass balance was always below 10%.

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7

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8

FULL PAPERS

Redox rocks: A series of nanocrystalline M–MOF-74 (M = Mn, Co, Ni, Cu, Zn) materials prepared at room temperature catalyze the oxidation of cyclohexene with *tert*-butylhydroperoxide. Radical oxidation is similar for any redox-active M, whereas epoxidation is preferred for M with slight oxidant properties. M–MOF-74 catalysts with the redox pairs M^{3+}/M^{2+} were stable and those with M^{2+}/M^+ were not.



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Nanocrystalline M-MOF-74 as Heterogeneous Catalysts in the Oxidation of Cyclohexene: Correlation of the Activity and Redox Potential