Selective oxidation of cyclooctene over copper-containing metal-organic frameworks

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ABSTRACT

The selective oxidation of cyclooctene with $tert$-butylhydroperoxide (TBHP) was studied over Cu-containing MOFs at 348 K in liquid toluene. With $Cu_3(BTC)_2$, complete conversion was achieved after 120 h. The epoxide selectivity steadily increases to >80%. The conversion is accelerated by a radical initiator and decelerated by a radical inhibitor. A radical-based mechanism is proposed with alkoxy- or polyperoxides being formed as intermediates to the epoxide. The comparison of the cyclooctene conversion with TBHP over $Cu_3(BTC)_2$ with FeBTC, the ion-exchanged zeolites Na,Cu-Y and Na,Fe-Y and TS-1 proves that $Cu_3(BTC)_2$ is active for radicals generation from TBHP, but less suitable for catalyzing alkene epoxidation. The two recently reported Cu-MOFs $^3_\infty[Cu(Me-4py-trz-ia)]$ and $^3_\infty[(Cu_4(\mu_4-O)(\mu_2-OH)_2(Me_2trz-pba)_4]$ are up to four times more active for cyclooctene oxidation than $Cu_3(BTC)_2$. This was attributed to the specific coordination geometry of the catalytically active Cu sites within these materials. Moreover, the liquid-phase conversion of cyclooctene with TBHP is shown to be a sensitive test reaction to evaluate the potential of new solid oxidation catalysts, especially of transition metal-containing MOFs.

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1. Introduction

Metal-organic frameworks (MOFs) are an attractive class of materials for a broad spectrum of applications like gas adsorption [1,2], separation [3] and heterogeneous catalysis. Especially because of their structural variety MOFs gain increasing interest as active materials in heterogeneous catalysis [4—11]. Among the most important features of MOFs are their tunable porosity as well as their structural and chemical functionality. Thus, highly active and selective catalysts can be designed by controlling the pore size and architecture on the one hand and the coordination of catalytically active metal centers on the other. This is evident, e.g., from the comparison of isoreticular MOFs. By variation of the molecular dimension of the linker with the same functional motif, it is possible to build up MOFs with a given structure, but different pore sizes [12—14]. Also, the incorporation of catalytically active metal clusters into the highly porous framework structure within a spatially confined geometry is attractive in terms of biomimetic design of solid catalysts [15—17]. Moreover, the coordination sphere of metal sites in MOFs can, in many cases, be extended to allow for reversible binding of reactants, predominantly by Lewis acid/base interactions while keeping the framework structure intact [13]. Compared to conventional zeolites, the major drawback of MOF catalysts is their limited thermal, hydrothermal and chemical stability, although improvements were reported in this respect [18—21]. This is particularly evident for applications in oxidation catalysis, where stability towards oxidizing conditions as well as towards water is often required. MOFs with nitrogen-containing aromatic moieties in the linkers exhibit a considerable robustness under these conditions [5,22].

Several studies on the selective oxidation of alkenes [23—25] were already reported. Mechanistic insight into the oxidation of cyclic alkenes over Cu(II)- and Co(II)-containing MOFs was recently reported. For example, Li et al. [26] proposed a mechanism for the cyclohexene oxidation with molecular oxygen over $[Cu_2(OH)(BTC)(H_2O)]_n \cdot 2nH_2O$ and $[Co_2(DOBDC)(H_2O)_2] \cdot 8H_2O$. Here, molecular oxygen is activated at the metal center of the MOF through the formation of a superoxo complex. Fundamental work

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by Volkmer and co-workers [27] proves for the oxidation of cyclkohexene with TBHP that Co-containing MFU-1 activates the oxidizing agent TBHP at its [Co$_4$O] sites by accepting a hydroxyl anion and leaving a *tert*-butoxyl radical. The conversion leads to the well known reaction products epoxycyclohexene, 2-cyclohexen-1-ol, 2-cyclohexen-1-one and cyclohexene hydroperoxide via the formation of *tert*-butyl peroxyl radicals catalyzed by the metal sites within the MOF.

Among the MOF-based catalysts for selective oxidations, those containing Cu as the active element bear particular potential. Thus, the well-known Cu$_3$(BTC)$_2$ was extensively studied, for example in the oxidation of xanthene [28], benzylic alcohols [29], thiols [30] and benzyl amines [31]. A mixed-linker metal-organic framework derivate of Cu$_3$(BTC)$_2$ has also shown catalytic activity in the hydroxylation of toluene [32]. Also other Cu-containing MOFs are promising for catalytic selective oxidations. These include the so called "Cu-MOFs" [Cu(bpy)(H$_2$O)(bpy)(BF$_4$)$_2$] [24], [Cu$_2$(bi-py)$_2$(btec)] [33], [Cu(bipy)(H$_2$btec)] [34,35] phenoxyacetic acid derivatives [Cu(L$_1$)$_2$(H$_2$O)$_2$], [Cu(L$_1$)$_2$(H$_2$O)(Py)$_2$], [Cu(L$_3$)(H$_2$O)Cl] [36] and [Cu$_2$(OH)(BTC)(H$_2$O)]$_n$·2nH$_2$O [26] which were used for the oxidation of linear or cyclic alkenes with molecular oxygen or TBHP.

The present work was, thus, devoted to more deeply understand the activity of Cu-containing MOFs for selective oxidation catalysis. As a test reaction, the selective oxidation of cyclooctene with *tert*-butyl hydroperoxide in the liquid phase was chosen, which was already studied in previous reports over silica supported Mn-salen complex catalysts [37], clay supported Schiff-base complexes [38], VSi$_2$ [39], mesoporous organo vanadosilicates [40], vanadium diboride [41], Cu$_3$(BTC)$_2$ and [Co$_x$Zn$_{1-x}$(tdc)(bipy)], [Co$_x$Zn$_{1-x}$(Me$_2$trz-*p*ba)$_2$] [42]. Compared to the widely studied cyclohexene oxidation, this conversion provides the advantage that the cyclooctene reactant is less volatile. This reduces losses during experiments in a stirred batch reactor open to the atmosphere, especially when gaseous streams are lead through the reaction mixture and when lower reactant concentrations are studied. First, the role of radicals during the conversion of cyclooctene with TBHP over Cu$_3$(BTC)$_2$ was investigated. Using both radical starters and scavengers as well as different gas streams, the possibility of utilizing molecular oxygen or air as an environmentally benign oxidant was studied. Secondly, the catalytic activity, selectivity and stability of Cu$_3$(BTC)$_2$ (crystal structure [43], see ESI Fig. 1) was directly compared to different reference materials including the corresponding Fe-containing MOF Fe(BTC), Cu- and Fe-ion exchanged zeolites Na-Y and TS-1 as a well-known catalyst for alkene epoxidation. Finally, two recently reported novel Cu-containing MOFs, i.e., $^3_\infty$[(Cu$_4$(μ_4 − O)(μ_2 − OH)$_2$(Me$_2$trz − pba)$_4$)] (Cu$_4$O(OH)$_2$(Me$_2$trz-*p*ba)$_4$) based on 4-(3,5-dimethyl-4*H*-1,2,4-triazol-4-yl)benzoate (Me$_2$trz-*p*ba)$^-$ [44] and $^3_\infty$[Cu(Me − 4py − trz − ia)] (Cu(Me − 4py − trz − ia)) based on 5-(3-methyl-5-(pyridine-4-yl)-4*H*-1,2,4-triazol-4-yl)isophthalate (Me-4py-trz-ia)$^{2-}$ [45] as the linkers (Fig. 1), were also investigated with respect to their catalytic activity in the conversion of cyclooctene with TBHP.

2. Experimental section

2.1. Catalyst synthesis

Cu$_3$(BTC)$_2$ ((BTC)$^{3-}$ = 1,3,5-benzenetricarboxylate) and Fe(BTC) were purchased from Sigma-Aldrich and activated at 393 K for 16 h in ambient air. The microcrystalline Cu-containing MOF $^3_\infty$[(Cu$_4$(μ_4 − O)(μ_2 − OH)$_2$(Me$_2$trz − *p*ba)$_4$)] (Cu$_4$O(OH)$_2$(Me$_2$trz-*p*ba)$_4$) was synthesized as described in Ref. [44]. In brief, 1.1 equivalents of copper acetate hydrate (*p.a.*, Riedel-de
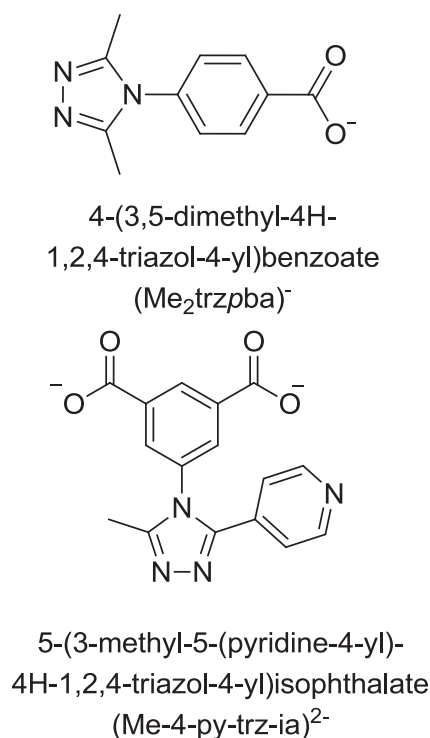

Fig. 1. Structures and abbreviations of the ligands (given in the anionic form) in the metal-organic frameworks Cu$_4$O(OH)$_2$(Me$_2$trz-*p*ba)$_4$ and Cu(Me-4py-trz-ia) respectively.

Haen) were refluxed with the protonated ligand H(Me$_2$trzpba) ((Me$_2$trzpba)$^-$ = 4-(3,5-dimethyl-4*H*-1,2,4-triazol-4-yl)benzoate, prepared according to [46]) in ethanol (96%, technical grade, Solvadis) for two days. The obtained solid was separated by filtration, washed with water/ethanol (volume ratio of 1:1) and dried. Subsequently, it was treated via Soxhlet extraction with methanol (96%, technical grade, Solvadis) for seven days. Before the catalytic experiments, Cu$_4$O(OH)$_2$(Me$_2$trz-*p*ba)$_4$ was activated at 373 K under vacuum for 16 h.

A third Cu-containing MOF $^3_\infty$[Cu(Me − 4py − trz − ia)] (Cu(Me-4py-trz-ia)) ((Me-4py-trz-ia)$^{2-}$ = 5-(3-methyl-5-(pyridine-4.yl)-4*H*-1,2,4-triazol-4-yl)isophthalate) was synthesized by refluxing H$_2$(Me-4-py-trz-ia) (prepared according to [45]) and copper sulphate pentahydrate (*p.a.*, Riedel-de Haen) in a molar ratio of 1:1 in acetonitrile (99,9%, BDH Prolabo)/water (volume ratio of 1:1) for 24 h. Again, the solid was removed by filtration, washed with acetonitrile/water (volume ratio of 1:1) and dried. Then, Cu(Me-4py-trz-ia) was activated at room temperature under vacuum for 48 h prior to the catalytic reaction.

For comparison, a Cu- and a Fe-containing zeolite, i.e., Na,Cu-Y and Na,Fe-Y were prepared via ion exchange. 10 g of zeolite Na-Y (VEB Chemiekombinat Bitterfeld; n$_{Si}$/n$_{Al}$ = 2.8) was suspended in 800 cm^3 of a 0.5 M aqueous solution of copper(II) nitrate (98%, Sigma-Aldrich) or a 0.33 M solution of iron(III) nitrate (99%, Merck), respectively, and stirred for three days at room temperature. Then, the ion-exchanged zeolites were filtered and washed with water until no copper or iron ions were detectable in the washing solution by adding ammonia solution or potassium ferrocyanide respectively. After drying at 353 K and calcination at 673 K in air for 4 h, the zeolites Na,Cu-Y and Na,Fe-Y were obtained with a cation exchanged degree of 70% for the Na,Cu-Y and 90% for the Na,Fe-Y (determined by back titration of the Cu^{2+} and Fe^{3+} ions remaining in the filtrate after the ion exchange). Furthermore, an industrial