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ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.9b02941 • Publication Date (Web): 25 Sep 2019 Downloaded from pubs.acs.org on September 25, 2019

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Protons make possible heterolytic activation of hydrogen peroxide over Zr-based metal-organic frameworks

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ABSTRACT: The catalytic performance of zirconium-based metal-organic frameworks (UiO-66, UiO-67, and MOF-801) in cyclohexene oxidation with aqueous hydrogen peroxide can be greatly improved by adding a source of protons directly into the reaction mixture. A blend of Zr-MOF and protons favors heterolytic activation of H₂O₂ and makes possible selective formation of epoxide and diol with negligible formation of allylic oxidation products. Additives of $HClO_4$ suppress the rates of H_2O_2 decomposition over Zr-MOF and increase oxidant utilization efficiency. No structural changes occur in the acid-activated Zr-MOF. The catalyst does not suffer metal leaching, reveals a truly heterogeneous nature of the catalysis and can be recovered and reused.

KEYWORDS: cyclohexene, epoxidation, heterogeneous catalysis, hydrogen peroxide, metal-organic frameworks, UiO, zirconium

The development of sustainable oxidation processes on the basis of environmentally benign oxidants is a demanding task of the modern chemical industry stimulated by increasing ecological concerns.1 Hydrogen peroxide can be the oxidant of choice because it contains 47% of potentially active oxygen and produces water as the sole byproduct.² The elaboration of new methods for the direct synthesis of H₂O₂ from H₂ and O₂ may open up the new prospects for the widespread use of this green oxidant.3

Metal-organic frameworks (MOFs) possess a unique blend of properties, such as intrinsic hybrid nature, open crystalline structures, ultrahigh surface areas, tunable pore dimensions, and surface functionality.⁴ All these fascinating features allow one to consider MOFs as prospective functional materials for gas storage and separation, molecular recognition, drug delivery, and heterogeneous catalysis.^{4,5} Zr-based MOFs are of particular interest for practical applications owing to their outstanding stability.⁶ The zirconium terephthalate UiO-66 first reported in 2008⁷ has attracted great attention due to its exceptional robustness to thermal treatments (up to 540 °C),⁷ acidic conditions (pH 1),8 and aqueous H₂O₂.8b

The absence of coordinatively unsaturated metal sites in UiO-66 and related materials initially caused doubts about the possibility of using such MOFs in catalysis. However, recent studies revealed that catalytic activity of UiO-66 and some other MOFs can be significantly enhanced through the generation of defects in their crystalline structure.9 Several 'defect engineering' methodologies have been suggested to increase the number of potential Lewis acid sites, including (i) adjusting synthetic conditions, e.g. metal to linker ratios,¹⁰ temperature^{10,11} or time of synthesis,¹² (ii) using modulators during the preparation,^{9a,13} and (iii) post-synthetic treatments.¹⁴ Recently, correlations between the number of missing-linker sites and catalytic activity of UiO-66 have been found for the

selective oxidation of benzyl alcohol and S-compounds with H₂O₂.¹⁵ Another way to design selective oxidation catalysts on the basis of UiO-66 and some other stable Zr-MOFs involves grafting of catalytically active species (Cr, Ti, V, Mo) onto the MOF surface¹⁶ or encapsulation of noble metal nanoparticles within the MOF cages.¹⁷ In this case, MOF serves more as a support rather than a true catalyst. A controlled exchange of linkers with chiral M(salen) linkers in a Zr-based MOF has led to asymmetric metallosalen heterogeneous catalysts.¹⁸

Here, we report on a simple tool that enables tuning the reactivity and selectivity of UiO-66 and other Zr-MOFs in H₂O₂-based oxidation of olefins through enhancing heterolytic pathway of hydrogen peroxide activation by means of proton additives, without evident changes in the MOF crystalline structure.

UiO-66 and isoreticular UiO-67 as well as MOF-801 were prepared by the procedure reported in the literature¹⁹ and characterized by XRD, elemental analysis, N2 adsorption, SEM, TGA, FT-IR and Raman spectroscopy (see Supporting Information (SI) for details). TGA measurements (Figure S5) showed that the dehydrated and desolvated sample of UiO-66 lost 52.1% of its weight (from 89.2% to 42.7 wt %) in the last step in contrast to 54.6% of the calculated weight loss based on the formula of ideal Zr₆O₆(CO₂C₆H₄CO₂)₆.²⁰ Therefore, the UiO-66 material used in this work could be considered as a slightly defective one with 11.4 terephthalate ligands per inorganic Zr₆O₄(OH)₄ cluster instead of 12 in the nondefective structure (see SI for calculations). This suggestion agrees with the ICP and CHNO-analyses data (Tables S2 and S3).

Catalytic performance of UiO-66 was first assessed in the oxidation of cyclohexene (CyH) with equimolar amounts of 30% aqueous H₂O₂ using acetonitrile as solvent (Table 1). found for the Note that CyH has become a conventional test substrate to ACS Paragon Plus Environment

evaluate contributions of homo- and heterolytic oxidation pathways by analyzing the composition of the reaction products.^{16c,d,21} UiO-66 promoted CyH oxidation (15 vs 6% conversion in the 'blank' experiment) and produced a mixture of epoxide, trans-cyclohexane-1,2-diol and allylic oxidation products, cyclohexenyl hydroperoxide (HP), 2-cyclohexene-1ol (enol), and 2-cyclohexene-1-one (enone). A high ratio (52%) of the allylic oxidation products unambiguously indicated a homolytic oxidation mechanism with the participation of radical species capable of H-atom abstraction.²² The addition of 1 molar equivalent (relative to Zr atoms in the MOF) of HClO₄ increased significantly the reaction rate and attainable CyH conversion and drastically altered the composition of products, favoring the formation of epoxide and diol (Scheme 1, Table 1), the products derived from heterolytic oxygen transfer to the C=C bond.

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Scheme 1. Effect of protons on selectivity of CyH oxidation with H_2O_2 catalyzed by UiO-66 (violet – Zr atoms, red – O atoms).

Table 1. Effect of acid on CyH oxidation with H_2O_2 over $UiO\text{-}66^{a}$

catalytic system	$\frac{\mathrm{TOF}^{b}}{(\mathrm{min}^{-1})}$	X ^c (%)	product selectivity ^d (%)		
			epoxide	diol	allylic ^e
_ <i>f</i>	-	6	16	16	65
H^{+g}	-	8	25	26	47
UiO-66	0.1	15^{h}	36	11	52
$UiO-66 + H^+$	1.3	$31^{i,j}$	77	21	2
	catalytic system -f H ^{+g} UiO-66 UiO-66 + H ⁺	catalytic system TOF^b (min ⁻¹) $-f$ - H^+g -UiO-660.1UiO-66 + H^+1.3	catalytic system TOF ^b (min ⁻¹) X^c (%) $-f$ - 6 H^+g - 8 UiO-66 0.1 15 ^h UiO-66 + H ⁺ 1.3 31 ^{ij}	catalytic system TOF^b (min ⁻¹) X^c (%)product sel epoxide $-f$ -616 H^+g -825UiO-660.115^h36UiO-66 + H^+1.331^{i,j}77	catalytic system TOF^b (min ⁻¹) X^e (%)product selectivity epoxidediol $-f$ -61616 H^+g -82526UiO-660.115^h3611UiO-66 + H^+1.3 31^{ij} 7721

^{*a*}Reaction conditions: 0.1 mmol CyH, 0.1 mmol 30% H₂O₂, 2 mg UiO-66 (7 µmol Zr), 7 µmol HClO₄ (if any), 1 mL CH₃CN, 50 ^oC, 1 h. ^{*b*}TOF (turnover frequency) = (moles of substrate consumed)/(moles of Zr × time), determined by GC from initial rates of substrate consumption. ^{*c*}CyH conversion. ^{*d*}GC yield based on CyH consumed. ^{*e*}Sum of allylic oxidation products (HP + enol + enone). ^{*f*}No catalyst was present. ^{*g*}7 µmol HClO₄. ^{*b*}H₂O₂ conversion 35%. ^{*i*}Reaction time 20 min. ^{*f*}H₂O₂ conversion 50%.

A similar trend was observed with the larger cage UiO-67 as well as another microporous Zr-MOF, MOF-801 (Table S4). The nature of acid produced no effect on the ratio of homo- to heterolytic oxidation products; however, use of anhydrous CF₃SO₃H increased the ratio of epoxide relative to diol (Table S5).

In the absence of Zr-MOF, acid produced only a minor effect on the product distribution and CyH conversion (see Table 1). The positive effect of protons could be observed in different reaction media, but the best solvent, in terms of attainable CyH conversion and heterolytic oxidation selectivity, was acetonitrile (Figure S6). Variations in the concentration of $HClO_4$ showed that the optimal amount of acid to achieve the highest total selectivity toward epoxide and diol (98%) and 77% selectivity toward epoxide is close to 1 equiv. relative to the amount of Zr (Figure 1). Reduction in the amount of acid led to a progressive increase in the ratio of allylic oxidation products and decrease in alkene conversion and TOF (Figure 1). On the other hand, the addition of an extra portion of acid (1.5 equiv.) favored the epoxide ring opening and enhanced the ratio of diol along with some increase in CyH conversion and TOF (Figure 1).



Figure 1. Effect of the amount of acid on CyH oxidation with H_2O_2 in the presence of UiO-66. Reaction conditions: 0.1 mmol CyH, 0.1 mmol H_2O_2 , 2 mg UiO-66 (7 µmol Zr), 0.7–10.5 µmol HClO₄, 1 mL CH₃CN, 50 °C.

With 1 equiv. of the oxidant, the maximal CyH conversion varied from 20 to 31%, depending on the reaction temperature, without a significant alteration in the product selectivity (Figure S7). The incomplete substrate conversion might be caused by competitive decomposition of H2O2 with the evolution of molecular oxygen. Indeed, the addition of an extra portion of the oxidant after the reaction stopped allowed the CyH conversion to be increased from 31 to 41%, but also augmented the yield of diol (Figure S8b). Interestingly, increase in the amount of H₂O₂ in the absence of acid reduced the ratio of homolytic oxidation products and improved epoxidation selectivity (Figure S8a), although H₂O₂ utilization efficiency decreased (31.5% for 0.2 M H_2O_2 vs 45% for 0.1 M H₂O₂). Such behavior is not typical in homogeneous catalysis, where epoxidation selectivity is normally decreased with increasing H₂O₂ concentration, but has been precedented for MOF catalysts.5a,23

Figure 2 shows that H_2O_2 degradation over UiO-66 in the absence of organic substrate occurs with an appreciable rate, which is quite typical of Zr-containing catalysts.²⁴ It has been documented in the literature,^{3,25} that acid additives (H_3PO_4 , H_2SO_4 , HNO_3 and some others) may retard H_2O_2 decomposition over various catalysts. However, the role of acid is not always evident and may depend on the specific catalyst system and the nature of the acid. For example, $HClO_4$, in contrast to H_2SO_4 , produced no effect on the hydrogen peroxide decomposition over a Pd-containing zeolite catalyst.²⁶ On the other hand, H_2O_2 degradation catalyzed by Keggin Zr-substituted polyoxometalates (Zr-POMs)²⁷ or Zr-silicate (Figure S9) revealed an acid-accelerated behavior, and a similar trend was observed for Ti-POMs.²⁸

The effect of acid on the rate of H_2O_2 degradation over Zr-MOFs was then investigated. Even small additives of $HClO_4$ resulted in a significant suppression of H_2O_2 decomposition over UiO-66 (Figure 2) and UiO-67 (Figure S10). Therefore, we can conclude that acid produced opposite effects on the 1

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rates of the target alkene oxidation reaction and the side reaction of H_2O_2 degradation, which may imply that different active sites are involved in these two reactions. Given that, one might anticipate that acid additives would increase oxidant utilization efficiency in Zr-MOF-catalyzed oxidations. Indeed, while CyH conversion was 31 and 15% in the experiments with and without acid, respectively, the corresponding H_2O_2 conversion reached the values of 50 and 35% (Table 1). As a result, H_2O_2 utilization efficiency improved from 45% to 63% due to the addition of protons.



Figure 2. Effect of acid on H_2O_2 decomposition over UiO-66. Reaction conditions: 0.4 mmol H_2O_2 , 10 mg UiO-66 (0.04 mmol Zr), 0.004–0.04 mmol HClO₄ (if any), 2 mL CH₃CN, 50 °C.

Since the reaction stopped before all H₂O₂ was consumed, we may suggest that accumulation of the reaction products within the micropores of UiO-66 is the main reason for the catalyst deactivation. Previously, oxidation products caused the catalyst deactivation in UiO-66-catalyzed oxidation of propylene glycol.²⁹ In fact, the catalyst separated after the CyH oxidation revealed some decrease in the specific surface area and pore volume (Table S1). Moreover, if the principal products, epoxide and water, were added during the reaction course in the amount close to that formed at the end of the catalytic reaction, the CyH oxidation stopped without reaching the expected substrate conversion (Figure S11). Washing the spent catalyst with methanol under elevated temperature allowed the catalyst to be regenerated completely. Plots of CyH conversion vs time (Figure 3) show that the catalyst retained its activity during, at least, three consecutive runs.



Figure 3. Reuse of UiO-66 (solid symbols) and hot catalyst filtration test (open squares) for CyH oxidation over UiO-66 in the presence of 1 equiv. $HClO_4$. Reaction conditions as in Table 1.

To understand the origin of the enhanced heterolytic pathway selectivity of UiO-66 in the presence of small acid additives, the catalyst stability was verified under the conditions employed for catalytic runs. Hot filtration tests unambiguously proved that the observed catalysis has the truly heterogeneous nature (Figures 3 and S12). Only traces of zirconium (< 0.1 ppm) were determined in the filtrate by ICP-AES, which also corroborates the absence of the metal leaching during the reaction course. The retention of the UiO-66 structure after the catalytic reaction was confirmed by XRD (Figure 4), FT-IR (Figure S3), and Raman (Figure S4) spectroscopy. Moreover, the IR and Raman spectra of the H₂O₂/acid-treated UiO-66 revealed no changes that might arise due to the formation of a peroxy acid from an uncoordinated carboxylate linker, which allowed us to exclude its participation in the epoxidation process.



Figure 4. XRD patterns for UiO-66: (A) simulated, (B) fresh, and (C) after CyH oxidation with H_2O_2 in the presence of 1 equiv. of HClO₄ (reaction conditions as in Table 1).

Given that defects can play a significant role in catalysis by Zr-MOFs,^{9,15} we compared TG profiles for the fresh and reused UiO-66 samples (Figure S5) and found that the latter was insignificantly more defective: the weight loss in the last step was 51.4% in contrast to 52.1% determined for the fresh sample, which corresponds to 11.3 and 11.4 linkers, respectively. Therefore, the positive effect of small additives of acid on the CyH epoxidation selectivity cannot be explained by the formation of a significant portion of new defects. Indeed, stability of UiO-66 under mild acidic conditions has been well-documented.⁸

In homogeneous catalysis, protonation is known to trigger the electrophilic reactivity of some peroxo complexes as oxygen-transfer agents.^{21,30} DFT calculations on transitionmetal-substituted Keggin-type POMs $(Bu_4N)_n[PM(OH)W_{11}O_{39}]$ (M = Ti(IV), Zr(IV), Nb(V), V(V), Mo(VI), W(VI), and Re(VII)) showed that the formation of epoxide via a hydroperoxo intermediate is energetically more favorable than through peroxo intermediates for such metals as Ti(IV), Zr(IV) and Nb(V).^{30c} More recently, the same trend was found for Ti- and Nb-monosubstituted tungstates of the $(Bu_4N)_3[(CH_3O)TiW_5O_{18}]$ Lindavist structure, and (Bu₄N)₂[(CH₃O)NbW₅O₁₈].^{30d} We could tentatively assume that protons may facilitate the formation of an active zirconium hydroperoxo species 'ZrOOH' upon interaction of a terminal Zr-OH bond (such sites might be present in the defects of UiO-66)^{9b,c,31} with H₂O₂ (Scheme 2, route A) and this species is responsible for oxygen atom transfer to the alkene. Note that feasibility of the formation of 'ZrOOH'

intermediates in UiO-66 was recently confirmed by DFT calculations.^{15b}

Alternatively, we may suggest the formation of a bridging μ - η^2 : η^2 -peroxo species (Scheme 2, route B) via a mechanism similar to that proposed by Mizuno and co-workers for a divanadium-substituted γ -Keggin polyoxotungstate, $(Bu_4N)_4[\gamma$ -PW₁₀O₃₈V₂(μ -O)(μ -OH)].³² Note that Zr peroxo complexes with the μ - η^2 : η^2 -arrangement of the peroxo ligand have been reported in the literature.³³



Scheme 2. Alternative mechanisms of the formation of active Zr-peroxo species.

So far, attempts to identify spectroscopically any Zr peroxo species in Zr-MOFs failed, most likely, because of their extremely high reactivity. Further experimental and computational studies on soluble molecular models, Zr-POMs, are in progress in our group to gain insights into the intimate mechanism of H_2O_2 activation on Zr(IV) sites.

In summary, we demonstrated that both catalytic activity and selectivity of Zr-MOFs, in particular UiO-66, UiO-67 and MOF-801, in epoxidation of CyH with aqueous H_2O_2 can be greatly enhanced by small acid additives. Protons disfavor homolytic degradation of the oxidant on Zr-MOF and oppositely facilitate heterolytic activation of H_2O_2 , which makes possible selective oxygenation of the C=C bond, avoiding allylic oxidation. Importantly, all these occur without evident changes in the MOF structure and the catalyst can be recycled and reused several times without loss of the catalytic activity.

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the

manuscript.

Notes

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The authors declare no competing financial interests.

ASSOCIATED CONTENT

Supporting Information. Full experimental procedures; characterizing data for UiO-66, UiO-67 and MOF-801; N₂ adsorption, ICP, EA, TGA, FT-IR and Raman data; SEM images; catalytic experiments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

ACKNOWLEDGMENT

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (project AAAA-A17-117041710080-4) and partially supported by the Russian Foundation for Basic Research (grant № 18-29-04022). J.S.C. and J.S.L. are grateful to Global Frontier Center for Hybrid Interface Materials (GFHIM) and ISTK for their financial support through the Global Frontier R&D Program and the Institutional Collaboration Research Program (SK-1301).

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SYNOPSIS TOC



