Contents lists available at ScienceDirect





Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Sulfonic-functionalized MIL-101 as bifunctional catalyst for cyclohexene oxidation



Weng-Jie Sun, En-Qing Gao*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, 200062, China

ARTICLE INFO	A B S T R A C T
Keywords: Metal-organic frameworks Difunctional catalyst Cyclohexene Oxidation Mechanism study	Metal-organic frameworks (MOFs) are newly emerging and versatile platforms for designing catalysts, and catalytic oxidation of cyclohexene has attracted much academic and industrial attention for the versatile re- activity of the substrate and the great importance of the various oxygenated products. Here we report the bifunctional catalytic properties of a sulfonic-containing MOF, MIL-101-SO ₃ H, for cyclohexene oxidation. The sulfonic group and the Cr(III) site acts in a complementary or collaborative way. The Cr(III) framework promotes the oxidation to 3-hydroperoxycyclohex-1-ene (perox) and 2-cyclohexen-1-one (1-one) (route A), whereas the sulfonic group in collaboration with the Cr(III) framework promotes the oxidation to diol (route B) and also enhances further conversions in route A: from perox to 1-one, to 2-cyclohexen-1,4-dione (dione) and even to benzoquinone. With the bifunctional MOF, molecular oxygen alone cannot oxidize cyclohexene but participates as oxidant cooperating with tert-butyl hydroperoxide (TBHP) to accelerate the reactions and to alter the product distribution in favor of dione.

1. Introduction

Cyclohexene is a cheap, abundant, and easily obtained industrial raw material and can be oxidized to different oxygenated chemicals that are important intermediates for the production of medicines, pesticides, spices, surfactants and polymers [1-4]. so the oxidation of cyclohexene has received great attention from both industrial and academical viewpoints [5,6]. Cyclohexene has two potential sites for oxidation transformation, usually giving rise to a mixture of products with different oxygenated functional groups. Oxidation at the allylic C-H bond can lead to unsaturated compounds such as 2-cyclohexen-1one (1-one), 2-cyclohexen-1-ol (1-ol), 3-hydroperoxycyclohex-1-ene (perox) or 3-(tert-butylperoxy)cyclohex-1-ene (Scheme 1, route A), whereas oxidation at the C=C bond usually produces cyclohexene epoxide (epox) and 1,2-cyclohexanediol (diol) (Scheme 1, route B) [6]. Many efforts have been made in recent years to explore the selectivity and mechanism of cyclohexene oxidation over various catalysts, including homogeneous or immobilized metal-based species [7-13] and non-metal ones (such as carbon nanotubes [4] and C₃N₄ [14,15]). The most popular oxidants have been molecular oxygen, hydroperoxide and tert-butyl hydroperoxide (t-BuOOH, TBHP), which are clean or relatively clean [10,16,17]. The choice of the oxidants is strongly dependent upon the nature of the catalysts.

Metal-organic frameworks (MOFs), constructed by linking metal ions or metal clusters with organic ligands and featured by well-defined crystalline structure, tunable porosity and functionalities, have recently emerged as versatile and attractive platforms for the design of heterogeneous porous catalysts and many other functional materials [18-21]. Some MOFs with different metal centers or topologies, such as MFU-1 [22], MIL-47 [23], MIL-101 [24], MOF-74 [25], and UiO-66-NH₂ [17], have been employed for catalytic oxidation of cyclohexene in the last decade, with diverse activity and selectivity [10,26,27]. MOF-based dior multifunctional catalysts for cyclohexene oxidation has seldom been explored. Polyoxometalates have been encapsulated inside MIL-101 to enhance the activity [28,29]. Mo(VI) [27,30], Nb(V) [31], Ti (IV) [32] oxide sites have been installed onto the metal cluster nodes by postsynthetic solvothermal deposition in NU-1000 or onto the organic linkers by postsynthetic coordination modification of HKUST-1 and MIL-47, the Mo(VI) oxide functionalized and showing high selectivity for epoxidation by hydroperoxide. In this article, we report the catalytic study of a facile difunctional MOF, MIL-101-SO₃H [33], for cyclohexene oxidation. It is demonstrated that the sulfonic group and the Cr(III) center acts in a complementary way to promote the oxidation reactions. In particular, the Cr(III) center promote the transformation to perox and

https://doi.org/10.1016/j.mcat.2019.110746 Received 7 September 2019; Received in revised form 9 December 2019; Accepted 16 December 2019 2468-8231/ © 2019 Published by Elsevier B.V.

^{*} Corresponding author at: Shanghai Key Laboratory of Green Chemistry and Chemical Processes, College of Chemistry and Molecular Engineering, East China Normal University, Shanghai, 200062, China.

E-mail address: eqgao@chem.ecnu.edu.cn (E.-Q. Gao).



Scheme 1. Possible reaction routes of cyclohexene oxidation.

1-one (route A), and the incorporation of the sulfonic group into the MOF enhances the conversion to diol (route B) and the further conversions in route A: from perox to 1-one and further to 2-cyclohexen-1,4-dione (dione). The dione product is rarely identified in cyclohexene oxidation [24], can become the major product in our catalytic system. We also demonstrate that molecular oxygen alone cannot oxidize cyclohexene but serves as co-oxidant in cooperation with TBHP. Tentative mechanisms for the formation of different products are proposed.

2. Experimental

2.1. Physical measurements

X-ray powder diffraction patterns of the samples were measured using a Rigaku Ultima IV X-ray diffractometer with Cu K_{α} radiation (λ =1.5418 Å) at a scanning rate of 10° /min, with accelerating voltage and current of 35 kV and 25 mA, respectively. Nitrogen adsorption and desorption isotherm measurements were performed on a Micromeritics ASAP2020 analyzer at 77 K. Scan electron microscopy (SEM) images were carried out with a S-4800 HITACHI scanning electron microscope. FT-IR spectra were recorded in the range $500 - 4000 \text{ cm}^{-1}$ using KBr pellets on a Nicolet NEXUS 670 spectrophotometer. The temperatureprogrammed desorption of ammonia (NH3-TPD) were performed on a Micromeritics autochem 2920 instrument. For the purpose, 0.050 g sample was put into a U-shaped quartz tube and treated in argon (20 mL/min) at 150 °C for 30 min. The TPD curves were obtained at the 10 °C / min rate. The catalytic products were analyzed by gas chromatography (Shimadzu: GC-2014) and gas chromatograph-mass spectrometer (Agilent Technologies, GC: 7890B, mass: 5977A). Elemental analysis was performed on an Elementar Vario ELIII analyzer. The metal amount was detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an IRIS Intrepid II XSP spectrometer.

2.2. Catalyst preparation and characterization

MIL-101-SO₃H was prepared under the hydrothermal conditions according to a procedure described [34] with some modification. Sulfoterephthalic acid (3.35 g, 12.5 mmol), CrO₃ (1.25 g, 12.5 mmol) and concentrated aqueous hydrochloric acid (0.8 mL, 25 mmol) was dissolved in water (50 mL) and then transferred to a Teflon-lined stainless steel autoclave. The solution was heated at 180 °C for six days. The reaction product was harvested by centrifugation, washed with deionized water (50 mL \times 3) and methanol (50 mL \times 3), and dried in air. Elemental analysis: Anal. calcd. for $[Cr_3O(OH)]$ (H₂O)₂(C₈H₄O₇S)₃]·12H₂O: Cr, 13.3; C, 24.5; S: 8.2 %. Found: Cr, 13.2; C, 24.8; S, 8.2 %. According to the analytic results, the amounts of Cr and SO₃H are both 2.55 mmol/g.

2.3. Typical procedure for cyclohexene oxidation

MIL-101-SO₃H (8.0 mg, corresponding to 0.020 mmol Cr and

0.020 mmol SO₃H, 4 mol% with respect to cyclohexene) was dried in vacuum at 110 °C for 4 h and added under stirring to a 10 mL vessel containing cyclohexene (0.5 mmol) and TBHP (5 mmol) in *n*-decane (5.5 mol/L). The mixture was stirred at 40 °C for 14 h. The catalyst was filtered and washed with chloroform (10 mL) for three times. The conversion and yield was determined by gas chromatography (GC) with the combined liquid phase. The washed catalyst was dried in vacuum at 110 °C for 4 h and used for recycle tests.

2.4. Control test with 1-one

The test was performed following the above procedure, using 1-one in the place of cyclohexene.

2.5. Control test with epox

TBHP (5 mmol) or H_2O (45 μ L, 2.5 mmol) was added under stirring to a 10 mL vessel containing epox (0.1 mmol) and MIL-101-SO₃H (8 mg, 4 mol%). The mixture was stirred at 40 °C for 14 h. The diol yield was determined by GC.

3. Results and discussion

3.1. Synthesis and characterization of MIL-101-SO₃H catalyst

MIL-101-SO3H was synthesized according to the procedures reported the literature before [34]. The powder X-ray diffraction (PXRD, Fig. 1a) is in good agreement with those of MIL-101 (simulated and experimental), indicating the formation of the MIL-101-type structure. Compare with MIL-101, MIL-101-SO₃H shows three new FTIR bands assignable to the sulfonic group (Fig. 1b). The asymmetric and symmetric stretching peaks of O=S=O appears at 1226 and 1179 cm⁻¹ respectively, and the peak at 1025 cm^{-1} is ascribable to the S–O stretching vibration [35-37]. The peaks at 1080 and 770 cm⁻¹ for MIL-101-SO₃H can be assigned to the in-plane and out-of-plane skeletal C-H vibrations of the benzene ring, which are blue shifted compared to the corresponding peaks (1018 and 748 cm⁻¹) for MIL-101 [35,38]. The changes should be due to sulfonation of the ligand. According to nitrogen adsorption isotherm at 77 K (Fig. 1c), the Brunauer – Emmett – Teller (BET) specific surface area is 1603 m^2/g . SEM (Fig. 1d) displayed an octahedral morphology with particle sizes of 100 – 250 nm.

3.2. Catalytic studies for cyclohexene oxidation

To evaluate the catalytic performance of MIL-101-SO₃H for cyclohexene oxidation, different reaction conditions were tested over MIL-101-SO₃H and TBHP. Two commercially available TBHP reagents, 70 wt% (water) and 5.5 mol/L (n-decane), were used as the oxidant to react with cyclohexene over MIL-101-SO₃H at 40 °C for 14 h under air atmosphere. According to the results, the reactions in both solvent systems produce 1-one, dione and diol, with similar product distributions (Table 1, entries 1 and 2). TBHP/n-decane leads to somewhat higher conversion than the aqueous solution. This can be explained by the blocking of active sites by water molecules. TBHP/n-decane was used for further investigation. Various additional solvents were tested to investigate the solvent effects. From Table 1 we can see that except CH₃CN, the additional solvents would greatly decrease the conversion of cyclohexene. The catalytic reactions without additional solvents gave the highest conversion. The negative effects of additional solvents could partially be attributed to the decreased concentrations of TBHP and cyclohexene. Another reason could be that the formation and stability of radical intermediates during the catalytic process is affected by the solvents (especially DMF and acetic acid).

The effects of the oxidant dosage were investigated. When TBHP was slightly in excess of cyclohexene, 1-one was the main product



Fig. 1. (a) PXRD profiles of MIL-101-SO₃H (fresh) and MIL-101 (observed and simulated). The profile for used MIL-101-SO₃H (after one catalytic run) is also included. (b) FTIR spectra of MIL-101 and MIL-101-SO₃H. The spectrum for used MIL-101-SO₃H (after one catalytic run) is also included. (c) Nitrogen adsorption and desorption isotherms of MIL-101-SO₃H, (d) SEM image of MIL-101-SO₃H.

 Table 1

 Conversion of cyclohexene and yields of various oxidation products in different solvent systems.^a

Entry	Solvent	Conv (%)	1-one (%)	dione (%)	diol (%)
1 ^b	-	91	56	24	11
2	-	95	57	22	16
3	acetonitrile	89	69	18	2
4	DMF	8	8	-	-
5 ^c	toluene	64	46	3	3
6	ethyl acetate	67	58	7	2
7	acetic acid	16	5	-	11

^a Reaction conditions: cyclohexene (0.5 mmol), TBHP (0.75 mmol, 1.5 equivalent) in *n*-decane (5.5 mol/L), MIL-101-SO₃H (4 mol%), additional solvent (0.5 mL, if added), air atmosphere, 40 $^{\circ}$ C, 14 h. ^b 0.75 mmol TBHP in water (70 wt %). ^c 12 % epox was also found.

Table 2

Conversion of cyclohexene and yields of various oxidation products with different TBHP dosages and under different atmospheres.^a

Entry ^a	TBHP (eqv.)	atmosphere	Conv (%)	1-one (%)	dione (%)	diol (%)
1	1.5	air	95	57	22	16
2	5	air	96	41	36	19
3	10	air	99	36	43	20
4 ^b	1.5	nitrogen	58	37	5	12
5	10	nitrogen	98	42	35	21
6	1.5	oxygen	96	54	19	23
7	10	oxygen	99	13	61	25
8	0	oxygen	0	-	-	-
9	0.5	oxygen	31	31	-	-

 a Reaction conditions: cyclohexene (0.5 mmol), TBHP with MIL-101-SO_3H (4 mol%) at 40 $^\circ C$ for 14 h. b 4 % epox was also found.

(Table 2, entry 1). Increasing the TBHP dosage leads to less 1-one, more dione and slightly more diol (entries 2 and 3). The results could suggest that dione be the secondary product arising from further oxidation of 1-one. The formation of a large amount of dione in the catalytic system is

worth noting. This product was rarely noticed in the literature of cyclohexene oxidation, except for only a few reports that mentioned it as a minor product [24,39–41]. According to the stoichiometry of the reactions [10,42], at least two equivalent TBHP is required to oxidize cyclohexene to 1-one or diol. Similarly, four equivalents of the oxidant are required to oxidize cyclohexene to dione. It is surprising that 1.5 equivalent TBHP leads to a 95 % conversion of cyclohexene, with the yields of 57, 22 and 16 % for 1-one, dione and diol, respectively. According to the stoichiometric proportions, the conversion would need nearly 2.3 equivalents of TBHP. This implies a utilization efficiency of TBHP is up to 156 %, which is unrealistic. To explain the phenomenon, we propose that dioxygen in the air should participate as additional oxidant. The dioxygen should be responsible for the conversion that at least corresponds to the actually nonexistent 56 % TBHP.

To further confirm the involvement of dioxygen, control reactions were performed in different atmospheres (dinitrogen, air and dioxygen) (Table 2). Under the dinitrogen atmosphere instead of air, 1.5 equivalent TBHP leads to sharp declines in conversion of cyclohexene (58 %) and yield of route-A products (42 % for 1-one + dione) (Table 2, entry 4). The reaction shows a reasonable efficiency of TBHP (79 %). Under dioxygen, the conversion is almost complete, the selectivity for diol being somewhat increased compared with that under air (Table 2, entries 1 and 6). Again, an unrealistic efficiency of TBHP (153 %) was obtained under dioxygen, indicating the participation of dioxygen. Excessive TBHP (10 eqv.) leads to decreased TBHP efficiency (~ 30 %) but complete conversions under the different atmospheres (entries 3, 5 and 7). The dione yield increases as the atmosphere changes from dinitrogen to air and to dioxygen, in line with the decrease in the 1-one yield. The yield of diol is relatively high under dioxygen. These results not only confirm that dioxygen is involved in the oxidation reactions but also suggest that it facilitates the production of dione and diol. We also performed the reaction under dioxygen in the absence of TBHP (Table 2, entry 8). No conversion was observed, which indicates that dioxygen alone cannot oxidize cyclohexene but serves as co-oxidant in cooperation with TBHP. A small amount of TBHP (0.5 eqv.) in the presence of pure dioxygen leads to only 1-one (Table 2, entry 9). The

Table 3

Conversion of cyclohexene and yields of various oxidation products with different catalyst amounts and at different temperatures.^a.

Entry ^a	MOF (mol%)	Temperature(°C)	Conv (%)	1-one (%)	dione (%)	diol (%)
1	2	40	98	52	40	6
2	4	40	99	13	61	25
3	6	40	99	11	60	28
4 ^b	4	30	99	37	51	6
5 °	4	50	99	-	52	37

 a Reaction conditions: cyclohexene (0.5 mmol), TBHP (5 mmol) with MIL-101-SO₃H in oxygen atmosphere for 14 h. b 5 % epox was also found. c 10 % benzoquinone was also found.

conversion (31 %) is higher than the value (25 %) expected for 0.5 eqv. TBHP, once again confirming participation of dioxygen in oxidation. The conversion is much lower than those for higher TBHP dosages, indicating that dioxygen cannot oxidize cyclohexene any more once the small dosage of TBHP is completely consumed up (entries 6 and 7). In addition, the absence of dione in the products implies that dioxygen alone cannot oxidize 1-one.

The effects of catalyst dosage and reaction temperature were tested (Table 3). When the catalyst dosage was increased from 2 to 4 mol%, the yields of dione and diol were significantly increased at the cost of less 1-one (entries 1 and 2). Therefore, more catalyst is more beneficial to route B and secondary oxidation of 1-one. The effects become weaker upon further increasing the catalyst dosage to 6 mol% (entry 3): a slight increase in diol yield and a slight decrease in 1-one yield were observed. When the temperature was reduced from 40 to 30 °C with 4 mol% catalyst, the yield of diol was significantly reduced, and the conversion from 1-one to dione was slowed down (entry 4). In addition, a small amount of epox was observed (5 %), which could be the precursor to diol. On the other hand, increasing the temperature to 50 °C leads to significant increase in diol yield, complete disappearance of 1-one (entry 5), which is presumed to be further oxidized to diol. A certain amount of benzoquinone was also detected (10 %) at 50 °C, which should arise from further oxidation of dione. On the whole, the product distribution is strongly dependent upon temperature. Increasing temperature facilitates route B and further conversion of the products of both routes.

To gain further insight into the reaction process and intermediates, the product distribution at different time was investigated (Fig. 2 and Table 4). The conversion of cyclohexene under dinitrogen reaches 42 % after 2h and is almost complete after 10h. An intermediate product, identified as perox by GC-MS, was found at the early stage of the reaction (Fig. 2a). The intermediate disappeared after 6 h through rapid conversion to 1-one [4,43,44], which increases rapidly in the first 4 h and then decreases. The decrease of 1-one is accompanied by the increase of dione, which was not detected within the first 2 h. The precursor to diol, epox, was also detected within 10 h and disappeared after prolonged reaction time, accompanied by an increase in diol yield. This suggests the conversion of epox to diol [4,45], The data confirm that the oxidation of cyclohexene proceeds through two routes: route A, through perox to 1-one and then to dione (and finally to DDQ at higher temperature); route B, through epox to diol. The total yield for each route increases at the early stage and remains unchanged after complete conversion of cyclohexene, indicating that the two route are independent without cross transformation (Fig. 2c and d). The kinetic data for the reaction under dioxygen atmosphere reveal the same intermediates and products (Fig. 2b). However, the reaction is significantly accelerated by dioxygen, the conversion of cyclohexene reaching 45 % after 1 h and almost completed after 6 h. Close inspection suggests that the effects of dioxygen are more significant on route A than on route B. Particularly, the production of perox from cyclohexene and of dione from 1-one is significantly enhanced.

Control reactions were performed to further confirm the two routes (Scheme 2). Under the typical catalytic conditions, 1-one can be oxidized to dione by TBHP under dinitrogen atmosphere (Scheme 2a). The reaction under dioxygen gave higher conversion but would not proceed if TBHP were not used. The results proved that, as mentioned above for oxidation of cyclohexene, dioxygen serves to oxidize 1-one only in cooperation with TBHP. To verify the epox-to-diol conversion in route B, epox was allowed to react with TBHP under the typical catalytic conditions (Scheme 2b). The yield of diol was 76 %. For comparison, using water instead of TBHP to react with epox, a significantly lower vield of diol (41 %) was observed. Obviously, the epoxide ring-open mechanism by TBHP should be different from that by water. The ringopen reaction is a catalytic process for the reaction does not proceed without MIL-101-SO3H. Furthermore, no diol (or dione) was detected in the catalytic reaction starting from 1-one (or epox), confirming that routes A and B are mutually independent without cross conversion.

When a radical inhibitor, BHT (butylated hydroxytoluene) was added to the reaction mixture at the beginning, no conversion of cyclohexene was observed within 14 h (Scheme 3a), suggesting the involvement of radical species in the oxidation processes. Furthermore, when BHT was added after the catalytic reaction proceeded for 1 h (19 % conversion to perox, 1-one and epox), no further conversion of cyclohexene was detected, and only the radical-independent elimination reaction from perox to 1-one proceeded to completion (Scheme 3b). It is worth noting that the addition of BHT suppress the ring-open reaction of epox, which indicates the epox-to-diol reaction also involves radicals. This was further confirmed by the results of the control reactions starting with epox (Schemes 2b and 3 c): the conversion of epox reacting with TBHP was dramatically reduced from 76 to 28 % when BHT was added.

Next, the effective catalytic sites in MIL-101-SO₃H were explored. Under catalyst-free conditions, 68 % cyclohexene converts to perox (56 %) and a small portion of 1-one (12%) in 14h (Table 5, entry 1). In the presence of MIL-101 (entry 2), the conversion is enhanced to 82 %, where perox remains to be the main product but the yield of 1-one increases obviously, with a little amount of dione (7 %). No products of route B appear in above reactions. For comparison, MIL-101-SO₃H leads to 99 % cyclohexene conversion (entry 3). Dione becomes the main product in the expense of 1-one, and a considerable amount of diol appears. According to the results, the Cr(III) center should promote route A but cannot trigger route B, whereas the introduction of the sulfonic acid group could trigger route B and meanwhile promotes perox decomposition and the 1-one-to-dione conversion. The effect of sulfonic acid was checked by using p-toluene sulfonic acid (PTSA) instead of the MOFs (entry 4). It seems that PTSA is an impediment to route A because it leads to lower conversion of cyclohexene and lower yields of perox and 1-one compared with the catalyst-free reaction. However, it indeed leads to diol formation, confirming the positive effect of sulfonic acid on route B. Using PTSA together with MIL-101 leads to much improved cyclohexene conversion through route A (entry 5). With either PTSA or MIL-101 alone, the major product is perox. With PTSA + MIL-101, however, perox disappears and 1-one becomes the major product, suggesting that the framework and the sulfonic acid act in synergy for the conversion from perox to 1-one. Compared with PTSA + MIL-101, MIL-101-SO₃H leads to higher conversion, more dione and more diol. All in all, combining the Cr(III) and sulfonic sites in the MOF can significantly enhance the activity for cyclohexene oxidation. In particular, the bifunctional MOF promotes the oxidation through route B and also the further reactions in route A (the elimination reaction of perox to 1-one and the deeper oxidation of 1-one to dione). It could be because the framework provides an appropriate environment for synergistic action of the different catalytic sites. Interestingly, the promotion of route B by the sulfonic group is similar to the results reported recently for cyclohexene oxidation with H₂O₂ as oxidant and with Ti or Zr MOFs as catalyst, where the addition of an acid leads to significantly increased selectivity for route-B products



Fig. 2. Time-dependent conversion and product distribution for cyclohexene oxidation in N_2 (a, c) and O_2 (b, d) atmosphere (other conditions: 0.5 mmol cyclohexene, 5 mmol TBHP, 8 mg MIL-101-SO₃H (4 mol%), 40 °C, 14 h). (a) and (b) show the yields for individual products, and (c) and (d) show the total yields for the two different routes.

Table 4 Conversion of cyclohexene and yields of various oxidation products in N_2 and O_2 atmosphere.^a.

Atmosphere	Time (h)	Conv (%)	1-one (%)	dione (%)	epox (%)	diol (%)
dinitrogen	2	42	24 (7 ^b)	-	10	-
	4	81	57 (3 ^b)	4	14	3
	6	89	56	13	14	6
	10	97	46	30	9	12
	14	98	42	35	-	21
dioxygen	1	45	15(24 ^b)	-	6	-
	2	58	36 (11 ^b)	-	11	-
	4	88	54 (4 ^b)	11	13	6
	6	95	45	28	9	13
	10	98	33	41	9	15
	14	99	13	61	-	25
	$1 + 5^{c}$	61	22(32 ^b)	-	6	-

 a Reaction condition: cyclohexene (0.5 mmol), TBHP (5 mmol) with MIL-101-SO₃H (8 mg, 4 mol%) at 40 °C for 14 h. b 3-hydroperoxycyclohex-1-ene (perox) yield. c The catalyst was removed after 1 h, and the filtrate was analyzed after standing under the same conditions for 5 h.

[46,47].

The heterogeneous nature of the catalysis was examined by "hot" filtration tests. The solid catalyst was removed by filtration after the catalytic reaction proceeded for 1 h (conversion 45 %), and the filtrate was stirred under the same conditions as those before filtration. As can be seen Fig. 3, the conversion in the filtrate stirred for 5 h is only 60 %, which is much lower than the value (95 %, 6 h) without filtration. The small increase of conversion after filtration is consistent with the fact that the reaction can proceed slowly under catalyst-free conditions (Table 5, entry 1). The reaction after catalyst filtration only led to increased yields for perox and 1-one. No further conversion of cyclohexene to epox occurred, and no secondary products (dione and diol) were observed (Table 4, the last entry). These are also consistent with the data obtained for the catalyst-free reaction and indicate that the



Scheme 2. Control tests with the intermediates. (a) 1-one. (b) epox. Conditions: 0.5 mmol 1-one (or 0.1 mmol epox), 5 mmol TBHP (or 2.5 mmol H_2O , if used), 8 mg MIL-101-SO₃H (4 mol%, unless otherwise specified), 40 °C, 14 h.

catalyst is required for route B and the 1-one-to-dione conversion in route A. The results of the filtration tests support that the catalytic process is heterogenous, with the active sites in the solid.

On the basis of our experimental results and previous reports, the oxidation processes of cyclohexene over MIL-101-SO₃H can be tentatively proposed in Scheme 4. First, different radical species are generated from TBHP [4,48], which is promoted by Cr(III) centers (eqn 1–4). Dioxygen participates in the oxidation by reacting with *tert*-butyl hydroperoxide to generate *tert*-butyl peroxyl and hydroperoxyl radicals (eqn 4). The fact that dioxygen alone cannot oxidize cyclohexene suggests that it cannot generate oxidative radicals by itself. In route A,



Scheme 3. The influence of radical inhibitor BHT. (a) and (b) Oxidation of cyclohexene. (c) Reaction of epox. Conditions: 0.5 mmol cyclohexene or 0.1 mmol epox, 5 mmol TBHP, 8 mg MIL-101-SO₃H (4 mol%), 5 mmol BHT, 40 °C, 14 h.

 Table 5

 Comparison of different catalytic systems for cyclohexene oxidation.^a

Entry	Catalyst	Conv. (%)	perox (%)	1-one (%)	dione (%)	diol (%)
1	no catalyst	68	56	12	-	-
2	MIL-101	82	43	32	7	-
3	MIL-101-SO ₃ H	99	-	13	61	25
4	PTSA	49	36	7	-	6
5	MIL-101 + PTSA	84	-	64	14	6
6	MIL-101-SO ₃ Na	99	-	50	37	6(6 ^b)

 a Reaction conditions: cyclohexene (0.5 mmol), TBHP (5 mmol) with MIL-101-SO_3H (4 mol%, 8 mg) at 40 $^\circ$ C in oxygen atmosphere for 14 h. b yield of epox.



Fig. 3. Filtration test for cyclohexene oxidation (solid symbols for the reaction without filtration and open symbols for the reaction after filtering off the catalyst). Conditions: 0.5 mmol cyclohexene, 5 mmol TBHP, 8 mg MIL-101-SO₃H (4 mol%), 40 °C, O₂ atmosphere, 14 h.

hydrogen transfer from an α -C-H of cyclohexene to ROO· or RO· radicals generates the cyclohexenyl radical (I), which combines with the hydroperoxyl radical to give perox. According to some previous reports [49–51], the cyclohexenyl radical could react with *tert*-butyl peroxyl to produce 3-(*tert*-butylperoxy)cyclohexene, but the product was not detected in our system. Perox undergoes the elimination reaction to produce 1-one, which is catalyzed by synergetic action of sulfonic acid and Cr(III). The 1-one to dione transformation occurs through a radical mechanism similar to that for cyclohexene to 1-one. For route B, the *tert*-butyl peroxyl radical is added to the C=C bond to generate the intermediate 2-peroxide cyclohexyl radical (III), which undergoes fast ring-closing to give epox [52,53]. For the formation of diol, the common route is the ring-opening hydrolyzation of epox, through a well-established acid-catalyzed mechanism without involvement of radicals. However, as discussed above, the epox to diol conversion in the MIL-101-SO₃H/TBHP system is even more efficient than that in MIL-101-SO₃H/water, and the process should involve radicals. A tentative radical mechanism can be speculated as follows (Scheme 4). Attack of epox by the hydroxyl radicals leads to ring-opening, and then the intermediate radical (IV) undergoes hydrogen exchange with TBHP to give diol. Nevertheless, the contribution from the hydrolyzation mechanism cannot be precluded because water is an inevitable coproduct in the reaction system. It is possible that the two mechanisms coexist in the catalytic reaction.

On the basis of the mechanisms, the functions of the sulfonic group in MIL-101-SO₃H can be satisfactorily explained as follows. MIL-101 structures show interconnecting mesopores up to 29 and 34 Å (free internal diameters) with entrances up to 16 Å, while cyclohexene and its oxidation products are only 7-8 Å in their maximum dimension. It is reasonable to assume that the large and open pore system should set no limitation on internal diffusion of the small molecules [46]. The sulfonic group makes the pore surface more polar and hydrophilic than the "bare" surface of MIL-101 and thus facilitates adsorption and retention of the oxidant and various oxygenated intermediates within the pores through electrostatic interactions and hydrogen bonding. The fact that MIL-101-SO₃H, compared with MIL-101, gives enhanced selectivity for route B could be due to stabilization of the peroxide radical intermediate (III) by the interactions afforded by the sulfonic-functionalized surface. The relatively reduced total selectivity for route A could be because the first radical intermediate (I) of the route is non-oxygenic and not favored by the sulfonic group. The promotion effects of the sulfonic group on further transformations along route A can be justified as follows. Perox can be activated by hydrogen bonding with the sulfonic group in favor of the elimination transformation to 1-one; the sulfonic group can also help to keep 1-one inside the pore to facilitate further oxidation to dione. The hydrogen-bonding catalytic activity of the sulfonic group has also been demonstrated elsewhere for oxidation of olefins to diols, where, however, the oxidant and the catalyst are H₂O₂ and silica-supported sulfonic acid, respectively [54]. To further reveal the effects, the MOF with neutralized sulfonate groups (MIL-101-SO₃Na [55]) was also tested for the reaction (entry 6, Table 5). Compared with MIL-101-SO3H, the deprotonated catalyst led to lower conversion (12 %) through route B and also lower secondary conversions (1-one to dione, and epox to diol) for both routes. The results corroborate the assumption that -SO₃H promotes route B and the secondary conversions through the OH group, which can form hydrogen bonds with the oxygenated intermediates involved in route B and the secondary reactions. The hydrogen bonds are absent for MIL-101-SO₃Na to the disadvantage of route B and the secondary reactions. Nevertheless, compared with the "bare" MIL-101 (entry 2), MIL-101-SO₃Na is more active, leading to higher conversions for both routes and for the perox-to-1-one and 1-one-to-dione reactions. This indicates that the electrostatic interactions enhanced by the sulfonate group also play important roles in promoting the reactions. The sulfonate group may also form hydrogen bonds with the OH-containing species (such as perox and TBHP) in favor of the reactions.

Finally, the recyclability of the catalyst was tested. As can be seen from Table 6, the conversion of cyclohexene remains almost unchanged in the recycle runs, but the product selectivity changes. The yield of 1-one increases and those of dione and diol decrease in the recycle run compared to those in

the preceding run, along with increasing total selectivity for route A relative to route B. The XRD, IR and N₂ adsorption for the used catalyst are compared with those for the fresh catalyst (Fig. 1). There are no essential changes in IR absorption, including the bands characteristic of the sulfonic group, so the chemical integrity of the material is retained. The XRD profiles are similar on the whole, but the used catalyst shows slightly decreased reflection intensity. The N₂ adsorption capacity decreases after use, and the surface area changes from 1603 to 1291 m²/g. According to ICP analysis with the supernatant obtained by filtering off



Scheme 4. Proposed reaction pathways of MIL-101-SO₃H catalyzed cyclohexene oxidation.

 Table 6

 Recycle tests of MIL-101-SO₃H catalyzed cyclohexene oxidation.^a.

Number of cycles	Conv. (%)	1-one (%)	dione (%)	epox (%)	diol (%)
1	99	13	61	-	25
2	99	29	49	10	11
3	97	52	34	8	3

 a Reaction condition: cyclohexene (0.5 mmol), TBHP (5 mmol) with MIL-101-SO_3H (8 mg, 4 mol%) at 40 $^\circ C$ for 14 h.

the catalyst, the amount of leached Cr(III) after one cycle accounts for 1.9 % of the total Cr(III) content in the catalyst. It is unlikely that the insignificant leaching can cause the obvious changes in catalytic properties. The XRD and N_2 adsorption data indicate that the porous MOF undergoes some degree of structural degradation, which could be responsible for the changes in catalytic properties. The details are open to further investigation.

4. Conclusions

In this study, MIL-101-SO₃H was demonstrated as a bifunctional catalyst for oxidation of cyclohexene. The catalytic oxidation proceeds through two independent routes to give various oxygenated products: perox (intermediate at early stage of the reaction), 1-one, dione, and even benzoquinone (at higher temperature) for route A; epox (at early stage) and diol for route B. Molecular oxygen is inactive if used alone, but it does act as supplementary oxidant cooperating with TBHP to accelerate the oxidation of cyclohexene to 1-one and further to dione. The sulfonic group and the Cr(III) framework behave in a complementary and collaborative way, so the oxidation processes and product distribution over the bifunctional MOF are very different from those over MIL-101. On the one hand, the Cr(III) framework promotes the oxidation to perox and 1-one in route A. On the other hand, the sulfonic group acts in synergy with the framework to enhance the conversion to diol (route B) and the further conversions in route A (from perox to 1-one and further to dione). This is the first time to demonstrate the bifunctional catalysis of sulfonic-containing MOFs for oxidation of olefins.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal

relationships which may be considered as potential competing interests:

CRediT authorship contribution statement

Weng-Jie Sun: Formal analysis, Investigation, Validation, Writing - original draft, Writing - review & editing. En-Qing Gao: Conceptualization, Methodology, Formal analysis, Funding acquisition.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (NSFC No. 21773070).

References

- [1] H. Sun, Y. Pan, S. Li, Y. Zhang, Y. Dong, S. Liu, Z. Liu, J. Energy Chem. 22 (2013) 710–716.
- [2] S. Liu, Z. Liu, S. Zhao, Y. Wu, Z. Wang, P. Yuan, J. Nat. Gas Chem. 15 (2006) 319–326.
- [3] Y. Cao, H. Yu, H. Wang, F. Peng, Catal. Commun. 88 (2017) 99-103.
- [4] Y. Cao, H. Yu, F. Peng, H. Wang, ACS Catal. 4 (2014) 1617–1625.
- [5] C. Li, Y. Zhao, T. Zhu, Yg. Li, J. Ruan, G. Li, RSC Adv. 8 (2018) 14870-14878.
- [6] H. Cao, B. Zhu, Y. Yang, L. Xu, L. Yu, Q. Xu, Chin. J. Catal. 39 (2018) 899-907.
- [7] R.A. Moretti, J. Du Bois, T.D. Stack, Org. Lett. 18 (2016) 2528–2531.
 [8] L. Li, S. Huang, J. Song, N. Yang, J. Liu, Y. Chen, Y. Sun, R. Jin, Y. Zhu, Nano Res. 9 (2016) 1182–1192.
- [9] G. Yang, H. Du, J. Liu, Z. Zhou, X. Hu, Z. Zhang, Green Chem. 19 (2017) 675–681.
 [10] T. Zhang, Y.O. Hu, T. Han, Y.O. Zhai, Y.Z. Zheng, ACS Appl. Mater. Interfaces 10
- (2018) 15786–15792.
- [11] A. Bhattacharjee, T. Das, H. Uyama, P. Roy, M. Nandi, ChemistrySelect 2 (2017) 10157–10166.
- [12] P. Daw, R. Petakamsetty, A. Sarbajna, S. Laha, R. Ramapanicker, J.K. Bera, J. Am. Chem. Soc. 136 (2014) 13987–13990.
- [13] N. Pal, E.B. Cho, D. Kim, C. Gunathilake, M. Jaroniec, Chem. Eng. J. 262 (2015) 1116–1125.
- [14] P. Zhang, Y. Wang, J. Yao, C. Wang, C. Yan, M. Antonietti, H. Li, Adv. Synth. Catal. 353 (2011) 1447–1451.
- [15] G.Y. Liu, R.R. Tang, Z. Wang, Catal. Lett. 144 (2014) 717-722.
- [16] F. Jin, C.C. Chang, C.W. Yang, J.F. Lee, L.Y. Jang, S. Cheng, J. Mater. Chem. A 3 (2015) 8715–8724.
- [17] J.C. Wang, Y.H. Hu, G.J. Chen, Y.B. Dong, Chem. Commun. 52 (2016) 13116–13119.
- [18] H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, Science 341 (2013) 974.
 [19] M. Wriedt, J.P. Sculley, A.A. Yakovenko, Y. Ma, G.J. Halder, P.B. Balbuena,
- H.C. Zhou, Angew. Chem. Int. Ed 51 (2012) 9804–9808.
- [20] J. Zhou, H. Li, H. Zhang, H. Li, W. Shi, P. Cheng, Adv. Mater. 27 (2015) 7072–7077.
- [21] Y. Liu, Z. Liu, D. Huang, M. Cheng, G. Zeng, C. Lai, C. Zhang, C. Zhou, W. Wang, D. Jiang, H. Wang, B. Shao, Coord. Chem. Rev. 388 (2019) 63–78.
- [22] M. Tonigold, Y. Lu, B. Bredenkotter, B. Rieger, S. Bahmuller, J. Hitzbleck,
- G. Langstein, D. Volkmer, Angew. Chem. Int. Ed 48 (2009) 7546–7550. [23] K. Leus, I. Muylaert, M. Vandichel, G.B. Marin, M. Waroquier, V. Van Speybroeck,
- P. Van der Voort, Chem. Commun. 46 (2010) 5085–5087.[24] N.V. Maksimchuk, K.A. Kovalenko, V.P. Fedin, O.A. Kholdeeva, Adv. Synth. Catal.
- 352 (2010) 2943–2948.
- [25] D. Ruano, M. Díaz-García, A. Alfayate, M. Sánchez-Sánchez, ChemCatChem 7

(2015) 674-681.

- [26] X. Zhang, N.A. Vermeulen, Z. Huang, Y. Cui, J. Liu, M.D. Krzyaniak, Z. Li, H. Noh, M.R. Wasielewski, M. Delferro, O.K. Farha, ACS Appl. Mater. Interfaces 10 (2018) 635-641.
- H. Noh, Y. Cui, A.W. Peters, D.R. Pahls, M.A. Ortuno, N.A. Vermeulen, C.J. Cramer, [27] L. Gagliardi, J.T. Hupp, O.K. Farha, J. Am. Chem. Soc. 138 (2016) 14720-14726.
- [28] N. Maksimchuk, M. Timofeeva, M. Melgunov, A. Shmakov, Y. Chesalov, D. Dybtsev, V. Fedin, O. Kholdeeva, J. Catal. 257 (2008) 315-323.
- N.V. Maksimchuk, K.A. Kovalenko, S.S. Arzumanov, Y.A. Chesalov, M.S. Melgunov, [29] A.G. Stepanov, V.P. Fedin, O.A. Kholdeeva, Inorg. Chem. 49 (2010) 2920-2930.
- [30] S. Abednatanzi, A. Abbasi, M. Masteri-Farahani, J. Mol. Catal. A: Chem. 399 (2015) 10-17.
- [31] S. Ahn, N.E. Thornburg, Z. Li, T.C. Wang, L.C. Gallington, K.W. Chapman,
- J.M. Notestein, J.T. Hupp, O.K. Farha, Inorg. Chem. 55 (2016) 11954-11961. [32] K. Leus, G. Vanhaelewyn, T. Bogaerts, Y.-Y. Liu, D. Esquivel, F. Callens, G.B. Marin, V. Van Speybroeck, H. Vrielinck, P. Van Der Voort, Catal. Today 208 (2013) 97-105.
- [33] G. Akiyama, R. Matsuda, H. Sato, M. Takata, S. Kitagawa, Adv. Mater. 23 (2011) 3294-3297
- [34] Y.X. Zhou, Y.Z. Chen, Y. Hu, G. Huang, S.H. Yu, H.L. Jiang, Chem. Eur. J. 20 (2014) 14976-14980.
- [35] L. Ma, L. Xu, H. Jiang, X. Yuan, RSC Adv. 9 (2019) 5692-5700.
- [36] M.G. Goesten, J. Juan-Alcañiz, E.V. Ramos-Fernandez, K.B. Sai Sankar Gupta,
- E. Stavitski, H. van Bekkum, J. Gascon, F. Kapteijn, J. Catal. 281 (2011) 177-187. [37] J. Juan-Alcañiz, R. Gielisse, A.B. Lago, E.V. Ramos-Fernandez, P. Serra-Crespo, T. Devic, N. Guillou, C. Serre, F. Kapteijn, J. Gascon, Catal. Sci. Technol. 3 (2013)
- 2311. [38] A. Chatterjee, X. Hu, F.L.-Y. Lam, Appl. Catal. A 566 (2018) 130-139.
- [39] X. Liu, C.M. Friend, Langmuir 26 (2010) 16552-16557.

- Molecular Catalysis 482 (2020) 110746
- [40] P. Chotmongkolsap, T. Bunchuay, W. Klysubun, J. Tantirungrotechai, Eur. J. Inorg. Chem. 2018 (2018) 703-712.
- [41] T. Bunchuay, R. Ketkaew, P. Chotmongkolsap, T. Chutimasakul, J. Kanarat, Y. Tantirungrotechai, J. Tantirungrotechai, Catal. Sci. Technol. 7 (2017) 6069-6079.
- [42] S. Mukherjee, S. Samanta, A. Bhaumik, B. Ray, Appl. Catal. B 68 (2006) 12-20.
- [43] M. Guidotti, C. Pirovano, N. Ravasio, B. Lázaro, J.M. Fraile, J.A. Mayoral, B. Coq, A. Galarneau, Green Chem. 11 (2009) 1421-1427.
- I.Y. Skobelev, A.B. Sorokin, K.A. Kovalenko, V.P. Fedin, O.A. Kholdeeva, J. Catal. [44] 298 (2013) 61-69.
- [45] C. Antonetti, A.M.R. Galletti, P. Accorinti, S. Alini, P. Babini, K. Raabova E. Rozhko, A. Caldarelli, P. Righi, F. Cavani, P. Concepcion, Appl. Catal. A 466 (2013) 21-31.
- [46] N. Maksimchuk, J. Lee, A. Ayupov, J.-S. Chang, O. Kholdeeva, Catalysts 9 (2019) 324/321-324/314.
- [47] N.V. Maksimchuk, J.S. Lee, M.V. Solovyeva, K.H. Cho, A.N. Shmakov, Y.A. Chesalov, J.-S. Chang, O.A. Kholdeeva, ACS Catal. 9 (2019) 9699-9704.
- [48] U. Neuenschwander, F. Guignard, I. Hermans, ChemSusChem 3 (2010) 75-84.
- [49] B. Govinda Rao, P. Sudarsanam, P.R.G. Nallappareddy, M. Yugandhar Reddy,
- T. Venkateshwar Rao, B.M. Reddy, Catal. Commun. 101 (2017) 57-61. [50] X. Li, D. Ma, B. Cao, Y. Lu, New J. Chem. 41 (2017) 11619-11625.
- [51] Q.X. Luo, M. Ji, S.E. Park, C. Hao, Y.-Q. Li, RSC Adv. 6 (2016) 33048-33054. [52] W. Nam, H.J. Kim, S.H. Kim, R.Y.N. Ho, J.S. Valentine, Inorg. Chem. 35 (1996) 1045-1049
- [53] A. Agarwala, D. Bandyopadhyay, Catal. Lett. 124 (2008) 256-261.
- [54] R. Maggi, G. Martra, C.G. Piscopo, G. Alberto, G. Sartori, J. Catal. 294 (2012) 19-28.
- [55] Y. Gu, C. Ogawa, J. Kobayashi, Y. Mori, S. Kobayashi, Angew. Chem., Int. Ed 45 (2006) 7217-7220.