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Merging *N*-hydroxyphthalimide into Metal−Organic Frameworks for Highly Efficient and Environmentally Benign Aerobic Oxidation

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Abstract: Two highly efficient metal−organic framework catalysts TJU-68-NHPI and TJU-68-NDHPI have been successfully synthesized through solvothermal reactions of which the frameworks are merged with *N*-hydroxyphthalimide (NHPI) units for the first time, resulting in the decoration of pore surfaces with highly active nitroxyl catalytic sites. When *t*-butyl nitrite (TBN) is used as co-catalyst, the as synthesized MOFs are demonstrated to be highly efficient and recyclable catalysts for a novel three-phase heterogeneous oxidation of activated C−H bond of primary, secondary alcohols and benzyl compounds under mild conditions. Based on the high efficiency and selectivity, an environmental benign system with good sustainability, mild condition, simple work-up procedure has been established for practical oxidation of a wide range of substrates.

Introduction

Oxidation, as one of the two most significant subjects in chemistry, has always been attracting great research interests due to the ubiquitous involving in the reactions. Initially the catalytic oxidation was developed with little environment and economy concerns using toxic or noble metals, corrosive protic acids, stoichiometric noxious oxidants and hazardous solvents, etc.[1] After the pioneering research was reported by Sharpless, *et al*. in 1976 using the noble Ru catalyst and amine-N-oxides to catalyze very efficient oxidation of various alcohols in mild condition,[2] significant progresses were made in the next few decades to develop environmentally benign catalytic oxidation systems such as using H_2O as solvent.[3] Except for the concerns over catalysts, solvents and reaction conditions, developing heterogeneous reaction system is very crucial for practical applications in virtue of the tedious purification process resulting from homogeneous reactions generally featuring high cost, undue energy consumption and challenges for complete removal of hazardous metal residuals. The heterogeneous systems can render simple filtration to the work-up procedure not only for facile separation of the product from the reaction mixture but also to collect the solid catalyst for recycling, which is essential to develop ideal catalytic systems.[4-8]

As a kind of new soft porous crystalline solid, Metal−Organic Frameworks (MOFs), also known as porous coordination polymers (PCPs),[9] have been emerging and booming in both the fundamental and application researches because of their enormous diversity in structures and functionalities.[10-18] MOFs have been considered and proved to be the most promising materials for building up ideal catalysts due to their characteristics mainly in four aspects,[19-22] i.e., heterogeneous nature for facile work-up process, large porosity facilitating diffusion of the substrates to render high efficiency, incorporation of metal and organic ligand in one single system with the confinement effect for elevated activity, and strong designability and functionalizability for specific catalysis such as size and shape selectivity.[23-29] Based on these concepts, we have developed a new free-radical decorated MOF (FRMOF) assembling from the copper and aminoxyl radical fused ligand [4,7-bis(4-pyridyl)-1,1,3,3-tetramethylisoindolin-2-yloxyl (DPIO)], which indeed showed prominent performance for highly efficient and selective oxidation of various alcohols.[23] However, the synthesis of DPIO is rather onerous with the usage of a large amount of oleum and bromine etc., yet only 9.3% total yield could be achieved.

Instead of the stable aminoxyl type radicals of which the classic representative is 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO), another kind of even more superb radicals are imidoxyl type, and the representative is phthalimido *N*-oxyl (PINO) which is not isolable at ambient temperature but can be readily generated from the stable organic molecule *N*-hydroxyphthalimide (NHPI).[30-31] Compared with the TEMPO, the synthesis of NHPI is much easier *via* one step condensation reaction of the very cheap *o*-phthalic anhydride and hydroxylamine, and the NHPI possesses higher oxidation capability.[32] Moreover, the catalytic mechanism studies have demonstrated that the key catalytic species of the TEMPO involved reaction is the oxoammonium salt while in the reactions of NHPI as catalyst the catalysis is dominated by hydrogen abstracting from C–H bonds *via* the generated active PINO intermediate.[32-36] In practical applications, NHPI has hitherto achieved excellent catalytic oxidation performance such as photocatalysis and electrocatalysis.[37-53] In order to avoid the disadvantage of NHPI as homogeneous catalyst, greener heterogeneous catalytic systems have been developed by immobilization or confinement of NHPI molecules into MOFs (solid catalysts) but suffered from the potential pore blocking, NHPI leaching and harsh catalytic condition problems.[54-60] Compared with the catalysts synthesized by simple NHPI wet-loading methods or NHPI anchored to the surface of the solid catalysts by chemical bonding, MOFs constructed by NHPI functionalized ligands ensure the high-density and regular distribution of catalytic sites as well as sufficient channel space for smooth diffusion of the reactants that provide an ideal platform for innovation of green, efficient and heterogeneous oxidation catalysts.

Herein, two Zr−based MOFs incorporated with new organic ligands functionalized with NHPI units have been successfully synthesized for the first time (Scheme 1 and Figure 1). The as-synthesized MOFs featuring high surface areas, good stability, uniform pores and highly dense organo-catalytic sites render us a green catalytic system for cost-effective, highly efficient and superior recyclable aerobic oxidations of various activated C−H compounds under mild conditions.

Results and Discussion

Synthesis and Characterization

Development of general method to merge the NHPI unit into the organic ligand is of great significance because it will pave the way for versatile functional materials covalently modified by the critical imidoxyl (INO) radicals. However in view of the synthetic route design it is very challenging to synthesize the ligands H_2L_{NOH} (with one NHPI group) and H_2L_{2NOH} (with two NHPI groups), since highly selective condensation of the hydroxylamine with carboxylic acid or anhydride is difficult and the general low solubility of the ligands with imide and carboxylic acid groups makes the purification formidable (Scheme 1 and Figure 1). Tremendous efforts have been devoted to the traditional strategies such as *N*-hydroxyl group protection and de-protection but all failed. Surprisingly, a straightforward condensation of the hydroxylamine with the corresponding tetracarboxylic acid compound **12** or hexacarboxylic acid compound **15** afforded the target compounds H_2L_{NOH} and H_2L_{2NOH} in 95.4% and 92.3% yields respectively (Scheme 1, S1 and S2, see the Supporting Information). Moreover, as shown in Scheme 1, only through three key steps of simple organic reactions including Suzuki−Miyaura coupling for multi-methyl substituted *p*-terphenyl **11** and **14**, subsequent $KMnO_4$ oxidation to its multi-carboxylic acids **12** and **15**, and selective condensation to the targets, the total yields of H_2L_{NOH} and H_2L_{2NOH} can achieve 78.6% and 64.4% respectively without necessitating the synthesis of phthalic anhydride intermediates, of which not only the synthesis is difficult but also the purification is laborious (see the Supporting Information). After the ligands were synthesized in gram scales, in consideration of the outstanding stability of UiO (Univeristy of Olso) MOFs the optimal solvothermal reaction conditions using these ligands to synthesize the corresponding UiO MOFs were screened out.[61] It was found that although the solvothermal reactions in the presence of modulator acetic acid at elevated temperature higher (e.g., 100 °C) could result in highly crystalline UiO MOFs, the pre-functionalized NHPI groups on MOF linkers were partially hydrolyzed which could be verified by NMR spectra of the HF digested samples (Figure S1). After a number of trials, the TJU-68-NHPI with intact NHPI groups could be synthesized by the solvothermal reaction of H_2L_{NOH} ligand with $ZrCl_4$ and acetic acid under 80 °C, while the

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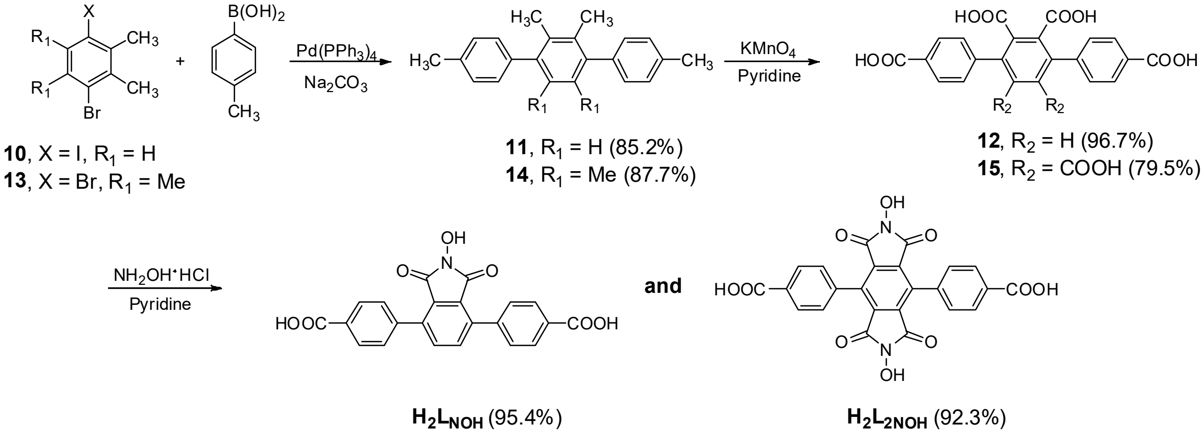
TJU-68-NDHPI with little hydrolyzed imide *N*-hydroxyl (INOH) groups could be only prepared by H_2L_{2NOH} ligand in the presence of benzoic acid modulator through a specific programmed temperature process (Figure 1a–b, and the Supporting Information).[62-63] Powder X−ray diffraction (PXRD) patterns of the as-synthesized TJU-68-NHPI and TJU-68-NDHPI are in good agreement with that of the simulated UiO-68 from single-crystal data, suggesting their high phase purity.[64] Both of the activated TJU-68 MOFs are liable to gradually lose the crystallinity intensity when exposed in the air moisture accompanied by color change from white to yellow, but they are very stable in common organic solvents such as acetonitrile and dichloromethane (Figure 1c–d).



Scheme 1. Synthetic scheme of ligand H_2L_{NOH} and H_2L_{2NOH}.

As shown in the Scanning Electron Microscopy (SEM) imagines, the TJU-68-NHPI and TJU-68-NDHPI crystals feature very regular octahedron shapes with uniform particle sizes of *ca.* 20 μm and 0.50 μm, respectively (Figure 1e–f). Based on these unambiguous characterizations the essential difference of TJU-68 to UiO-68 MOFs is the central phenyl group of the ligand modified by one or two INOH groups at the molecular level.[64] Due to the features of the organic linkers, the precursors of PINO free radical are periodically integrated onto the pore surface of the TJU-68 MOFs. It is worth mentioning that this approach will give inspiration for conceiving of multifunctional MOFs bearing high-density active catalytic sites for sensing, catalysis and energy storage, etc.

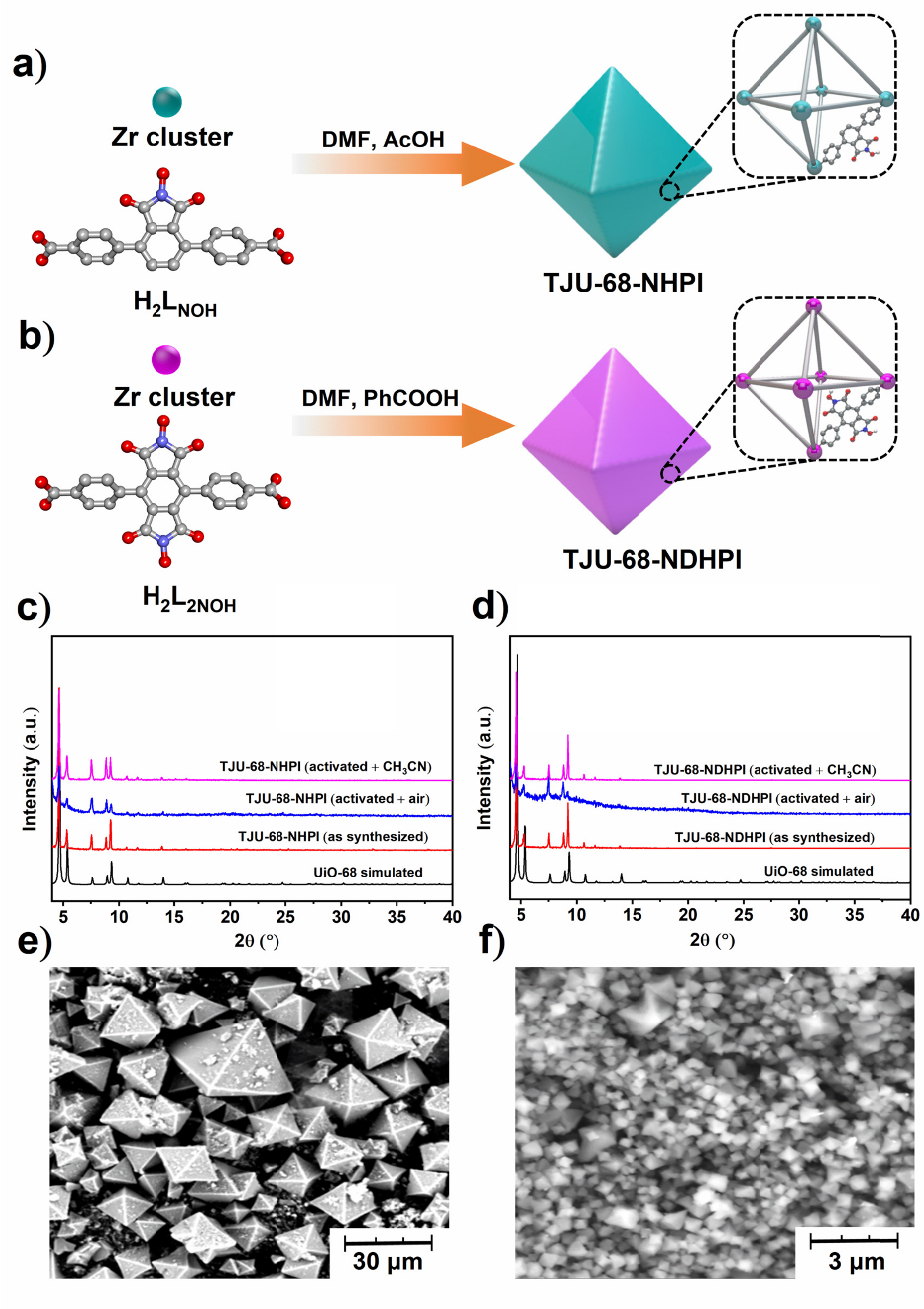


Figure 1. Synthetic scheme of (a) TJU-68-NHPI and (b) TJU-68-NDHPI. (O, red; C, gray; N,

blue; H atoms have been omitted). PXRD patterns of (c) TJU-68-NHPI and (d) TJU-68-NDHPI. Simulated from the UiO-68 (black), as synthesized sample (red), activated by drying under vacuum at 120 °C for 12 h (blue), re-soaked in CH_3CN after the activation (purple). SEM images of (e) TJU-68-NHPI and (f) TJU-68-NDHPI.

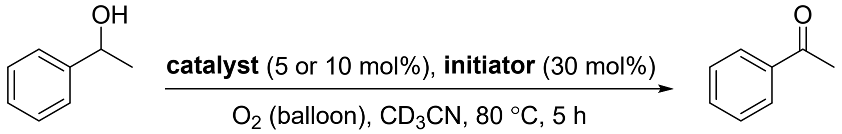
In order to investigate the porosity of activated TJU-68-NHPI and TJU-68-NDHPI, gas sorption studies of N_2 and CO_2 were conducted at different temperatures (Figure S2a–b). For compounds TJU-68-NHPI and TJU-68-NDHPI, the N_2 adsorption isotherms manifest type I with high uptake at low pressure and little hysteresis, indicating the robustness and no strong interactions between the N_2 gas molecules and porous frameworks.[65] The Brunauer−Emmett−Teller (BET) surface areas of TJU-68-NHPI and TJU-68-NDNPI calculated from the N_2 adsorption isotherms are 2558 $m^2\ g^{-1}$ and 1470 $m^2\ g^{-1}$ respectively, appreciably decreasing from that of the UiO-68 (without INOH functionalization, 4240 $m^2\ g^{-1}$).[66] In addition, the pore volumes of TJU-68-NHPI and TJU-68-NDHPI are calculated to be 0.9741 $cm^3\ g^{-1}$ and 0.5996 $cm^3\ g^{-1}$ respectively, which also decrease drastically from that of UiO-68 (1.82 $cm^3\ g^{-1}$)[66], attributed to the densely functionalized INOH groups and futher proving the success of this bottom-up functionalization strategy.

Catalytic Performance Tests

The ideal porous structure with high density of accessible organocatalytic sites decorated on the pore surface and good stability of the TJU-68 MOFs encouraged us to employ them as heterogeneous catalysts for oxidation reactions. At first, we choose 1-phenylethanol as the model substrate to screen the optimal reaction condition by changing the additives/initiators and solvents (Table S1). Without the initiators the oxidation could not proceed under O_2

atmosphere, indicating that the NHPI groups on MOF frameworks could not be directly activated by the molecular O_2 to generate PNIO radicals for oxidation. By addition of various inorganic and organic initiators including $Co(OAc)_2$, $Mn(OAc)_2$, $Co(NO_3)_2$, $Cu(OAc)_2$ and dimethylglyoxime (DMG), the catalytic reactions gave trace to low yields of the acetophenone product, which might be attributed to their very slow accessing to the INOH functional sites. However, facilitated by AIBN additive 52% and 76% moderate yields were achieved. The yields were further improved to be quantitative when 30 mol% of *t*-butyl nitrite (TBN) was used. Not only that, the low boiling point and high volatility (i.e., easy removability) of the TBN and resultant degraded product *t*-butyl alcohol could make the work-up procedure straightforward and eco-friendly.[67] And then, with the TBN as initiator various common solvents were tested and the relatively green solvent acetonitrile was found to be optimal (Table S1 and Table 1, entry 1). Finally, the oxidants were examined by using atmospheric air, pure oxygen and nitrogen gas, affording moderate (63%, 68%), quantitative and trace amount of the product respectively, which prove that oxygen gas is the terminal oxidation source (Table 1, entries 1−3). It is worth mentioning that using 5 mol% of the TJU-68-NDHPI possessing twice of the catalytic site density exhibited similar high efficiency compared with that of using 10 mol% of the TJU-68-NHPI catalyst, suggesting the density of the catalytic site is appropriately proportional to the catalytic efficiency in this heterogeneous system (Table 1, entries 1−2). The reaction in the absence of MOF catalyst afforded 8% yield induced by TBN (Table 1, entry 4). The attempts to a homogeneous catalysis by the ligands led low yields (42% and 36%) probably attributed to the insufficient solubility of the H_2L_{NOH} and H_2L_{2NOH} in acetonitrile (Table 1, entry 5). In addition, to evaluate the effect of Zr metal, catalytic reactions in the presence of ligand and $ZrCl_4$ were performed to give a complex mixture with the yields of target acetophenone in 76% and 82%, respectively, further indicating the superiority of MOF catalysts (Table 1, entry 6 and Figure S3). Based on the above screening experiments, the optimal condition for this heterogeneously catalytic system is that 10 mol% of TJU-68-NHPI or 5 mol% of TJU-68-NDHPI with 30 mol% TBN under the atmospheric pressure of O_2 gas in acetonitrile at 80 °C for 5 h.

Table 1. Catalytic Oxidation of 1a with difference initiators.[a]



Entry	Initiator	Catalyst	Yield[b] (%)
1	TBN	TJU-68-NHPI	99
		TJU-68-NDHPI	99
2[c]	TBN	TJU-68-NHPI	63
		TJU-68-NDHPI	68
3[d]	TBN	TJU-68-NHPI	Trace
		TJU-68-NDHPI	Trace
4	TBN	/	8
5[e]	TBN	H_2L_{NOH}	42
		H_2L_{2NOH}	36
6[f]	TBN	$H_2L_{NOH} + ZrCl_4$	76
		$H_2L_{2NOH} + ZrCl_4$	82

[a] Reaction conditions: 0.5 mL CD_3CN, 0.075 mmol 1-phenylethanol, TJU-68-NHPI (10 mol%)/TBN (30 mol%) or TJU-68-NDHPI (5 mol%)/TBN (30 mol%). [b] Determined by ^{1}H NMR spectroscopy and GC−MS using nitrobenzene or naphthalene as internal standard. [c] Reaction carried out under air. [d] Reaction carried out under nitrogen. [e] Reaction conditions: 0.5 mL CD_3CN, 0.075 mmol 1-phenylethanol, H_2L_{NOH} (10 mol%)/TBN (30 mol%) or H_2L_{2NOH} (5 mol%)/TBN (30 mol%). [f] Reaction conditions: 0.5 mL CD_3CN, 0.075 mmol 1-phenylethanol, H_2L_{NOH} (10 mol%)/$ZrCl_4$ (10%)/TBN (30 mol%) or H_2L_{2NOH} (5 mol%)/$ZrCl_4$ (5%)/TBN (30 mol%).

Under the optimized reaction condition a broad scope of secondary alcohols have been explored and oxidized to the corresponding ketone products (Table 2). Notably, a series of substituted secondary alcohols containing aromatic and aliphatic alcohols can be successfully oxidized by TJU-68 MOFs to desired products with excellent yields (92% − 100%, Table 2, entries 1−16). The longer or cyclic alkyl chains make the oxidation of benzylic alcohols slightly adverse. However excellent yields (95% − 99%) can still be obtained by prolonging the reaction time to 5 h (Table 2, entries 1−4). On the basis of quantitative yields of the corresponding ketones, the reaction times of phenyl secondary alcohols substituted with electron-donating groups are shorter than that of electron-withdrawing group substituted ones (3 h *vs* 4 h, Table 2, entries 5−8). The extended π−conjugation all enable the oxidation reactions to accomplish in shorter times (Table 2, entries 9−10). It is notable that the diphenylethanediol **1k** featuring diol groups smoothly underwent the bis-oxidation to the benzil **2k** in 95% and 92% yields respectively, necessitating reaction times over 10 h (entry 11). A variety of other linear or cyclic aliphatic secondary alcohols can also be oxidized to the

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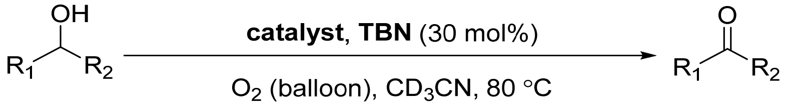
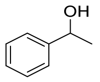
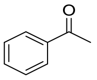
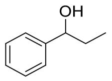
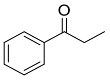
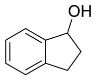
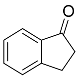
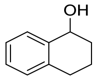
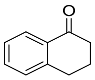
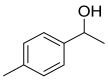
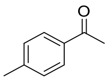
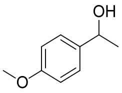
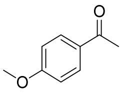
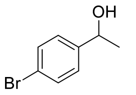
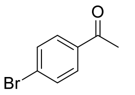
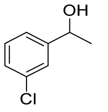
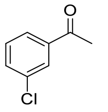
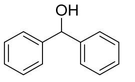
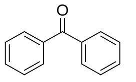
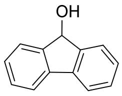
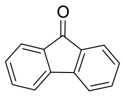
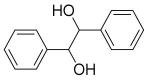
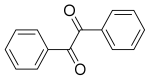
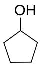
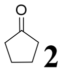
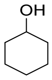
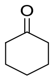
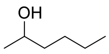
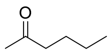
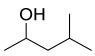
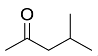
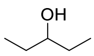
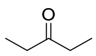
corresponding ketones in longer reaction times (8 h or 10 h), affording very good yields (Table 2, entries 12−16). Strikingly, the oxidation of secondary alcohols by this TJU-68 MOFs system reveals broad substrate applicability, excellent yield, outstanding selectivity and much higher efficiency compared with previously documented MOF catalytic oxidation systems, which generally demand much longer reaction time with lower conversion efficiency.[68-69]

Table 2. TJU-68-NHPI (TJU-68-NDHPI) Catalyzed Oxidation of the Secondary Alcohols.[a]



1 **2**

Entry	Alcohol	Product	Catalyst	Time (h)	Yield[b] (%)
1	 **1a**	 **2a**	TJU-68-NHPI	4	99
			TJU-68-NDHPI	4	99
2	 **1b**	 **2b**	TJU-68-NHPI	4	98
			TJU-68-NDHPI	4	97
3	 **1c**	 **2c**	TJU-68-NHPI	5	96
			TJU-68-NDHPI	5	95
4	 **1d**	 **2d**	TJU-68-NHPI	5	97
			TJU-68-NDHPI	5	95
5	 **1e**	 **2e**	TJU-68-NHPI	3	99
			TJU-68-NDHPI	3	99
6	 **1f**	 **2f**	TJU-68-NHPI	3	99
			TJU-68-NDHPI	3	99

7	 **1g**	 **2g**	TJU-68-NHPI	4	100
			TJU-68-NDHPI	4	100
8	 **1h**	 **2h**	TJU-68-NHPI	4	100
			TJU-68-NDHPI	4	100
9	 **1i**	 **2i**	TJU-68-NHPI	4	98
			TJU-68-NDHPI	4	99
10	 **1j**	 **2j**	TJU-68-NHPI	3	98
			TJU-68-NDHPI	3	97
11	 **1k**	 **2k**	TJU-68-NHPI	12	95
			TJU-68-NDHPI	10	92
12	 **1l**	 **2l**	TJU-68-NHPI	10	92
			TJU-68-NDHPI	10	94
13	 **1m**	 **2m**	TJU-68-NHPI	8	89
			TJU-68-NDHPI	8	92
14	 **1n**	 **2n**	TJU-68-NHPI	8	95
			TJU-68-NDHPI	8	90
15	 **1o**	 **2o**	TJU-68-NHPI	8	94
			TJU-68-NDHPI	8	93
16	 **1p**	 **2p**	TJU-68-NHPI	8	97
			TJU-68-NDHPI	8	98

[a] Reaction conditions: 0.5 mL CD_3CN, 0.25 mmol alcohol, TJU-68-NHPI (10 mol%)/TBN (30 mol%) or TJU-68-NDHPI (5 mol%)/TBN (30 mol%). [b] Determined by ^{1}H NMR

spectroscopy and GC−MS using nitrobenzene or naphthalene as internal standard.

Furthermore, the primary benzyl alcohols can also be oxidized efficiently by this catalytic system. As shown in Table 3, all the oxidations catalyzed by TJU-68-NHPI achieved very high conversion with good to excellent selectivity. It was found that aromatic primary alcohols regardless of the electron-donating and electron-withdrawing substituents are oxidized to the corresponding aldehydes as the major products and the carboxylic acid as the minor products (Table 3). Neither decreasing the reaction temperature nor increasing the catalyst and TBN amounts gave improved selectivity to the aldehyde or acid product. However, the higher electron-donating ability of the substituents, the alcohol substrates is more propitious to be oxidized to the carboxylic acid products. The trimethoxybenzyl alcohol **3d** could be completely oxidized to give 43% of acid product **5d** (Table 3, entry 4). The oxidation of the substrates with electron-withdrawing groups (i.e., NO_2, F, Cl, Br, I) always leads to excellent conversion, however it is not inevitable that the stronger the electron-withdrawing ability of the substrates, the higher the selectivity of conversion to carboxylic acid products (Table 3, entries 5−10). The nitro substituted benzyl alcohol **3e** was oxidized in high conversion of 98% and selectivity of 89% to the aldehyde **4e** (Table 3, entry 5), whereas the strong electron-withdrawing group fluoro substituted benzyl alcohol **3f** was oxidized in 99% conversion with low selectivity of 50% to the acid **5f** (Table 3, entry 6). The oxidation of furan-2-ylmethanol **3l** resulted in a moderate conversion of 76% with supreme selectivity of 99% to the aldehyde **4l** (Table 3, entry 12). The thiophen-2-ylmethanol **3m** was readily oxidized in 99% conversion to 84% yield of the aldehyde **4m** and 16% yield of the acid **5m** (Table 3, entry 13). In addition, the chemo-selectivity of this oxidation system was

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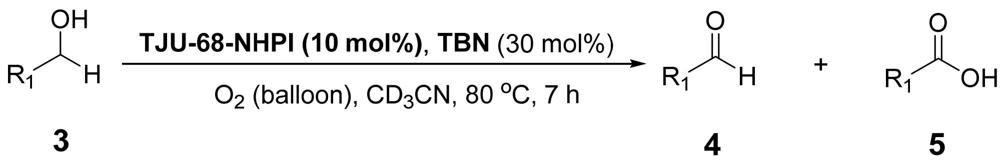
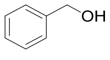
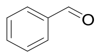
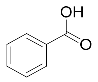
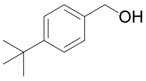
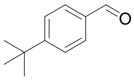
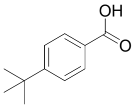
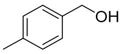
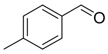
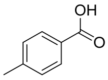
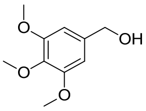
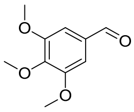
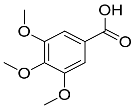
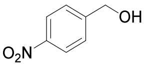
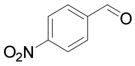
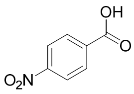
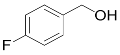
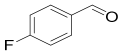
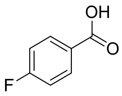
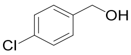
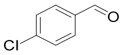
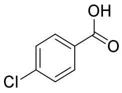
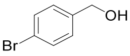
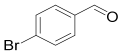
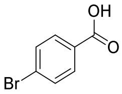
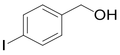
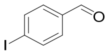
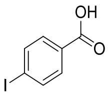
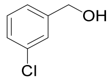
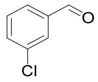
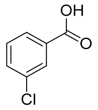
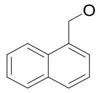
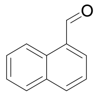
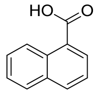
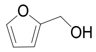
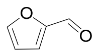
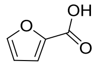
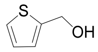
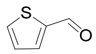
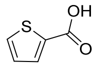
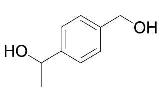
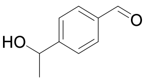
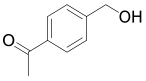
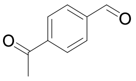
investigated by **3n** with primary and secondary alcohol groups, and the results revealed that the primary alcohol was more easily oxidized than the secondary alcohols (43% vs 32%, Table 3, entry 14). Albeit the reaction conditions were desperately optimized by prolonging the reaction time, decreasing the dosage of the catalyst and additive, etc., the oxidation of primary alcohols to achieve excellent conversion as well as selectivity was elusive because the degree of the oxidation strongly depends on the oxidation capability of the catalytic systems. Compared with the homogeneous oxidation catalyzed by NHPI which can only oxidize the primary benzyl alcohols to the aldehydes, our heterogeneous oxidation systems exhibited higher oxidation capability to partly over-oxidize them to the corresponding acids, probably due to the confinement effect of the TJU-68 MOFs.[38] Base on the same INOH functional groups, similar oxidations of all the primary alcohols catalyzed by 5 mol% of TJU-68-NDHPI were implemented, affording comparable conversion and selectivity to that of TJU-68-NHPI (Table S3).

Table 3. TJU-68-NHPI Catalyzed Oxidation of the primary alcohols.[a]



Entry	Substrate	Product	Conversion[b] (%)	Selective[b] (%)
1	 **3a**	 **4a**	97	51
		 **5a**		49

2	 **3b**	 **4b**	99	90
		 **5b**		10
3	 **3c**	 **4c**	97	84
		 **5c**		16
4	 **3d**	 **4d**	100	56
		 **5d**		43
5	 **3e**	 **4e**	98	89
		 **5e**		11
6	 **3f**	 **4f**	99	50
		 **5f**		50
7	 **3g**	 **4g**	93	77
		 **5g**		23
8	 **3h**	 **4h**	99	73
		 **5h**		27
9	 **3i**	 **4i**	99	74
		 **5i**		26

10	 **3j**	 **4j**  **5j**	99	82 18
11	 **3k**	 **4k**  **5k**	80	72 28
12	 **3l**	 **4l**  **5l**	76	99 0
13	 **3m**	 **4m**  **5m**	99	84 16
14	 **3n**	 **4n**  **4n′**  **4n″**	82	43 32 25

[a] Reaction conditions: 0.5 mL CD_3CN, 0.075 mmol alcohol, TJU-68-NHPI (10 mol%)/TBN (30 mol%). [b] Determined by ^{1}H NMR spectroscopy and GC−MS using nitrobenzene or naphthalene as internal standard.

In order to further unveil the oxidation capability of this catalytic system, a variety of substrates with less activated benzyl C−H bonds were subjected to this oxidation system and the results are presented in Table 4. The ethylbenzene **6a** was smoothly oxidized to the acetophenone **7a** in 10 h in good yield and conversion (Table 4, entry 1). In particular, oxidation of the diphenylmethane derivatives **6b**, **6c**, **6d** successfully produced the

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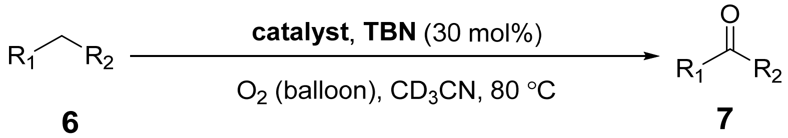
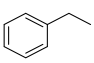
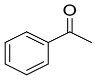
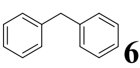
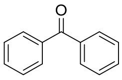
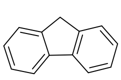
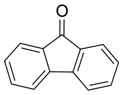
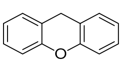
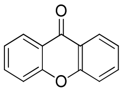
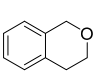
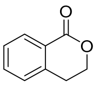
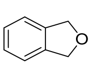
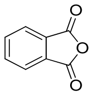
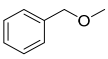
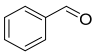
corresponding ketones in quantitative yield with superb selectivity (Table 4, entries 2−4). The benzyl ether derivatives could be readily oxidized quantitatively but the selectivity varied from 36% to 97% (Table 4, entries 5−7).

Table 4. TJU-68-NHPI (TJU-68-NDHPI) Catalyzed Oxidation of Benzyl C−H bonds.[a]



6 **7**

Entry	Substrate	Product	Catalyst	Time (h)	Conversion[b] (%)	Selective[b] (%)
1	 **6a**	 **7a**	TJU-68-NHPI	10	71	80
			TJU-68-NDHPI	10	76	86
2	 **6b**	 **7b**	TJU-68-NHPI	10	94	95
			TJU-68-NDHPI	8	93	97
3	 **6c**	 **7c**	TJU-68-NHPI	8	98	99
			TJU-68-NDHPI	6	99	98
4	 **6d**	 **7d**	TJU-68-NHPI	8	96	99
			TJU-68-NDHPI	6	97	94
5	 **6e**	 **7e**	TJU-68-NHPI	8	97	97
			TJU-68-NDHPI	8	98	96
6	 **6f**	 **7f**	TJU-68-NHPI	8	100	36
			TJU-68-NDHPI	6	100	58
7	 **6g**	 **7g**	TJU-68-NHPI	8	91	74
			TJU-68-NDHPI	6	95	81

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[a] Reaction conditions: 0.5 mL CD_3CN, 0.20 mmol substrate, TJU-68-NHPI (20 mol%)/TBN (50 mol%) or TJU-68-NDHPI (10 mol%)/TBN (50 mol%). [b] Determined by ^{1}H NMR spectroscopy and GC−MS using nitrobenzene or naphthalene as internal standard.

Heterogeneity and Recyclability

The most important advantage of these MOF catalysts constructed by bottom-up strategy is their sophisticated integration of the merits of homogeneous and heterogeneous catalysts, i.e., comparable or even higher efficiency than the homogeneous catalysts, good recyclability and resultant simple purification procedure as the heterogeneous catalysts, etc. The heterogeneous characteristic of this catalytic system was elucidated by control experiments. As shown in Figure 2a, 1-phenylethanol was oxidized smoothly in 2 hours to give 38% conversion. The reaction after catalyst filtration kept on heating for another 2 hours and gave an almost constant conversion of 40%, indicating the reaction of filtrate mixture ceased after the MOF catalyst was filtered out, while the parallel reaction without performing catalyst filtration afforded a conversion of 99%, proving that the reaction can only proceed with the MOF catalyst (see the Supporting Information). Additionally, the recyclability of the TJU-68 MOF catalysts was also evaluated by consecutive runs in the same reaction condition using the catalyst recycled *via* centrifugation. After ten cycles of the consecutive reactions, still a yield of no less than 88% could be obtained (Figure 2b). Furthermore, the Zr contents in the filtrate of the first and fifth cycles were detected to be 0.00638 and 0.00627 wt% of the total amount respectively by inductively coupled plasma−optical emission spectroscopy (ICP−OES) analyses, indicating negligible metal leaching to the reaction solution (Table S2, entries 1−2). The carboxylic acid product in this catalytic oxidation system resulted in a little Zr leaching

(0.185 wt%, Table S2, entries 3) but the catalyst was not poisoned to lose its catalytic capability. The PXRD patterns of the TJU-68 MOFs before and after the catalytic reactions are in good agreement and without appreciable decreasing of the intensity, suggesting good stability of these TJU-68 MOF catalysts in this aerobic oxidation condition (Figure 2c−d). Moreover, the outstanding selectivity, efficiency, conversion and volatile solvent and side products of this heterogeneous catalysis system endowed us with an economic and eco-friendly product purification process. Taking the oxidation of alcohol **1f** as an example, after the general reaction procedure for 3 hours, the MOF catalyst was collected by simple centrifugation or filtration, and the filtrate was concentrated to recover the reaction solvent acetonitrile and dried under vacuum to give the product **2f** in 91% yield (theoretically shall be 99%) with over 99% purity, avoiding the tedious purification by chromatography or high energy-consuming distillation process (Figure S4−6).

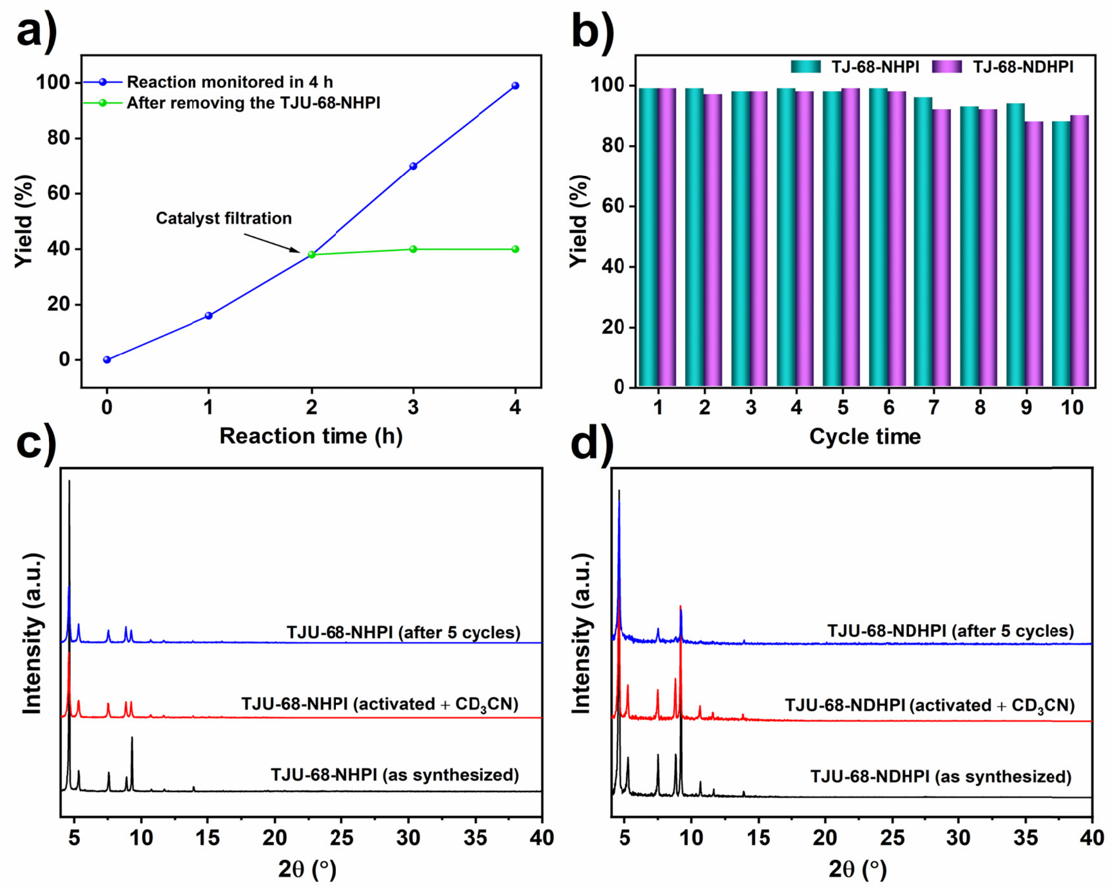

Figure 2. (a) Plots of conversions versus reaction time of the 1-phenylethanol oxidation catalyzed by TJU-68-NHPI. (b) Recycle tests of TJU-68-NHPI (green bars) and TJU-68-NDHPI (purple bars). PXRD profiles of the TJU-68-NHPI (c) and TJU-68-NDHPI (d) before and after the catalytic reactions.

Mechanistic Studies

The reaction mechanism of this NHPI catalyzed oxidation has been intensively studied and demonstrated in various systems, mainly for homogeneous ones.[38, 70-71] In this heterogeneous system, intrinsically the mechanism is similar (Figure 3). First of all, under elevated temperature the TBN will decomposed to generate NO species which will directly react with molecular oxygen gas to produce the very active NO_2 oxidant.[72] And then the small NO_2 molecules will readily diffuse into the solution and MOF pores, transforming the

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INOH groups on the pore surface to the INO radical active sites, that is, conversion of the TJU-68-NHPI to TJU-68-PINO. Simultaneously the NO_2 molecules are reduced to NO molecules furnishing the other half of the cycle in the gas phase. The high density INO radicals can efficiently abstract the hydrogen of activated C−H bonds on the alcohols or benzylic positions to generate C radical intermediates **RI1**, which subsequently activate the molecular O_2 to form the α–hydroxyl peroxyl radical intermediates **RI2**. Finally, the metastable **RI2** convert to the stable products by redox decomposition. The product aldehydes (R_2 = H) are potentially over-oxidized to the corresponding acids *via* the same pathway. To examine the involvement of the radicals in this oxidation system, 0.5 equivalents of radical scavenge 2,6-diterbutul-4-methylphenol was added to the oxidation reaction of 1-phenylethanol resulting in little conversion (3%) to the acetophenone product (see the Supporting Information). A straightforward evidence for the existence of critical radical species was obtained by electron paramagnetic resonance (EPR) spectra of the solid catalyst in the reaction system, showing a free radical signal at $g = 2.0073$ which is an essential characteristic of PINO radical in the pore.[73-75] The broadening of the EPR spectra was observed and indicated that the very active PINO radicals were successfully generated and confined on the TJU-68 frameworks under the reaction conditions (Figure S7a–b).[68] Most strikingly, this is a novel three-phase heterogeneous catalytic system first stated in this work, manifesting very high efficiency, outstanding selectivity, facile work-up procedure with green chemistry characteristics (Figure 3).

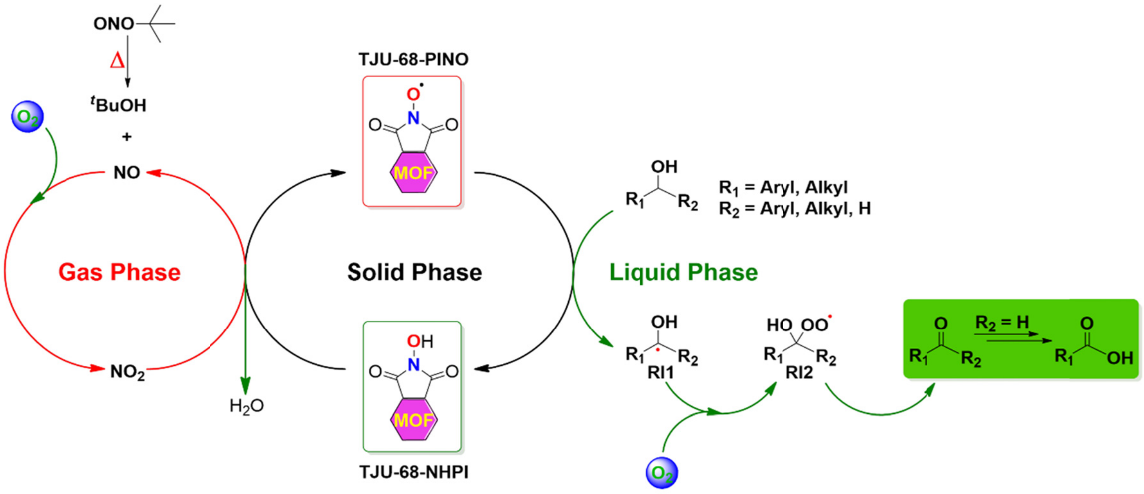

Figure 3. Proposed mechanism of the oxidation catalyzed by the TJU-68-NHPI/TBN/O_2 system.

Conclusions

In conclusion, a straightforward synthetic strategy has been developed to merge the NHPI unit as radical precursor sites into the organic ligand for bottom-up construction of novel free-radical TJU-68 MOFs. By comprehensive studies on the MOF characteristics and optimal reaction condition and mechanism, an unprecedented three-phase heterogeneous system has been established for catalytic oxidation of a wide scope of primary, secondary alcohols and benzyl compounds. The highly dense radical sites orderly decorated on the pore surfaces render the catalytic oxidation high efficiency, excellent selectivity, mild condition and environmental friendliness with molecular O_2 as terminal oxidant. Moreover, these MOF catalysts with satisfactory stability can catalyze the oxidation for ten cycles with little decrease of the conversions. The universal synthetic method reported here to functionalize the MOFs with the critical NHPI units will amalgamate the active radical chemistry with versatile MOF materials. Further efforts towards development of sophisticated MOFs with synergic effect of the organic catalytic sites and open metal sites for ideal catalysis are currently underway.

Experimental Section

Materials and Methods

All the solvents used in both synthesis and performance testing were purchased and used without further purification. The synthetic procedures of the ligands for the MOFs were described in the Supporting Information. Nuclear magnetic resonance (NMR) data were obtained by Bruker ARX400 and ARX600 spectrometer (400 MHz/600 MHz). Powder X−ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer at 40 mA, 40 kV for Cu $K\alpha$ (λ = 1.5418 Å) at room temperature with 2° min^{-1} at the range of 4 − 40°. Scanning Electron Microscopy (SEM) images were performed on a Hitachi S−4800 instrument. Gas adsorption measurements were conducted using the adsorption equipment TRISTAR 3020. The reaction products of aerobic oxidation were analyzed in Gas Chromatography Mass Spectrometry (GC−MS, SHIMADZU GCMS−QP2010 SE W). The Zr^{4+} concentrations were analyzed by an inductively coupled plasma−optical emission spectroscopy (ICP−OES, PerkinElmerOptima 8300). Electron Paramagnetic Resonance (EPR) spectrum were obtained by Bruker A300 spectrometer at the following experimental parameters: frequency, 9.852609 GHz; power, 18.26 mW; modulation amplitude, 0.1 G; modulation frequency, 100 kHz; sweep Time, 41.94 s; center field, 3510 G; sweep width, 50 G.

Synthesis of TJU-68-NHPI

A mixture of $ZrCl_4$ (3.00 mg, 0.01 mmol) and H_2L_{NOH} (5.00 mg, 0.01 mmol) in DMF (2.5

mL) was ultrasonically dissolved in a 10 mL Pyrex vial. Acetic acid (150 μL) was added to the reaction mixture followed by sonication. The clear solution was heated at 80 °C in an oven for 3 days to give white powder after filtration (yield 72%, based on the ligand).

Synthesis of TJU-68-NDHPI

A mixture of $ZrCl_4$ (2.40 mg, 0.01 mmol) and benzoic acid (0.10 g, 0.82 mmol) in DMF (3 mL) was dissolved in a 10 mL Pyrex vial by shaking. H_2L_{2NOH} (5.00 mg, 0.01 mmol) and deionized water (12 μL) were added subsequently to the reaction mixture followed by sonication. The clear solution was heated at 70 °C for 48 h, then temperature was elevated to 85 °C for 24 h, finally the temperature was increased to 100 °C and kept for another 48 h. The resulting white powder was obtained by filtration (yield 68%, based on the ligand).

Catalytic Reactions

To a 10 mL glass tube was added the alcohol (75.00 μmol), catalyst (7.50 μmol of TJU-68-NHPI or 3.75 μmol of TJU-68-NDHPI, or 7.50 μmol of other catalyst), *tert*-butyl nitrite (22.50 μmol) and 0.5 mL CD_3CN. The glass tube was sealed with rubber stopper and connected to an O_2 balloon through a long needle. After smoothly discharging the air in the glass tube by oxygen bubbling, the reaction mixture was fixed in a thermoshaker for and heated at 80 °C with a shaking speed of 900 rpm for a set time, and the conversions were checked by ^1H NMR spectra and GC−MS using nitrobenzene or naphthalene as internal standard.

Supporting Information

Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: N-hydroxyphthalimide, metal−organic frameworks, heterogeneous catalysis, aerobic oxidation, nitroxyl radical

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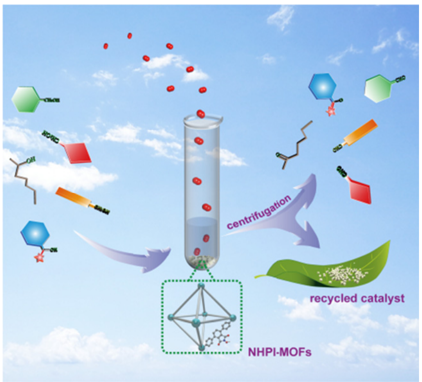

NHPI engaged MOFs: Two UiO metal–organic frameworks covalently merged with *N*-hydroxyphthalimide organocatalytic sites have been synthesized for the first time. By comprehensive studies on the MOF characteristics, optimal reaction condition and mechanism, an unprecedented three-phase heterogeneous system has been established for catalytic oxidation of a wide scope of primary, secondary alcohols and benzyl compounds. The catalytic oxidation manifests high efficiency, excellent selectivity, mild condition and environmental friendliness with molecular O_2 as terminal oxidant.