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Ordered Mesoporous Metal–Organic Frameworks Incorporated with Amorphous TiO_2 As Photocatalyst for Selective Aerobic Oxidation in Sunlight Irradiation

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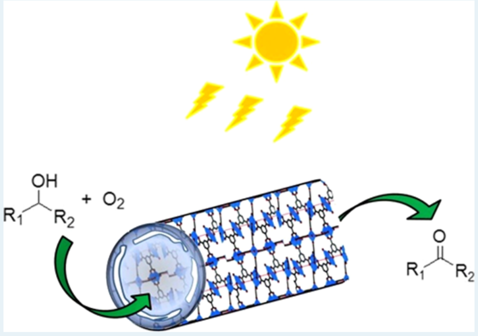
Supporting Information

ABSTRACT: Among the very few efforts for preparation of stable mesoporous metal–organic frameworks (MOFs), there is no report of an additive-free example via a surfactant-assisted templating method. On the other hand, photocatalytic aerobic oxidation of alcohols mediated by crystalline TiO_2 has been known as a green route, which has the potential to replace current technology with transition-metal-containing heterogeneous systems. Here, a simple procedure for preparation of HKUST-1 containing ordered mesoporous domains has been developed using nonionic block copolymer in DMF as the solvent. All materials have been thoroughly characterized by FTIR, FESEM, HRTEM, XRPD, EDS, and TG analysis. Subsequently, it has been demonstrated that incorporation of amorphous TiO_2 within the prepared mesoporous MOF could successfully develope a new type of photocatalyst system for selective aerobic oxidation of benzylic alcohols with moderate to high yields in sunlight irradiation.



KEYWORDS: *metal–organic framework, heterogeneous photocatalysis, amorphous TiO_2, aerobic oxidation, sunlight*

Metal–organic frameworks (MOFs) are very useful porous solid materials that have attracted much attention because of their potential applications for gas storage,[1] luminescent properties,[2] magnetic materials,[3] separation,[4] chemical sensing,[5] drug delivery, and heterogeneous catalysis.[6] Even though heterogeneous catalysis is one of the earliest demonstrated applications for MOFs,[7] compared with the reported crystalline MOFs,[8] the number of catalytically active structures is really limited.[9] Nevertheless, unique structural properties, such as a relatively large microporous surface area, high thermal and mechanical stability, and high transition metal site content as well as adjustable functionality, have attracted numerous chemistry scientific groups to investigate them for new catalytic aspects of these materials to be discovered.[9a]

Titanium dioxide (titania) plays a prominent role in fundamental studies and has both potential and demonstrated applications in solar energy conversion,[10] photocatalysis,[11] photochromic devices,[12] and gas sensing.[13] Among the three natural crystalline forms of titanium dioxide (anatase, brookite, and rutile), anatase has superior optoelectronic and photochemical properties.[14] One of the most important previous approaches to growing photocatalytic properties of crystalline titania was aimed at mesoporous materials (specially SBA-15)[15] for dispersing the TiO_2 nanoparticles within their interconnected channels. These types of titanosilicate composites prevent agglomeration of the fine titania nanoparticles, predominant formation of the crystalline anatase TiO_2, and eventually improve the accessible effective surface area of the photocatalytic active centers.[16] Another valuable aspect in this area which has been rarely investigated to date is applying amorphous titania instead of its crystalline phases, which can be simply prepared and has a relatively high surface area, leading to high adsorptivity properties. Very recently, within a periodic mesoporous organosilica (PMO) bearing an appropriate photoresponsive and photoresistance organic group, amorphous titania was coated, and the photocatalytic performance of the resulting materials was investigated in the aerobic regeneration of carbonyl compounds from oximes under sunlight irradiation.[17]

Recoverable transition-metal-mediated heterogeneous catalyst systems for aerobic oxidation of alcohols,[18] as one of the most important organic transformations, have provided the main breakthrough instead of traditional environmentally undesired stoichiometric oxidation systems. Moreover, photocatalytic aerobic oxidation of alcohols into carbonyl compounds using molecular oxygen in the presence of TiO_2 has attracted much attention as a potential and promising strategy because of the high oxidation capability and environmentally friendly properties of titania, in addition to the advantage of using O_2 as a green oxidant and light as the reaction driving force.[19] Recently, among evolution of TiO_2-mediated photocatalytic systems[20] to achieve high selectivity in aerobic oxidation of

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alcohols, high selectivity (>98%) was obtained by employing both anatase TiO_2 and titanosilicate, even in UV light irradiation.[21] Isotope labeling along with surface spectroscopic techniques accordingly showed that in the presence of an oxygen atmosphere and in organic solvents, both the ·OH radical production and autoxidation that traditionally has been thought to decrease the reaction selectivity do not form, and the reaction pathway proceeds through the side-on peroxide titanium intermediate in which the oxygen atom of a dioxygen has been transferred to the α-carbon atom of the alcohol.[22] In parallel with these studies by Zhao and co-workers, other investigations developed by the Palmisano group[23] interestingly indicated that in aqueous media, which inevitably results in the formation of high-power oxidative radicals such as ·OH, conducting the reaction to degradation in addition to the partial oxidation, the selectivity issue could be aided by using less crystalline rutile TiO_2 structures instead of more crystalline commercial ones.[24]

Herein, we demonstrate that selective photocatalytic activity in aerobic oxidation of alcohols under sunlight irradiation could be addressed by a simply prepared mesoporous structure of a photoresponse metal–organic framework, HKUST-1[25] decorated by amorphous TiO_2. To our knowledge, there has been no precedent example of MOFs used for immobilization of amorphous TiO_2 under such mild reactions as well as optical conditions for selective aerobic oxidation of alcohols.

Among particular efforts on the chemical foundation of crystalline MOFs for improving the substantial potential applications of these porous materials, preparation of mesoporous MOFs (mesoMOFs) has yet remained a phenomenally challenging area.[26] Mesoporous MOF structures as a new approach in material science combine the advantages of both mesoporous materials and MOF materials. The diffusion problem of the larger molecules leading to the lack of accessing the interpore active sites of the infinitely microporous framework of these materials significantly demonstrates the necessity of more in-depth studies to establish mesoporous MOFs. To date, few noteworthy mesoMOF structures have been reported via the most common synthetic approaches, including surfactant-assisted supramolecular templating[27] or, rarely, incorporating expanded organic linkers.[28] However, instability and interpenetration of the linear expanded ligands has caused inevitable reduction of the porosity and pore diameters of the framework. Few non-interpenetrated mesoMOF structures have been obtained by supramolecular template techniques.[27a,29] Recently, in a remarkable way using expanded and/or mixed organic linkers, high porosity was induced into the microporous MOF frameworks.[30] For larger pore diameters to be formed through the former approach, a cooperative template system containing cationic surfactant (CTAB) has been designed to prepare mesoporous MOFs using citric acid as a chelating agent.[31] Moreover, a well-ordered mesoMOF was synthesized using a three-component ionic liquid/CO_2/surfactant system.[32]

The most commonly used low-cost and biocompatible block copolymers are those belonging to the family of EO–PO–EO nonionic surfactants [PO and EO standing for poly(propylene oxide) and ethylene oxide, respectively]. To the best of our knowledge, although nonionic block copolymer surfactants have been widely used for preparation of the mesoporous silica,[33] alumina,[34] and other types of metal oxides[35] in aqueous solution, there is no report of using them for synthesis of mesoMOF in organic solvents. Knowing the fact that polar organic solvents are considered to be better than water for micellization of these block copolymers,[36] they logically can directed the construction of mesoMOF in organic media.

To shed light on this issue, herein, we present a direct simple method to prepare a mesoporous structure of HKUCT-1 via a combination of nonionic triblock surfactant pluronic P123, organic solvent, DMF, and the precursors of the MOF structure.[25] It is demonstrated that in an additive-free media in the presence of an appropriate amount of block copolymer surfactant in DMF solution, ordered mesoporous domains are actually constructed within the MOF framework.

Four separate experiments were designed according to different amounts of P123, and the final solids were denoted as SHK0.3, SHK1, SHK2, and SKH3, which represent surfactant assisted HKUST-1 prepared in the presence of 0.3, 1, 2, and 3 g of P123 during the same preparation stages. Another HKUST sample was also synthesized without the structure-directing agent that was denoted as HK (vida infra and the Supporting Information). Comparison of simulated and experimental powder X-ray diffraction (PXRD) patterns of all the prepared samples confirmed the HKUST-1 structure estimated from the basic crystallographic data (Figure S1 in the Supporting Information). The FTIR spectra and SEM images of the prepared samples have been shown in Supporting Information Figures S2, S3 and S4, verified the XRD analysis, as well.[25]

Interestingly, as evidenced by hysteresis in the N_2 adsorption–desorption isotherm and the pore size distribution, (Figure 1), in the presence of 0.3–2 g of P123, mesopores have been produced within the MOF framework. Type IV isotherm, characteristic of mesoporous materials, represented their mesoporous structures constructed under the mentioned preparation conditions. As represented in Figure 1, HK and SHK3 have no hysteresis in their N_2 adsorption–desorption isotherms, but the others have hysteresis that is clearly formed and growth by decreasing the concentration of the used surfactant. As calculated from the Barrett–Joyner–Halenda (BJH) method (Table 1), the average pore size of 2.4 nm was obtained for all three samples: SHK0.3, SHK1, and SHK2. Furthermore, although broad distribution of mesoporous sizes has been dictated in SHK0.3 and SHK1, in the case of SHK2, a relatively narrow pore size distribution can be observed around the meso region. Transmission electron microscopy (TEM)

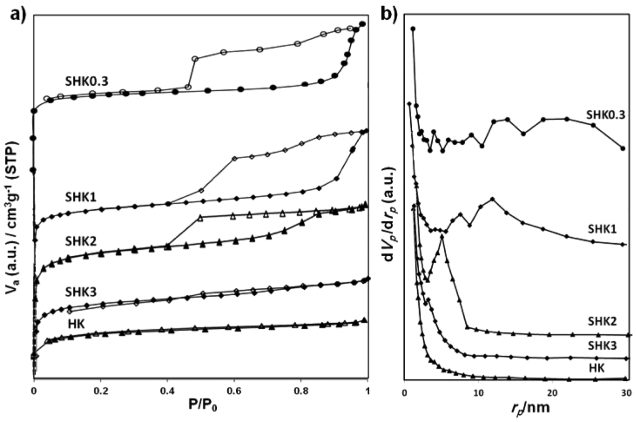


Figure 1. (a) N_2 adsorption–desorption isotherms and (b) pore size distributions of mesoMOFs synthesized in the presence of different amounts of P123.

Table 1. Lattice Parameters of HKUST-1 Structures Prepared in the Absence or Presence Different Amounts of P123

sample	S_{BET} ($m^2 g^{-1}$)[a]	D_{micro} (nm)[b]	D_{meso} (nm)[c]	V_{meso} ($cm^3 g^{-1}$)[c]
HK	927	0.6		
SHK0.3	662	0.6	2.4 (3.8)	0.176
SHK1	595	0.6	2.4 (4.2)	0.178
SHK2	732	0.6	2.4 (3.7)	0.099
SHK3	941	0.6	2.4 (3.3)	0.074
70Ti@HK	415	0.8	2.4 (2.4)	0.158
70Ti@SHK2	568	1.5	2.4 (3.8)	0.869

[a] The Brunauer–Emmett–Teller (BET) surface area. [b] The mesopore size distributions were calculated using MP plot. [c] The mesopore pore volume and the mesopore size distributions were calculated using the BJH method of adsorption branch; data in parentheses are calculated from the desorption branch.

images of SHK2 provided strong evidence that relatively ordered mesoporous domains were formed within the whole microporous structure of the parent MOF (Figure 2 a, b; see more images in the Supporting Information). All observations show that although the presence of nonionic triblock surfactant did not affect the origin of MOF structure, it could direct the construction of mesoporous structures in this manner.

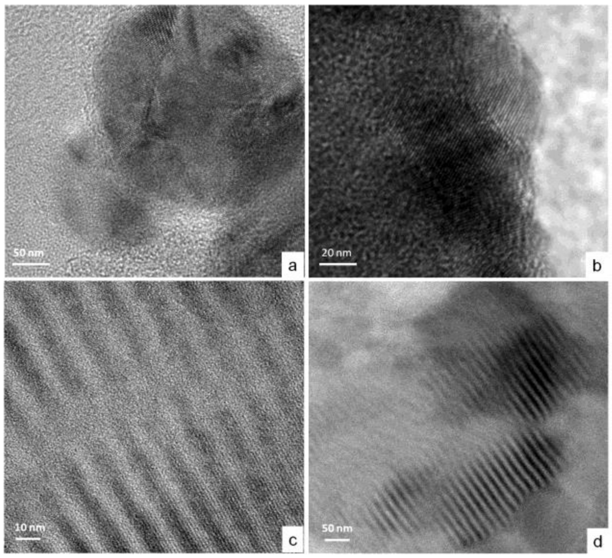


Figure 2. HRTEM images of (a, b) SHK2, (c) 70Ti@SHK2, and (d) 70Ti@SHK2R.

In the first investigations, the most ordered structure, SHK2, was chosen, and its surface was decorated with amorphous titania through a layer-by-layer coating procedure.[37] *x*Ti@SHK2 solids with four different nominal metal loadings (*x*: 25, 50, 70, and 85 wt %; actual loading indicated by ICP analysis) were prepared. As illustrated in Supporting Information Figure S2, considerable changes were not seen in any of the distinct XRPD patterns of all the prepared composites, which definitely showed the amorphous character of the coated TiO_2 layer. Moreover, the IR spectroscopy and SEM analysis confirming the XRPD analysis unanimously indicated that the structure of the parent MOF remained intact after titania embedding.

Afterward, the catalytic performance of these nanocomposite materials was compared in the photochemical aerobic oxidation of alcoholes under sunlight irradiation. The photocatalytic aerobic oxidation of 4-methylbenzyl alcohol was tested as a probe in dry CH_3CN, which was selected as the best solvent during the survey of reaction media. With 25Ti@SHK2, 50Ti@SHK2, 70Ti@SHK2, and 85Ti@SHK2 as photocatalysts, 21, 35, 89 and 63% of 4-methyl benzaldehyde, respectively, were surprisingly obtained with high selectivity (>93%). As can be seen in Table 2 (entries 1–2), in the presence of bare MOF, no obvious transformation of the alcohol was found after 15 h of irradiation. It definitely shows that the excitation of the photoresponse support could not alone be effective to continue the reaction. In addition, no reactivity was observed when the reaction took place in the absence of the catalyst, light, or oxygen atmosphere. All these observations not only proved the photocatalytic character of our system, but also proved that amorphous TiO_2 layer or copperic centers in the MOF matrix acting as Lewis acid catalyst in the reaction did not play a role in the reaction.

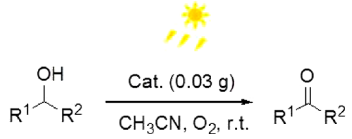
The obtained individual photocatalytic activity of 70Ti@SHK2 encouraged us to investigate more about this new type of photocatalytic system; therefore, 70Ti@HK, 70Ti@SHK0.3, and 70Ti@SHK1 were also prepared in the same manner as 70Ti@SHK2 and characterized with IR and XRPD analysis (Supporting Information Figures S2 and S5), and subsequently, the photocatalytic reaction of 4-methylbenzyl alcohol was performed using the same optimum conditions mentioned in Table 2, entries 8–10. Interestingly, 38, 36, and 54% of the corresponding aldehyde was produced in the presence of 70Ti@HK, 70Ti@SHK0.3, and 70Ti@SHK1 and 15 h of irradiation, respectively. Because all these materials are different only in their porosity properties, the discrepancy of the observed reactivity narrowly refers to the relatively uniform mesostructure of the former and is also a criterion of continuing the reaction inside the pores of the mesoporous structure.

The high-resolution TEM (HRTEM) image of 70Ti@SHK2 represented in Figure 2c accordingly confirms highly ordered amorphous titania arrayed toward the ordered mesochannels in the parent MOF, which was not observed in the other cases.

The high selectivity obtained in our photocatalyst system under such mild reaction conditions prompted us to investigate whether the reaction mechanism might be predominant here and the possibility of an undesired degradation process. It was determined that in specific photocatalytic reactions of 4-methylbenzyl alcohol with 70Ti@SHK2 in the presence or absence of catalytic amounts of 1,4-benzoquinone as a radical scavenger, the difference in the reactivity with 70Ti@SHK was actually negligible (Table 2, entries 17 and 18). To minimize the fluctuations, both compared reactions were performed in 1 day under the same sunlight irradiation conditions and daily temperature. Therefore, the inevitable role of $^\bullet OH$ radicals which can be easily formed in the presence of fully crystalline TiO_2 in aqueous medium and induce undesired degradation reaction was accordingly addressed and confirmed that the side-on peroxide formation in photocatlytic conditions[22] is the major path in our photocatalyst system. Although it needs more precise investigatios, it can be ascribed to the concerted contribution effect of h_{vb}^+ and e_{cb}^-,[22b] which is the predominant route under these conditions~~,~~ and raises the selectivity of the partial oxidation process.

It well-known that a high recombination rate of the charge carried (h_{vb}^+ and e_{cb}^-) within the amorphous titania bulk is responsible for its ineffectiveness to carry on the organic

Table 2. Aerobic Oxidation of Aromatic Alcohols Using MOF-Based Amorphous TiO_2 in Sunlight Irradiation



entry	cat.	R^1	R^2	concn (%)	select. (%)[a]
1	HK	4-MeC_6H_4	H		
2	SHK2	4-MeC_6H_4	H		
3(b)	70Ti@SHK2	4-MeC_6H_4	H		
4	35Ti@SHK2	4-MeC_6H_4	H	21	95
5	50Ti@SHK2	4-MeC_6H_4	H	35	95
6	70Ti@ SHK2	4-MeC_6H_4	H	89	95
7	85Ti@ SHK2	4-MeC_6H_4	H	63	95
8	70Ti@HK	4-MeC_6H_4	H	38	95
9	70Ti@SHK0.3	4-MeC_6H_4	H	36	95
10	70Ti@SHK1	4-MeC_6H_4	H	54	95
11	70Ti@SHK2	Ph	H	67	97
12	70Ti@SHK2	4-$MeOC_6H_4$	H	100	93
13	70Ti@SHK2	4-ClC_6H_4	H	65	98
14	70Ti@SHK2	4-$NO_2C_6H_4$	H	32	95
15	70Ti@SHK2	Ph	Me	100	99
16	70Ti@SHK2	Ph	Ph	30	99
17(c)	70Ti@SHK2	4-MeC_6H_4	H	51 (22)(d)	98
18(e)	70Ti@SHK2	4-MeC_6H_4	H	54 (26)(d)	98
19(f)	70Ti@SHK2R	4-MeC_6H_4	H	55	95
20(g)	amorph TiO_2	4-MeC_6H_4	H	6	

[a] Reaction conditions: 0.01 M solution of alcohol in absolute CH_3CN (10 mL), 30 mg of the catalyst, O_2 atmosphere (1 atm.), room temperature (25−35 °C) and sunlight irradiation (intensity =75−95 × 10^3 lux). Selectivity= $c_p/(c_{r0}\text{-}c_r)$ 100%, c_{r0}: the initial concentration of the reactant; c_r: the concentration of the reactant during the reaction; c_p: the concentration of the product during the reaction. GC yield based on an internal-standard method. (b)in dark. (c)irradiation in sunlight during 8 h in the presence of 0.003 mmol (3.3 × 10^{-4} g) of 1,4-benzoquinone, (d)after 4 h sunlight irradiation. (e)irradiation in sunlight during 8 h in the absence 1,4-benzoquinone; both reactions (entries 17 and 18) were performed in the same day, (f)70Ti@SHK2R is the recycled catalyst. (g)in the presence of 30 mg of amorphous titania.

transformations.[38] Herein, it is proved that incorporation of amorphous titania within the relatively ordered metal−organic framework not only could rectify this known weakness but also successfully introduce this kind of activated amorphous titania for the accomplishing selective oxidative organic transformation.

As summarized in Table 2, (entry 6 and entries 11−16) primary and secondary substituent electron-rich and electron-poor benzylic alcohols successfully transformed into their corresponding carbonyl compounds with high selectivities (93−99%) and moderate to high conversions (32−100%).

These significant and meaningful results persuaded us to keep our studies a step ahead and evaluate for the recycling ability of the catalyst, which is very important for practical purposes. To examine this issue, 70Ti@SHK2 was collected from various oxidation reactions, washed with 1:1 MeOH and CH_3CN, and then dried in air (see the Supporting Information). The reaction of 4-methylbenzyl alcohol with the recycled photocatalyst denoted as 70Ti@SHK2R under the same conditions mentioned in Table 2 afforded a 55% yield of 4-methylbenzaldehyde with 95% selectivity after 15 h of sunlight irradiation (Table 2, entry 19). As expected and then confirmed by IR, XRPD, and TG analyses (Supporting Information Figures S2, S5 and S11, respectively), the structure of HKUST has enough stability in this mild photooxidation condition. Decreasing photocatalytic activity was indicated by changes that appeared in the structure of the recycled catalyst. As is clear in Supporting Information Figures S17 and S18, a white layer of amorphous titania segregated from the basic ordered MOF is observed after the oxidation reaction. Precisely, the HRTEM shown in Figure 2d indicates some disjointed titania domains, which are clearly recognized to have lost their connectivity to the basic mesoporous MOF support. This finding in combination with the poor reactivity obtained with pure amorphous titania as the photocatalyst under the same reaction conditions (Table 2, entry 20) verified the credible synergistic role of the basic ordered mesoporous MOF structure and incorporated amorphous titania phase.

In conclusion, we were able to successfully prepare, for the first time, a relatively ordered mesoporous metal−organic framework via a simple template method. Then, selective aerobic photooxidation of benzylic alcohols was separately addressed via incorporation of unmerited amorphous titania into the meso-MOFs under sunlight irradiation and an oxygen atmosphere. With 70Ti@SHK2, which included a suitable amount of amorphous titania (70 wt %) incorporated into the most ordered obtained MOF structure, high selectivities (93−99%) with moderate to high conversions (32−100%) were subsequently deduced from the reaction of other electron-rich and electron-poor benzylic alcohols using this mild reaction condition. In addition, all experimental results, in addition to comparison of the HRTEM images of 70Ti@SHK2 with the recycled catalyst, interestingly revealed that a synergistic effect of both a photoresponse ordered meso-MOF and amorphous titania are surprisingly responsible for the uncommon reactivity observed in this new type of photocatalyst system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of MOF synthesis and incorporation of TiO_2, powder XRD, FTIR, SEM, HRTEM, TGA, EDS analysis, and images of the catalyst appearance. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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