Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.journals.elsevier.com/molecular-catalysis

Zirconium-based metal-organic framework as an efficiently heterogeneous photocatalyst for oxidation of benzyl halides to aldehydes

Ping Xue, Jiming Huang, Liguang Lin, Rong Li, Mi Tang*, Zhengbang Wang*

Ministry of Education Key Laboratory for the Green Preparation and Application of Functional Materials, Hubei Key Laboratory of Polymer Materials, School of Materials Science and Engineering, Hubei University, Wuhan, 430062, PR China

ARTICLE INFO	A B S T R A C T				
<i>Keywords:</i> Metal organic frameworks UiO-66-NH ₂ Photocatalysis Benzyl halides	The development of efficient heterogeneous catalysts for fine chemical synthesis is critical for practical appli- cations. Herein, for the first time, the zirconium-based metal-organic framework (UiO-66-NH ₂) is applied as an efficiently heterogeneous photocatalyst for conversion of benzyl halides to corresponding aldehydes with high selectivity (about 80 %) and conversion (up to 99 %) in the presence of oxygen and DMF as solvent. Through a series of experiments and analysis, the reaction mechanism is proposed to involve nucleophilic attack of the <i>N</i> - oxide. This study provides a general, environmental and high selective method to prepare benzaldehydes and broadens the application fields of UiO-66-NH ₂ .				

1. Introduction

Aromatic aldehydes and its derivatives are extensively used as important precursors in synthetic, pharmaceutical, and materials chemistry [1,2]. To date, variety of methods have been developed to access aromatic aldehydes, including the direct oxidation of benzyl alcohol [3-6], benzyl halides [7,8] or toluene [9,10] into corresponding aldehydes, transition-metal-catalyzed/mediated formation of aromatic aldehydes [11] and so on. Among them, the direct oxidation of benzyl halides to aldehydes has attracted widespread attention because of its convenience, excellent selectivity and efficiency. However, the classical oxidation approaches, such as Kornblum oxidation [12,13] and Sommelet oxidation [14], either generate unpleasant and difficult-separating sulfide byproducts or require excessive hexamine with low yield and inevitable side reaction (Delepine reaction), which severely limit their practical applications. Very recently, it was reported that benzyl halides could be oxidized to corresponding aldehydes catalyzed by benzo[*c*]cinnoline [15] with molecular oxygen, which showed excellent conversion and environmentally friendly. We reasoned that the recently emerging visible-light photocatalysis could promote this redox process under sustainable and mild conditions. Although there have been sporadic reports that photocatalysis could promote oxidation reactions of halides to aldehydes, the reported methods either suffered from poor selectivity [8] or required the long reaction time [7]. It is extremely urgent to develop efficient, high selectivity and recyclability

photocatalysis for the preparation of corresponding aldehydes from benzyl halides.

Recently, metal-organic frameworks (MOFs) as a new class of crystalline porous materials are attracting considerable attention in the field of heterogeneous catalysis due to their designable structure, large surface area and porosity, abundant catalytic sites and adjustable pore size [3,16,17]. A variety of well-designed MOF-based heterogeneous catalysts have been prepared and applied in many types of chemical conversion processes, not only for energy chemistry [18,19], but also in classic organic synthesis including name reactions and up-to-date functional reactions [20,21]. In particular, MOFs offer unique features in heterogeneous photocatalysis that have no comparison with other types of inorganic or organic photocatalysts, like the well-defined crystalline structure with uniform channels and nanopores that is beneficial for catalyst-substrate interaction, and the tunable light absorption properties via modular interaction between the inorganic metal clusters and the organic linkers, which could enhance the photoelectrons transfer. In addition, MOFs are also easy to separate from the reaction mixtures to avoid the costly separation step for reusing. Based on the above, MOF-based photocatalysts exhibited advantages in many catalytic reactions, such as hydrogen generation [18,22], CO₂ reduction [23], and other organic conversion [24]. However, the direct oxidation of benzyl halides to aldehydes catalyzed by MOFs has been rarely explored.

Hence, we apply the zirconium-based MOFs (UiO-66-NH₂) as the

* Corresponding author. *E-mail addresses:* mtang@huhu.edu.cn (M. Tang), zhengbang.wang@hubu.edu.cn (Z. Wang).

https://doi.org/10.1016/j.mcat.2021.111542

Received 30 December 2020; Received in revised form 11 March 2021; Accepted 21 March 2021 Available online 7 April 2021 2468-8231/© 2021 Published by Elsevier B.V.









Fig. 1. a. PXRD patterns of fresh and simulation UiO-66-NH₂; b. FT-IR spectroscope of UiO-66-NH₂ and 2-aminoterephthalic; c. SEM image of UiO-66-NH₂; d. TEM image of UiO-66-NH₂; e. N₂ adsorption-desorption isotherm of fresh UiO-66-NH₂; f. Pore size of fresh UiO-66-NH₂.

heterogeneous photocatalyst for the oxidation of benzyl halides to aldehydes, which is operationally simple and works under mild and environment-friendly conditions. UiO-66-NH₂ is a well-known functional MOF with high chemical and thermal stability [25], which showed excellent photocatalytic activity for selectivity oxidation of benzyl alcohols into aldehydes [26–28]. Under visible light irradiation, the UiO-66-NH₂ catalyst was excited to produce photogenerated electrons and holes, and then the electrons combined with the oxygen to form superoxide radical anion (O_2^-). Benzyl alcohol was oxidized to benzaldehyde by the combined action of O_2^- and holes with a selectivity of 100 % [27]. And such catalytic reaction could be improved with higher conversion and shorten reaction time by adding rGO into the UiO-66-NH2 catalyst and the reason was attributed to the effective separation and transport of photogenerated electrons and holes, consequently improving the photocatalytic activity [26,28]. In this study, we further reveal that the O_2^- , which is produced by photoelectrons transfer from UiO-66-NH₂ to O₂, could promote the oxidation of benzyl halides to aldehydes under mild and environment friendly conditions. In addition, the possible photocatalytic reaction mechanism is also proposed.

2. Experimental

2.1. Synthesis

The anhydrous zirconium chloride (ZrCl₄), 2-aminoterephthalic acid, 1,4-benzenedicarboxylic and benzyl bromide were purchased from Aladdin. Other reagents, such as *N*, *N*-dimethylformamide (DMF), acetonitrile (CH₃CN), 1,4-dioxane and methanol (CH₃OH), etc. are analytical reagent grade from Sinopharm Chemical Reagents Co., Ltd. The above reagents were used without further purification.

UiO-66-NH₂ was synthesized by the reported method [29]. Typically, 1.04 mmol ZrCl₄ (0.244 g) and an equimolar amount of 2-aminoterephthalic acid (0.188 g) were dissolved in 60 mL DMF. Thereafter, 1.8 mL glacial acetic acid as a modulator was added to the mixture and then sonication for 20 min. The resulting homogeneous was obtained and transferred into 100 mL Teflon-lined stainless steel autoclave. Then, the autoclave was placed to oven and heated at 120 °C for 24 h. After cooled naturally, the pale-yellow particles were separated by centrifugation and washed three times with DMF and CH₃OH. Finally, the particles dried overnight at 80 °C under vacuum. UiO-66 was prepared by replacing 2-aminoterephthalic acid with 1,4-benzenedicarboxylic under the same conditions.

A mixture of benzyl bromide (0.2 mmol), UiO-66-NH₂ (20 mg) and DMF (8 mL) in 25 mL glass reactor was stirred at 90 $^{\circ}$ C for 18 h in the air

under visible light irradiation (26 W helical bulb) to obtain the corresponding aldehydes. At the end of reaction, the mixture was centrifuged, the liquid phase was used to test the conversion and selectivity, and the solid phase was used to the next catalytic. The solid catalyst was washed three times with DMF and CH₃OH, respectively, and then placed in vacuum oven to dry at 80 $^{\circ}$ C.

2.2. Characterization

X-ray diffraction (XRD) measurements were performed on the Bruker D8 with a Cu K α radiation (40 KV, 40 mA, λ =1.5418 Å). The morphology of catalyst was performed over field emission scanning electron microscope (FESEM, Sigma 500, ZEISS, Germany), field emission transmission electron microscope (FETEM, Talos F200X, America) and high resolution transmission electron microscope (HRTEM, JEM-ARM200 F, Japan). The ultraviolet-visible (UV-vis) absorption spectrum was obtained by Ultraviolet-visible spectrometer (UV3600, SHI-MADZU, Japan), while Fourier-transform infrared (FT-IR) spectra were recorded on the Thermo Fisher Nicolet iS50 FT-IR spectrometer by KBr pellets. Specific BET surface area and pore volumes were determined from nitrogen adsorption-desorption isotherms of nitrogen at -196 °C using automatic Micromeritics apparatus (HJ-BW200B, JWGB Sci & Tech Ltd., China), the samples were degassed under vacuum at 150 °C for 12 h prior to measurement. The pore size distribution of samples was calculated by the Brunauer-Emmett-Teller (BET) model. The O_2^- was confirmed by electron paramagnetic resonance spectrometer (EPR, Bruker EMXplus, Germany). The electrochemical characterization was tested on a Autolab electrochemical workstation (Autolab PGSTAT302 N, Metrohm, Switzerland). A standard three-electrode system was used, Ag/AgCl as the reference electrode, Pt as the counter electrode and the sample as the working electrode in 0.2 M Na₂SO₄ solution. To prepare working electrodes, 10 mg sample was added to 1 mL 0.05 % Nafion ethanol solution. Then, the obtained suspension was fully dispersed by ultrasound for 30 min. Finally, the slurry was coated on a piece of FTO glass (1 \times 1 cm²) and dried at 80 °C for 12 h. The conversion and selectivity were determined by gas chromatography (GC-2014C, SHI-MADZU, Japan, FID detector and Rtx-5 chromatographic column). The temperature of gasification and detector was 300 °C while the initial column was set at 100 $^\circ C$ and kept for 1 min, then the temperature was raised to 200 °C at a rate of 10 °C/min and kept for 2 min. GC-MS (GCMS-QP2010 Ultra, SHIMADZU, Japan) was used for the detection of side products.

3. Results and disscussion

The structures and morphology of UiO-66-NH₂ were confirmed by XRD, FT-IR, SEM images, TEM images and HRTEM images. As shown in Fig. 1a, the as-synthesized material showed the characteristic diffraction peaks at 20 values of 7.33°, 8.47°, 12.03°, 17.04° and 22.15° corresponding to the (111), (002), (022), (004) and (115) crystal plane, respectively, which was consistent with previous reports and simulation [30]. The FT-IR spectroscopes also confirmed the successful acquisition of UiO-66-NH₂ (Fig. 1b). The absorptions at 3458 cm⁻¹ and 3369 cm⁻¹ were assigned to asymmetrical and symmetrical stretching vibration of amino group, while the band at 1570 cm⁻¹ suggested the coordination between carboxyl group and Zr⁴⁺. The SEM and TEM images (Fig. 1c and d) displayed that UiO-66-NH2 has uniform and regular spherical morphologies with about 0.6 µm diameter. The relative large particle size of UiO-66-NH₂ could be attributed to the addition of regulator (acetic acid) in the process of preparing UiO-66-NH₂ based on the competitive reaction between the regulator and ligands in the coordination process [31,32]. The lattice fringes had an interplanar spacing of 0.99 nm, corresponding to (002) fringes of UiO-66-NH₂, as shown in Fig. S1, which could further confirm the structure of UiO-66-NH₂.

The porous properties of the catalysts have an important effect on the catalytic performance. High surface area was benefit for effective

Table 1

Optimization of the UiO-66-NH₂-catalyzed conversion of benzyl bromide to benzaldehyde a .

	Br	UiC	90 °C, <i>hv</i> , 18 h	- U H		
Entry	Solvent	T (°C)	Catalyst (mg)	Time (h)	Conv. (%)	Sel. (%)
1	DMF	25	MOF, 20	18	15.17	trace
2	DMF	70	MOF, 20	18	54.84	30.78
3	DMF	90	MOF, 20	18	> 99	79.29
4	DMF	100	MOF, 20	18	> 99	65.36
5	DMF	90	MOF, 20	12	74.09	72.36
6	1,4- dioxane	90	MOF, 20	18	10.30	66.78
7	CH ₃ CN	90	MOF, 20	18	2.44	17.93
8	DMF	90	0	18	> 99	42.53
9	DMF	90	2-aminoterephthalic acid, 20	18	70.53	13.64
10^{b}	DMF	90	NaHCO ₃	18	> 99	5.00
11 ^c	DMF	90	MOF, 20	18	45.72	trace
12 ^d	DMF	90	MOF, 20	18	67.55	29.89
13 ^e	DMF	90	MOF, 20	18	59.88	8.96
14 ^e	DMF	90	0	18	60.68	36.64
15	DMF	90	UiO-66, 20	18	> 99	59.12

 a Reaction conditions: 0.2 mmol of benzyl bromide, 20 mg UiO-66-NH_2, DMF (8 mL), under visible light (26 w helical bulb) for 18 h at 90 $^\circ C.$

^b 2.0 eq NaHCO₃ was added.

^c the reaction was in a sealed tube.

^d Avoid light.

^e 15 mol% benzoquinone was added. Con. (%) = $(C_0 - C_i) / C_0$ (C_0 and C_i are the molar concentrations of benzyl bromide before and after the photocatalytic reaction, respectively.) Sel. (%) = $C_a / (C_a + C_b)$ (C_a and C_b are the molar concentrations of benzaldehyde and side products, respectively).

adsorption of reactants or guest molecular, hence accelerated the reaction progress. Therefore, the porosity of UiO-66-NH₂ was characterized by nitrogen adsorption-desorption isotherms. As shown in Fig. 1e and f, UiO-66-NH₂ demonstrated the characteristic Type I shape, indicating the microporosity. The BET surface area of UiO-66-NH₂ was calculated to be 997.714 m² g⁻¹, and the average pore was estimated to be 8.0 Å. These results showed that the obtained UiO-66-NH₂ is highly porous with large surface area.

Next, we probed the catalytic activity of UiO-66-NH₂ for the direct conversion of benzyl bromide to benzaldehyde. As shown in Table 1 (entries 1-15), catalytic reactions were conducted under different conditions, including different reaction temperatures and time, possible solvents, catalyst amounts, base, visible light and oxygen. Under the visible light and air as oxidant, the conversion reaction of benzyl bromide to benzaldehyde exhibited the best result in DMF with UiO-66-NH₂ (20 mg) at 90 °C for 18 h (Table 1, entry 3). The lower (25 and 70 °C) or a higher temperature (100 °C) resulted in reduced selectivity and conversion (Table 1, entry1, 2 and 4). Shortening the reaction time was also found to prohibit conversion and selectivity (Table 1, entry 5). Other relative low polar solvents, such as 1,4-dioxane and CH₃CN would lead to a very low conversion (less than 11 %, Table 1, entry 6 and 7). In addition, without UiO-66-NH₂, the reaction showed a very low selectivity although it had over 99 % conversion (Table 1, entry 8, the possible explanation would be discussed in the mechanism part). Other alkaline catalysts, such as homogeneous ligand 2-aminoterephthalic acid and inorganic base NaHCO₃, dramatically decreased selectivity (Table 1, entry 9 and 10). Lack of air or visible light would lead to poor conversion and selectivity (Table 1, entry 11 and 12), indicating that visible light and oxygen were essential for the conversion of benzyl bromide to benzaldehyde.

As a heterogeneous catalyst, as shown in Fig. 2a, UiO-66-NH₂ could be recycled, and the conversion and selectivity also could maintain up to



Fig. 2. a. Cycle performance of UiO-66-NH₂ for the selective oxidation of benzyl bromide to benzaldehyde; b. PXRD patterns of fresh and reused UiO-66-NH₂. c. EPR spectra of UiO-66-NH₂ dispersed in methanol under dark or light irradiation; d. Leaching tests for benzyl bromide reaction by UiO-66-NH₂.



 $^a\,$ Reaction conditions: 0.2 mmol of substrate, 20 mg UiO-66-NH_2, DMF (8 mL), under visible light (26 w helical bulb) for 18 h at 90 $^\circ C.$

F₂C

about 100 % and 80 %, respectively. However, comparing with the first cycle, the selectivity of the second and third cycle slightly decreased, which could be attributed to some degree of blockage in the micropores of UiO-66-NH₂. As shown in Fig. S2, the BET surface area of UiO-66-NH₂ reduced from 997.714 to 302.138 m² g⁻¹ and lost some microporous properties after three runs. We speculated that the generation of byproducts for example bromine ions in the reaction progress coordinated with the free Zr sites, which can't be removed easily, causing the

blockage of the pores. The crystallinity or structural integrity of MOF didn't change during cycles as revealed by XRD pattern and FT-IR spectroscopes. After three cycles, both of XRD pattern and FT-IR spectroscopes of UiO-66-NH₂ showed negligible changes (Figs. 2b and S3), indicating that the crystallinity and structure were well maintained after multiple reuses.

The scope of UiO-66-NH₂-catalyzed conversion of benzyl bromides to benzaldehydes was further investigated utilizing various substrates. The results were summarized in Table 2. In the presence of electrondonating groups, such as methyl group and methoxy group (Table 2, entry 1 and 2), the selectivity of corresponding aldehyde was higher, while electron-withdrawing groups (Table 2, entry 3–6) were converted into corresponding aldehyde with moderate selectivity. The possible explanation will be discussed in the reaction mechanism.

In order to explore the reaction mechanism, a series of control experiments were carried out. As we know, UiO-66-NH₂ has good photocatalytic activity. Therefore, we initially inspected the performance of UiO-66-NH2 in producing 'O2. On one hand, UV-vis and electrochemical experiments were performed to demonstrate that the UiO-66-NH₂ could be excited by visible light and had the ability to produce O_2^- under the investigated conditions. As shown in Fig. S4, the absorption edges and the band gap of UiO-66-NH₂ located at 443 nm and 2.80 eV, respectively. The flat-band potential of UiO-66-NH2 was measured to be -1.06 V versus Ag/AgCl (-0.86 V vs. NHE, Fig. S5). The conduction band (CB) of UiO-66-NH₂ was estimated to be -0.96 V, since the bottom of CB of ntype semiconductors is more negative 0.1 V than the flat-band potential [33,34]. The CB of UiO-66-NH₂ is much more negative than the standard redox potential of O2/O2 (-0.33 V vs. NHE) [35], meeting the production requirements for O_2^- . On the other hand, EPR test also showed the UiO-66-NH₂ had the ability to produce O_2^- under light irradiation, as shown in Fig. 2c. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as superoxide radical anion trap, UiO-66-NH2 methanol dispersed solution displayed remarkable O_2^- signals under light irradiation, which was in accord with the reported results [27]. In contrast, if we removed the light source, the signals immediately disappeared. These results reconfirmed that UiO-66-NH₂ did produce O_2^- under light irradiation.

To explore the catalytic site, the catalyst leaching test was designed and the result was shown in Fig. 2d. After reacting for 6 h or 12 h, UiO-



Scheme 1. Proposed mechanism for selective oxidation of benzyl bromide to benzaldehyde by UiO-66-NH₂ in DMF.

66-NH₂ was separated from the reaction mixture by centrifugation. After removing catalyst, the reaction was continued for an additional 12 h or 6 h, respectively. Although the conversion could still be up to 99 %, the selectivity was only 45.72 % and 64.25 %, which clearly showed that the actual catalytic site for the selective oxidation of benzyl bromide to benzaldehyde was located on UiO-66-NH2. The nanometer-sized cavities in UiO-66-NH₂ could be regarded as microphotoreactors for the formation of superoxide radical and reactive intermediates. The amino group in UiO-66-NH₂ have three key functions in the reaction [4,27]: 1) act as an auxochromic and bathochromic group to promote the optical response; 2) as strong electron-donating functional groups to reduce the band gap. Upon light irradiation, electrons on the HOMO composed of O, C and N 2p orbitals jump to the LUMO, and transfer to O₂ molecules adsorbed on the Zr^{3+} sites to form O_2 ; 3) stabilizing the reactive intermediates. The O_2^- could be stabilized in the cavities of UiO-66-NH₂ due to its interaction with the amine groups. In addition, under the same conditions, the catalyst performance of UiO-66 was also explored, as shown in Table 1 entry 15. The result showed that the conversion of benzyl bromide was over 99 % while the selectivity of benzaldehyde was only about 59.12 %. In fact, UiO-66 could not be excited under visible-light irradiation. Therefore, photogenerated electrons and holes did not generate under this condition [27]. Slightly improving the selectivity of benzaldehyde was possibly associated with the porosity of UiO-66. Accelerating the reaction rate and improving the selectivity by using the porous catalysts were usually found in some heterogeneous catalytic processes [36,37].

To further illustrate how UiO-66-NH₂ improve the selectivity, we conducted more capture assay. It should be noted that the reaction showed some selectivity without catalyst UiO-66-NH₂ (entry 8, Table 1). However, this selectivity possibly was not attributed to O_2^- (detailed discussions seen below). In the absence of UiO-66-NH₂, benzoquinone was also added to the reaction. The results showed that the selectivity of entry 14 (Table 1, 36.64 %) slightly decreased comparing with entry 8 (Table 1, 42.53 %), which suggested that the O_2^- was not involved in the

formation of benzaldehyde without adding catalyst. In fact, the benzyl radical probably took part in the actual reaction without catalyst. Moreover, in the above discussion, we have proved that O_2^- was being produced in the reaction. After adding benzoquinone into reaction mixture (entry 13, Table 1), the selectivity of benzaldehyde significantly reduced to 8.96 % because of the almost total consumption of O_2^- . Therefore, O_2^- produced by UiO-66-NH₂ catalyst was the key to improve the selectivity.

Next, air was essential oxidant. As shown in Table1 entry 11, if there was no oxygen, benzaldehyde can hardly be detected. EPR spectra showed that UiO-66-NH₂ can transfer electronic to O_2 to form O_2^- under visible light. The O_2^- acted as efficient oxidant to oxidize substrates. The O_2^- also could be confirmed by capturing test by using benzoquinone (Table 1, entry 13). If benzoquinone was added into reaction mixture, the selectivity of benzaldehyde significantly reduced to 8.96 % because of the almost total consumption of O_2^- . Hence, the oxygen was concerned in the reactions.

Finally, we also found DMF might be involved in the reaction. Firstly, DMF would react with water in the air to produce formic acid and dimethylamine in the presence of photogenerated electrons and holes generated by UiO-66-NH₂ under visible-light irradiation [38]. The decomposition product dimethylamine was oxidized by the O_2^- to generate N-oxide, which has been proved as an effective oxidant for the oxidization of halides to aldehydes [39-41]. The in situ generating N-oxide as actual oxidant here reacted with benzyl bromides. Secondly, in order to confirm the hydrolysis of DMF, we analyzed the side products. Benzyl formate, which possibly come from the esterification reaction of formic acid and benzyl alcohol (It comes from the hydrolysis of benzyl bromide.) was found by GC-MS and gas chromatographic (the retention time was consistent), as shown in Fig. S6. This result reconfirmed the decomposition of DMF. Lastly, the replacement of solvents would greatly reduce the yield of benzaldehyde (entry 6 and 7 in Table 1). Therefore, we proposed that DMF might be involved in the reaction.

Based on the above experimental results and discussions, we proposed a plausible mechanism, as shown in Scheme 1. Under visible-light and heating, UiO-66-NH₂ generated photoelectrons and holes, photoelectrons immediately transferred into O_2 to form ' O_2^- . Photogenerated electrons and holes promoted DMF to react with water in the air to produce formic acid and dimethylamine. Dimethylamine was further oxidized to *N*-oxide by ' O_2^- . Then, *N*-oxide would undergo nucleophilic attack on benzyl bromide to deliver intermediate 1. Finally, intermediate 1 undergone a basic hydrolysis with assist of UiO-66-NH₂ to afford the desired product. At the same time, side reaction that benzyl alcohol reacted with formic acid also could be occurred to get benzyl formate.

In view of this plausible mechanism, it is not difficult to find that electron-donating groups on the benzene ring are favourable to the elimination of bromine and thus would promote the reaction and contribute to good conversion, as shown in Table 2. While electron-withdrawing groups reduce the electron density of benzene ring, which was adverse to the leaving of bromine. However, the selectivity of substituted substrates was lower than that of benzyl bromide, which could be due to the increased volume of substituted that was not conductive to diffuse through the pore apertures of UiO-66-NH₂.

4. Conclusion

In summary, we have reported efficient MOF-based heterogenetic photocatalytic oxidation of benzyl bromides to corresponding aromatic aldehydes. In this transformation, the photoelectrons generating from UiO-66-NH₂ under visible light catalyzed O₂ to form O_2^- , which mediated oxidation of benzyl bromides to afford the corresponding benzal-dehydes with high conversion and selectivity. Moreover, this strategy is suite for a wide substrate scope and the benzyl bromides with different substituent groups could be efficiently oxidized into corresponding aromatic aldehydes. We believe that this synthetic strategy provides general, environmental and high selective preparation of benzaldehydes and significantly broadens the application scope of UiO-66-NH₂ catalysts.

CRediT authorship contribution statement

Ping Xue: Investigation, Data curation, Writing - original draft. Jiming Huang: Validation, Investigation. Liguang Lin: Investigation. Rong Li: Formal analysis. Mi Tang: Writing - review & editing, Data curation. Zhengbang Wang: Conceptualization, Writing - review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgements

This work was supported by National Science Foundation of China (Grant No. 201802036 and Grant No. 21801071), Hubei Provincial Natural Science Foundation of China (Project No. 2018CFB110, 2020CFB404), Youth Science Foundation of Hubei University (202011303000001), Overseas Expertise Introduction Center for Discipline Innovation (D18025) and State Key Laboratory of Advanced Technology for Materials Synthesis and Processing (Wuhan University of Technology).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

online version, at doi:https://doi.org/10.1016/j.mcat.2021.111542.

References

- [1] P.J. O'Brien, A.G. Siraki, N. Shangari, Crit. Rev. Toxicol. 35 (2005) 609-622.
- [2] W. Chen, A.M. Viljoen, S. Afr. J. Bot. 76 (2010) 643-651.
- [3] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, ACS Catal. 1 (2011) 48-53.
- [4] T.W. Goh, C.X. Xiao, R.V. Maligal-Ganesh, X.L. Li, W.Y. Huang, Chem. Eng. Sci. 124 (2015) 45–51.
- [5] X.W. Zhang, W.J. Dong, Y. Luan, M. Yang, G. Wang, J. Mater. Chem. A 3 (2015) 4266–4273.
- [6] Y.Z. Chen, Z.U. Wang, H.W. Wang, J.L. Lu, S.H. Yu, H.L. Jiang, J. Am. Chem. Soc. 139 (2017) 2035–2044.
- [7] D. Liu, C.W. Qiu, M.B. Li, Y.Y. Xie, L. Chen, H.X. Lin, J.L. Long, Z.Z. Zhang, X. X. Wang, Catal. Sci. Technol. 9 (2019) 3270–3278.
- [8] A. Itoh, T. Kodama, S. Inagaki, Y. Masaki, Org. Lett. 2 (2010) 2455–2457.
- [9] X.L. Li, T. Wang, X.Q. Tao, G.H. Qiu, C. Li, B.X. Li, J. Mater. Chem. A 8 (2020) 17657–17669.
- [10] S.S. Fan, Y.P. Pan, H.X. Wang, B. Lu, J.X. Zhao, Q.H. Cai, Mol. Catal. 442 (2017) 20–26.
- [11] M. Tanaka, H. Ando, M. Fujiwara, J. Org. Chem. 60 (1995) 3846-3850.
- [12] N. Kornblum, J.W. Powers, G.J. Anderson, W.J. Jones, H.O. Larson, O. Levand, W. M. Weaver, J. Am. Chem. Soc. 79 (1957) 6562.
- [13] N. Kornblum, W.J. Jones, G.J. Anderson, J. Am. Chem. Soc. 81 (1959) 4113-4114.
- [14] M. Sommlet, Compt. Rend. 157 (1913) 852–854.
- [15] I.B. Stone, J. Janis, S.N. Macmillan, L.T. Hayes, Angew. Chem. Int. Ed. 57 (2018) 12494–12498.
- [16] J. Liang, Z.B. Liang, R.Q. Zou, Y.L. Zhao, Adv. Mater. 29 (2017) 1701139.
- [17] C.D. Wu, M. Zhao, Adv. Mater. 29 (2017) 1605446.
- [18] F.M. Zhang, J.L. Sheng, Z.D. Yang, X.J. Sun, H.L. Tang, M. Lu, H. Dong, F.C. Shen, J. Liu, Y.Q. Lan, Angew. Chem. Int. Ed. 57 (2018) 12106–12110.
- [19] Y. Chen, D. Yang, B.B. Shi, W. Dai, H.J. Ren, K. An, Z.Y. Zhou, Z.F. Zhao, W. J. Wang, Z.Y. Jiang, J. Mater. Chem. A 8 (2020) 7724–7732.
- [20] Y. Gong, Y. Yuan, C. Chen, P. Zhang, J. Wang, A. Khan, S. Zhuiykov,
- S. Chaemchuen, F. Verpoort, J. Catal. 375 (2019) 371–379.
 [21] D.R. Sun, M.P. Xu, Y.T. Jiang, J.L. Long, Z.H. Li, Small Methods 2 (2018) 1800164.
 [22] Y. Chen, D. Yang, B. Shi, W. Dai, H. Ren, K. An, Z. Zhou, Z. Zhao, W. Wang,
- [22] T. Chen, D. Tang, B. Shi, W. Dai, H. Ken, K. An, Z. Zhou, Z. Zhao, W. Wang, Z. Jiang, J. Mater. Chem. A 8 (2020) 7724–7732.
- [23] Z. Jiang, X. Xu, Y. Ma, H.S. Cho, D. Ding, C. Wang, J. Wu, P. Oleynikov, M. Jia, J. Cheng, Y. Zhou, O. Terasaki, T. Peng, L. Zan, H. Deng, Nature 586 (2020) 549–554.
- [24] D. Sun, M. Xu, Y. Jiang, J. Long, Z. Li, Small Methods 2 (2018) 1800164.
- [25] M. Tilset, C. Larabi, E.A. Quadrelli, F. Bonino, K.P. Lillerud, M. Kandiah, M. H. Nilsen, S. Usseglio, S.R. Jakobsen, U. Olsbye, Chem. Mater. 22 (2010) 6632–6640
- [26] L.J. Shen, S.J. Liang, W.M. Wu, R.W. Liang, L. Wu, J. Mater. Chem. A 1 (2013) 11473–11482.
- [27] J.L. Long, S.B. Wang, Z.X. Ding, S.C. Wang, Y.G. Zhou, L. Huang, X.X. Wang, Chem. Commun. 48 (2012) 11656–11658.
- [28] J. Xu, S. He, H.L. Zhang, J.C. Huang, H.X. Lin, X.X. Wang, J.L. Long, J. Mater. Chem. A 3 (2015) 24261–24271.
- [29] Z.G. Wang, H. Ren, S. Zhang, F. Zhang, J. Jin, J. Mater. Chem. A 5 (2017) 10968–10977.
- [30] Q. Chen, Q.Q. He, M.M. Lv, Y.L. Xu, H.B. Yang, X.T. Liu, F.Y. Wei, Appl. Surf. Sci. 327 (2015) 77–85.
- [31] A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke, P. Behrens, Chem. Eur. J. 17 (2011) 6643–6651.
- [32] T. Tsuruoka, S. Furukawa, Y. Takashima, K. Yoshida, S. Isoda, S. Kitagawa, Angew. Chem. Int. Ed. 48 (2009) 4739–4743.
- [33] L. Liao, Q. Zhang, Z. Su, Z. Zhao, Y. Wang, Y. Li, X. Lu, D. Wei, G. Feng, Q. Yu, X. Cai, J. Zhao, Z. Ren, H. Fang, F. Robles-Hernandez, S. Baldelli, J. Bao, Nat. Nanotechnol. 9 (2014) 69–73.
- [34] A. Ishikawa, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi, K. Domen, J. Am. Chem. Soc. 124 (2002) 13547–13553.
- [35] C. Liu, D. Kong, P.C. Hsu, H. Yuan, H.W. Lee, Y. Liu, H. Wang, S. Wang, K. Yan, D. Lin, P.A. Maraccini, K.M. Parker, A.B. Boehm, Y. Cui, Nat. Nanotechnol. 11 (2016) 1098–1104.
- [36] R. Fang, R. Luque, Y. Li, Green Chem. 18 (2016) 3152–3157.
- [37] X. Wang, Y. Li, J. Mater. Chem. A 4 (2016) 5247–5257.
- [38] X. Feng, Z. Li, J. Photochem. Photobiol. A: Chem. 337 (2017) 19-24.
- [39] P.W. Zheng, L. Yan, X.J. Ji, X.M. Duan, Cheminform 41 (2010) 16-19.
- [40] S. Chandrasekhar, M. Sridhar, Tetrahedron Lett. 31 (2010) 5423–5425.
- [41] D.X. Chen, C.M. Ho, Q.Y. Wu, P.R. Wu, F.M. Wong, W. Wu, Tetrahedron Lett. 49 (2008) 4147–4148.