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Fe-based Metal-Organic Frameworks (MOFs) for Highly Selective Photocatalytic Benzene Hydroxylation to Phenol

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Abstract

Phenol is one of the most important chemicals in industry. One-step selective benzene hydroxylation is an attractive yet challenging method for phenol production, especially when such a reaction can be driven by solar energy. Herein, we reported that a highly selective benzene hydroxylation to phenol can be achieved over two Fe-based metal-organic frameworks (MIL-100(Fe) and MIL-68(Fe)) under visible light irradiations using hydrogen peroxide (H_2O_2) as an oxidant. An optimum benzene conversion of 30.6% was achieved with a H_2O_2 /benzene ratio of 3:4 over MIL-100(Fe) after 24 h irradiations. ESR results and the kinetic studies suggested that a successful coupling of the photocatalysis of Fe-O clusters in Fe-based MOFs with a Fenton-like route is involved in this benzene hydroxylation process. The comparison of the structure of MOFs are highly tunable, this study highlights the great potential of using Fe-based MOFs for photocatalytic benzene hydroxylation to form phenol, which may result in an economical, sustainable and thus green process for phenol production.

Keywords: benzene hydroxylation; phenol; photocatalysis; Fe-based metal-organic frameworks; H₂O₂

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Introduction

Phenol is one of the most important chemicals in industry.¹ Currently, phenol production is based upon the three-step cumene process, which involves a hazardous cumene hydroperoxide intermediate and produces nearly equimolar amounts of acetone as co-product.^{1,2} An attractive route in phenol production is the direct one-step selective hydroxylation of benzene using environmentally friendly oxidants such as O₂, N₂O and H₂O₂.³ In particular, the direct hydroxylation of benzene to form phenol with H₂O₂ has attracted extensive recent research attention since this process is green and clean, producing only water as a byproduct. However, the direct introduction of hydroxyl functionality into benzene is challenging. Almost all the developed catalytic systems require elevated temperature and suffer from low conversion due to the notoriously low reactivity of aromatic C–H bonds.⁴ Moreover, increased reactivity of phenol relative to benzene makes the selective oxidation of benzene to phenol very difficult, especially under heating conditions.⁵

The utilization of solar light to drive chemical reactions is extremely appealing.⁶ Especially, the selective hydroxylation of benzene to phenol via photocatalysis has attracted increasing research interest.⁷ A few photocatalysts, including homogeneous and metal-doped heterogeneous catalysts, have already been reported on the selective hydroxylation of benzene to phenol.⁸ However, the performance of the currently developed photocatalytic systems for the benzene hydroxylation reaction is far from satisfactory. In addition to low benzene conversion and inferior phenol selectivity, homogeneous photocatalysts are difficult to be separated from the reaction system, while the leaching of the active species from metal-doped heterogeneous catalysts is unavoidable. The development of new type of photocatalysts with superior performance for highly selective hydroxylation of benzene is important, yet it is challenging.

Metal-organic frameworks (MOFs) are a class of crystalline micro-mesoporous hybrid materials which have already shown a variety of applications.⁹ Previous studies have revealed that MOFs can be described as an array of self-assembled molecular catalysts. The light irradiations on the MOFs can lead to the generation of electrons and holes which can take part in the redox reactions in close vicinity even though their mobility is low as compared with those in semiconductors.¹⁰ This, in combination with the inherent large surface areas, uniform but tunable cavities of

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MOFs and their tailor-able chemistry, make MOFs to be promising photocatalysts. Actually, although studies on the photocatalysis based on MOFs is still in its infancy stage, the applications of MOFs in photocatalytic CO₂ reduction,¹¹ organic transformations,¹² hydrogen evolutions,¹³ as well as pollutants degradations¹⁴ have already been demonstrated. Among all the reported MOF-based photocatalysts, Fe-containing MOFs are extremely attractive since Fe is an earth-abundant element and Fe-based MOFs show intensive absorption in visible light region due to the existence of iron-oxo (Fe-O) clusters.^{11a,14} In addition, the activation of H₂O₂ to radicals (·OH) via Fenton-like route over Fe-based MOFs as well as Fe-containing complexes have been documented.¹⁵ Given the coupling of photocatalysis based on the Fe-O clusters with activation of H₂O₂ over Fe-based MOFs is successful, the Fe-based MOFs would be promising photocatalysts for benzene hydroxylation to produce phenol.

Herein, we report the photocatalytic benzene hydroxylation to phenol with H_2O_2 over two water-stable Fe-based MOFs, MIL-100(Fe) and MIL-68(Fe). Factors influencing the performance were investigated and a possible photocatalytic mechanism of benzene hydroxylation over Fe-based MOFs was proposed. This is the first demonstration that MOF material can be used for photocatalytic benzene hydroxylation and highlights the great potential of developing MOFs as photocatalyst for organic synthesis.

Results and discussion

 MIL-100(Fe), a three-dimensional porous MOF material, was first chosen in the photocatalytic benzene hydroxylation reaction. MIL-100(Fe) is built up from supertetrahedra consisting of trimers of FeO₆ octahedra sharing a common vertex μ_3 -O, which delimits two types of mesoporous cages (Figure 1a).¹⁶ The preparation of MIL-100(Fe) followed a modified procedure reported previously.^{16b} The XRD patterns and the N₂ adsorption/desorption isotherms of the as-prepared product confirm that pure phase of MIL-100(Fe) with high quality has been obtained (Figure 2a and S1). The UV-vis spectrum of MIL-100(Fe) shows an absorption edge extending to around 600 nm, in agreement with its orange color (Figure 2b).

The benzene hydroxylation reaction was initially carried out in acetonitrile (CH_3CN) with a H₂O₂/benzene ratio to be 1:2 under visible light irradiations (Table 1, entry 1). It was found that MIL-100(Fe) can effectively hydroxylate benzene to give

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phenol in the presence of H_2O_2 as oxidant. The conversion of benzene reached 10.3% and a high selectivity to phenol (>99%) was achieved after irradiated for 8 h. No over-oxidation products such as diphenol or quinone derivatives were detected. Control experiments carried out in absence of MIL-100(Fe) or without light irradiations did not give any detectable products, suggesting that the hydroxylation of benzene to phenol over MIL-100(Fe) is really induced by photocatalysis (Table 1, entry 2 and 3).

Solvent played an important role in this reaction. As shown in Table 1 (entry 4-7), the benzene conversion ratio over MIL-100(Fe) as well as its selectivity to phenol varied in different solvents. Among all the solvents investigated, a mixed solvent containing CH_3CN/H_2O (v/v =1:1) gave the best performance by showing the highest benzene conversion ratio at 13.6% without sacrificing the selectivity to phenol (98%) (Table 1, entry 7). It is obvious that the reaction carried out in the mixed solvent is more effective in benzene hydroxylation in view of both the benzene conversion and phenol production as compared with that in CH₃CN or H₂O only. An explanation to its superior performance in this biphasic system is that the benzene hydroxylation occurs in the aqueous phase in the cavity of the MOFs since the large inner surface area of MIL-100(Fe) is hydrophilic and is easy for the aqueous phase component to diffuse into the cavities (Figure S2).^{17a} Moreover, the presence of suitable amount of CH₃CN not only increases the concentration of benzene in the aqueous phase which is favorable for the aqueous benzene hydroxylation reaction, but also can extract phenol produced into organic phase to minimize the over-oxidation of phenol by reducing the contact between phenol and catalyst. Such a promoting effect played by the mixed solvent was also observed previously in the benzene hydroxylation with H2O2 over some Fe-containing homogeneous complexes.^{17b}

Since the ratio of H_2O_2 /benzene can influence the efficiency of the benzene hydroxylation, the performance of MIL-100(Fe) for the benzene hydroxylation was investigated in different H_2O_2 /benzene ratio. When H_2O_2 /benzene ratio increased from 1:2 to 3:2, the conversion of benzene in 8 h increased from the original 13.6% to 22.5%, but a slightly reduced selectivity to phenol from the original 98% to 92% was also observed (Table 1, entry 7-10). The reduced selectivity in the presence of excessive H_2O_2 with a H_2O_2 /benzene ratio at 3:2 was mainly due to the hydroxylation of phenol by H_2O_2 to form hydroquinone at ca. 5% yield as well as the oxidation of

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 phenol to form *p*-benzoquinone at ca. 2.3% yield. This phenomenon was also observed in benzene hydroxylation catalyzed by TS-1.¹⁸ However, no byproducts were detected over the reactions in other H₂O₂/benzene ratio. A H₂O₂/benzene ratio at 3:4 gave a benzene conversion of 20.1%, a value only slightly lower than that observed over a H₂O₂/benzene ratio of 3:2 (22.5%), but can still maintain a high selectivity (98%) to phenol production (Table 1, entry 8). Therefore, a H₂O₂/benzene ratio of 3:4 was used in the following experiments. Figure 3a shows the time-dependent conversion of benzene during the hydroxylation reaction. The conversion of benzene increased with the reaction time and, due to the depletion of H₂O₂, reached a maximum benzene conversion of 30.6% after 24h illumination. The addition of H₂O₂ into the system can recover the reaction (Figure S3).

The current photocatalytic system showed superior performance in terms of both benzene conversion and selectivity to phenol as compared with those reported previously, like Fe-g-C₃N₄/SBA-15 (11.9%), Fe-CN/TS-1 (10.4%) and Au/Ti_{0.98}V_{0.02}O₂ (18.0%).¹⁹ Unlike the above mentioned photocatalytic systems which require heating or UV light irradiations, only visible light is necessary for the current system. Moreover, H₂O₂ efficiency in the current photocatalytic system (26%) is higher as compared with the above mentioned systems (Table S1), such as Fe-g-C₃N₄/SBA-15 (20.7%), Fe-CN/TS-1 (18%) and Au/Ti_{0.98}V_{0.02}O₂ (10.7%).

No further conversion of benzene occurred when MIL-100(Fe) was removed from the reaction system at 4 h (Figure 3b). The ICP analysis on the filtrate revealed no detectable Fe, indicating that the benzene hydroxylation is truly induced by heterogeneous MIL-100(Fe). Cycling test showed that there was no obvious loss of the photocatalytic activity after three runs of reactions (Figure 4). Besides these, the XRD and N₂ adsorption of the photocatalyst after the reaction did not show much change (Figure S4 and S5). All these suggest that MIL-100(Fe) can hydroxylate benzene to produce phenol under visible light and is stable during the photocatalytic reaction.

Furthermore, it was found that the experiment can be scaled up without obvious decrease of the performance. A comparable benzene conversion (19.8%) was still observed in 8h when the reaction was scaled up by a factor of 10 (Table 1, entry 11).

To gain insight into the reaction mechanism, the kinetic isotope effect (KIE) was examined. The KIE was defined as $k_{\rm H}/k_{\rm D}$, in which $k_{\rm H}$ and $k_{\rm D}$ referred to the rate

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constant for the benzene hydroxylation reaction carried out over benzene and benzene- d_6 , respectively. A plot of $\ln C_t/C_0$ (C_0 and C_t are the concentration of benzene or benezene- d_6 at 0 and t time, respectively) versus time was obtained (Figure 5). The KIE value was determined to be 1.67, which was close to the value (1.7) for Fenton-type hydroxylation.²⁰ This suggests that a Fenton-type reaction is likely to be involved in the photocatalytic benzene hydroxylation over MIL-100(Fe). The benzene hydroxylation to produce phenol by H_2O_2 is generally believed to be proceeded via an oxygenation pathway induced by the in-situ formed OH.⁷ The ESR spectrum of the irradiated reaction system containing MIL-100(Fe), benzene and H₂O₂ in the presence of 5.5-dimethyl-1-pyrroline N-oxide (DMPO) as a trapping agent shows four typical signals for the DMPO-OH adduct and thus confirmed the formation of OH radicals during the photocatalytic reaction (Figure 6a). Moreover, the addition of ethanol, a OH radical scavenger, into the catalytic system completely inhibited the benzene hydroxylation and no phenol was detected (Figure 3c). This gives another confirmation that benzene hydroxylation over MIL-100(Fe) truly follows a OH radical mediated oxygenation pathway. It was proposed that the OH radical in this system can be generated via the reduction of H_2O_2 by Fe^{2+} formed over the irradiated MIL-100(Fe), similar to that observed in the homogeneous Fe-containing complex via a Fenton-like reaction.^{15b} Actually, the ESR signal corresponding to Fe³⁺ observed in a suspension of MIL-100(Fe) and benzene was quenched when visible light was irradiated, implying that upon the light irradiation, Fe^{3+} was reduced to generate Fe^{2+} (Figure 6b). A similar reduction of Fe^{3+} to form Fe^{2+} upon light irradiation was previously observed over MIL-101(Fe), another Fe-based MOFs, and was found to be responsible for its photocatalytic CO₂ reduction.^{11a}

Based on the above observations, the mechanism for photocatalytic benzene hydroxylation to phenol over MIL-100(Fe) was proposed (scheme 1). First, when irradiated, an excited charge separation state occurs in MIL-100(Fe) by transferring electrons from O^{2-} to Fe^{3+} in the Fe-O clusters and Fe^{3+} is thus reduced to Fe^{2+} (step i). The as-formed Fe^{2+} can reduce H_2O_2 to generate active $\cdot OH$ via a Fenton-like reaction, while itself was oxidized back to Fe^{3+} (step ii). The $\cdot OH$ radical can attack benzene ring to form hydroxycyclohexadienyl radical (step iii). The release of the proton and electron from the hydroxycyclohexadienyl radical leads to the formation of phenol and regenerates the Fe-based MOF to fulfill the photocatalytic cycle (step

iv).

To further explore how the structure of the MOFs can influence its photocatalytic performance for benzene hydroxylation, MIL-68(Fe), another water-stable Fe-based MOFs, was chosen and its photocatalytic activity for benzene hydroxylation was also investigated. Unlike MIL-100(Fe), MIL-68(Fe) is assembled from the infinite straight chains of corner-sharing $FeO_4(OH)_2$ octahedra connected through a terephthalate linker, defining two types of one-dimensional channels (Figure 1b).²¹ The XRD patterns and N₂ adsorption/desorption of as-synthesized MIL-68(Fe) confirmed that MIL-68(Fe) with high quality was obtained (Figure S6). Although benzene was also hydroxylated to form phenol over the irradiated MIL-68(Fe) (Table 1, entry 12), a lower benzene conversion (14%) and phenol selectivity (90%) were observed over MIL-68(Fe) as compared with those over MIL-100(Fe) (benzene conversion, 20.1%, selectivity to phenol 98%). It is generally known that the light absorption by the photocatalyst to generate the charge carriers is the initial step for photocatalysis. The comparison of the DRS spectra of MIL-100(Fe) and MIL-68(Fe) reveals that MIL-100(Fe) shows much intensive absorption in the visible light region (Figure 2b). Therefore, an enhanced light absorption of MIL-100(Fe) as compared with MIL-68(Fe) may contribute to its superior photocatalytic performance for benzene hydroxylation. Besides this, previous studies on the catalytic activities for aerobic oxidation of alcohols over a trinuclear ruthenium carboxylate catalyst $Ru_3O(O_2CCH_3)_6(H_2O)_3$, revealed that framework containing μ_3 -O played an important role in its catalytic performance. It was believed that the existence of μ_3 -O could promote the formation of a pronounced electronic delocalized state in Ru₃O cluster, which could help the electron transfer from metal ion to oxidant (O_2) to form active species $(O_2^{-1})^{22,23}$ Since MIL-100(Fe) also contains μ_3 -O in its framework, the formation of the electronic delocalized state in Fe₃O cluster can also promote the electron transfer from the metal center to the substrate. Actually, in addition to showing higher activity for benzene hydroxylation to form phenol, MIL-100(Fe) also exhibited improved performance in the oxidation of benzyl alcohol. The conversion of benzyl alcohol to benzaldehyde over MIL-100(Fe) (44.4%) was much higher than that over MIL-68(Fe) (32.7%) in 12 h. These facts indicated that structures of MOFs indeed affect the catalytic performance. Since the composition, structure of MOFs as well as its light absorption capability can be facilely tailorable, an enhanced

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photocatalytic performance for benzene hydroxylation over the Fe-based MOFs can be expected via a judicious selection of the organic ligand to form an optimum MOF structure.

Conclusions

In conclusion, we demonstrated that MIL-100(Fe) and MIL-68(Fe), two Fe-based MOFs, can selectively hydroxylate benzene to produce phenol under visible light irradiations using aqueous H_2O_2 as oxidant. This study highlights Fe-based MOFs to be promising photocatalysts for benzene hydroxylation, which may result in an economical, sustainable and thus green process for phenol production. Considering the diversified MOF structure due to the availability of different varieties of organic linkers as well as the versatile coordination chemistry of the metal cations, we believed that more efficient Fe-based MOF photocatalysts for selective benzene hydroxylation to produce phenol can be developed.

Experimental Sections

Materials. 1,3,5-Benzenetricarboxylic acid were provided by J&K Scientific Co. 1,4-Benzenedicarboxylic acid were provided by Aladdin Co. Iron(III) nitrate nonahydrate and iron (III) chloride hexahydrate were provided by Shanghai Chemical Reagent Co. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) were provided by TCI Co. All the reagents were analytical grade and used without further purifications.

Synthesis. MIL-100(Fe) was prepared following the procedure described in the literature with slight modification.^{16b} Typically, iron(III) nitrate nonahydrate (484 mg, 1.2 mmol) and 1,3,5-benzenetricarboxylic acid (210 mg, 1.0 mmol) were dissolved in deionized water (5 mL). Then, the resulting solution was stirred and transferred to a Teflon autoclave liner and sealed to heat at 180 °C for 12 h. After a period time, the autoclave was cooled down to room temperature in air. The obtained yellow solid was recovered by filtration and washed with deionized water and methanol for several times. The synthesized MIL-100(Fe) was finally dried overnight at 60 °C in oven.

MIL-68(Fe) was prepared according to the method reported in the literature.^{15a} Typically, a mixture of iron (III) chloride hexahydrate (1.2 mmol, 324 mg), 1,4-benzenedicarboxylic acid (2.4 mmol, 798 mg), hydrofluoric acid (5 mol/L, 0.12 mL), and hydrous hydrochloride (1 mol/L, 0.12 mL) was dissolved in N,N-dimethylformamide (18 mL) in a Teflon-lined autoclave. After sonication to be a

 homogeneous solution, the mixture was heated at 100 °C for 120 h. After a period time, the autoclave was cooled down to room temperature in air. The obtained solid was recovered by filtration and washed with N,N-dimethylformamide and methanol for several times. The synthesized MIL-68(Fe) was finally dried overnight at 60 °C in oven.

Characterizations. The as-prepared sample was characterized by X-ray diffraction (XRD) patterns on a D8 Advance X-ray diffractometer (Bruker, Germany) using Cu K_{α} (λ = 1.5406 Å) radiation at a voltage of 40 kV and 40 mA. XRD patterns were scanned over the angular range of 5-30° (20) with a step size of 0.02°. N₂ adsorption/desorption experiments were measured with an ASAP 2020 M (Micromeritics Instrument Corp). After the sample was degassed in a vacuum at 150°C for 10 h, the nitrogen adsorption and desorption isotherms were measured at -196°C. UV-vis diffuse reflectance spectrum (UV-vis DRS) was obtained by a UV-vis spectrophotometer (Varian Cary 500). Barium sulfate (BaSO₄) was used as a reference. The ESR spectra were performed on a Bruker A300 ESR spectrometer. Fe content in filtrate was determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Perkin-Elmer, OPTIMA 8000).

Photocatalytic reaction. The photocatalytic benzene hydroxylation was performed as follows. In a typical catalytic process, a mixture of acetonitrile (2 ml), water (2 ml) and benzene (44 μ L, 0.5 mmol) was transferred into a 10 mL schlenk tube containing 10 mg of catalyst. The resulting biphasic system was stirred with dropwise addition of hydrogen peroxide (30 wt%, 39µL, 0.38mmol) and irradiated with a 300 W Xe lamp with a UV-cut filter to remove light with wavelengths less than 420 nm and an IR-cut filter to remove all wavelengths longer than 800 nm (Figure S7). After the reaction, the whole system was cooled down with ice-water, followed by the addition of ice-cooled ethanol (2 mL) to quench the reaction, which turn the biphasic system to a single-phase system. The products of the reaction were analyzed by a gas chromatograph (Shimadzu GC-2014) and GC-MS with toluene as the internal standard. H₂O₂ concentration was determined by colorimetric titration method based on the formation of a yellow colored $Ti(IV)-H_2O_2$ complex. The reaction solution $(210 \ \mu L)$ was added to Ti(SO₄)₂ solution (25 mmol/L, 5 mL) and was diluted to 50 mL. The resultant solution was analyzed using a UV/Vis spectrophotometer and the adsorption peaks at 430 nm for Ti(IV)-H₂O₂ complex were monitored.

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Upscaling experiment was conducted under the similar conditions in a home-made reactor. Briefly, a mixture of acetonitrile (20 ml), water (20 ml) and benzene (440 μ L, 5 mmol) was transferred into the home-made reactor containing 100 mg of catalyst. The resulting biphasic system was stirred with dropwise addition of hydrogen peroxide (30 wt%, 390 μ L, 3.8mmol) and irradiated with a 300 W Xe lamp with a UV-cut filter to remove light with wavelengths less than 420 nm and an IR-cut filter to remove all wavelengths longer than 800 nm. After the reaction, the process of treatment and products detection are similar to the previous reported.

The labeling experiments were performed over benzene and benzene- d_6 , respectively, under standard reaction conditions. The kinetic isotope effect (KIE) is defined as $k_{\rm H}/k_{\rm D}$, in which $k_{\rm H}$ and $k_{\rm D}$ is the rate constant for the benzene hydroxylation reaction carried out over benzene and benzene- d_6 respectively.

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Supporting Information Available: Detailed experimental protocols and additional characterization data are included in the supporting information. 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.

References

- Weber, M.; Weber, M.; Kleine-Boymann, M. Phenol. Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2004; Vol. 26, p 503.
- (2) Hock, H.; Lang, S. Ber. Dtsch. Chem. Ges. 1944, 77, 257-264.
- (3) (a) Acharyya, S. S.; Ghosh, S.; Tiwari, R.; Pendem, C.; Sasaki, T.; Bal, R. ACS Catal. 2015, 5, 2850-2858. (b) Navarro, R.; Lopez-Pedrajas, S.; Luna, D.; Marinas, J. M.; Bautista, F. M. Appl. Catal. A-Gen. 2014, 474, 272-279. (c) Morimoto, Y.; Bunno, S.; Fujieda, N.; Sugimoto, H.; Itoh, S. J. Am. Chem. Soc. 2015, 137, 5867-5870.
- (4) Herrerías, C. I.; Yao, X. Q.; Li, Z. P.; Li, C. -J. Chem. Rev. 2007, 107, 2546-2562.
- (5) Piera, J.; Bäckvall, J. -E. Angew. Chem. Int. Ed. 2008, 47, 3506-3523.
- (6) (a) Lang, X. J.; Chen, X. D.; Zhao, J. C. *Chem. Soc. Rev.* 2014, 43, 473-486. (b) Tong, H.; Ouyang, S. X.; Bi, Y. P.; Umezawa, N.; Oshikiri, M.; Ye, J. H. *Adv. Mater.* 2012, 24, 229-251.
- (7) Brillas, E.; Sirés, I.; Oturan, M. A. Chem. Rev. 2009, 109, 6570-6631.
- (8) (a) Ohkubo, K.; Kobayashi, T.; Fukuzumi, S. *Angew. Chem. Int. Ed.* 2011, 50, 8652-8655. (b) Ohkubo, K.; Fujimoto, A.; Fukuzumi, S. *J. Am. Chem. Soc.* 2013, 135, 5368-5371. (c) Devaraji, P.; Sathu, N. K.; Gopinath, C. S. *ACS Catal.* 2014, 4, 2844-2853.
- (9) (a) Zhu, Q. -L.; Xu, Q. Chem. Soc. Rev. 2014, 43, 5468-5512. (b) Cui, Y. J.; Yue, Y. F.; Qian, G. D.; Chen, B. L. Chem. Rev. 2012, 112, 1126-1162. (c) Zhang, T.; Lin, W. B. Chem. Soc. Rev. 2014, 43, 5982-5993. (d) Gao, W. -Y.; Chrzanowski, M.; Ma, S. Q. Chem. Soc. Rev. 2014, 43, 5841-5866. (e) Zhou, H. -C.; Kitagawa, S. Chem. Soc. Rev. 2014, 43, 5415-5418. (f) Xuan, W. M.; Zhu, C. F.; Liu, Y.; Cui, Y. Chem. Soc. Rev. 2012, 41, 1677-1695.
- (10) (a) Alvaro, M.; Carbonell, E.; Ferrer, B.; Llabrés i Xamena, F. X.; Garcia, H. *Chem. Eur. J.* 2007, 13, 5106-5112. (b) Tachikawa, T.; Choi, J. R.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. C* 2008, 112, 14090-14101. (c) Wang, J. -L.; Wang, C.; Lin, W. B. *ACS Catal.* 2012, 2, 2630-2640. (d) Nasalevich, M. A.; Goesten, M. G.; Savenije, T. J.; Kapteijn, F.; Gascon, J. *Chem. Commun.* 2013, 49, 10575-10577. (e) Nasalevich, M. A.; Veen, M. van der; Kapteijn, F.; Gascon, J. *CrystEngComm* 2014, 16, 4919-4926. (f) Nasalevich, M. A.; Becker, R.; Ramos-Fernandez, E. V.; Castellanos, S.; Veber, S. L.; Fedin, M. V.; Kapteijn, F.; Reek, J. N. H.; Vlugt, J. I. van der; Gascon, J. *Energy Environ. Sci.* 2015, 8, 364-375.

ACS Catalysis

- (11) (a) Wang, D. K.; Huang, R. K.; Liu, W. J.; Sun, D. R.; Li, Z. H. ACS Catal.
 2014, 4, 4254-4260. (b) Fu, Y. H.; Sun, D. R.; Chen, Y. J.; Huang, R. K.; Ding, Z. X.; Fu, X. Z.; Li, Z. H. Angew. Chem. Int. Ed. 2012, 51, 3364-3367. (c) Sun, D. R.; Fu, Y. H.; Liu, W. J.; Ye, L.; Wang, D. K.; Yang, L.; Fu, X. Z.; Li, Z. H. Chem. Eur. J. 2013, 19, 14279-14285.
- (12) (a) Wang, D. K.; Li, Z. H. *Catal. Sci. Technol.* 2015, 5, 1623-1628. (b) Sun, D. R.; Ye, L.; Li, Z. H. *Appl. Catal. B: Environ.* 2015, 164, 428-432. (c) Manna, K.; Zhang, T.; Greene, F. X.; Lin, W. B. *J. Am. Chem. Soc.* 2015, 137, 2665-2673.
- (13) (a) Silva, C. G; Luz, I.; Llabrés i Xamena, F. X.; Corma, A.; García, H. *Chem. Eur. J.* 2010, 16, 11133-11138. (b) Horiuchi, Y.; Toyao, T.; Saito, M.; Mochizuki, K.; Iwata, M.; Higashimura, H.; Anpo, M.; Matsuoka, M. *J. Phys. Chem. C* 2012, 116, 20848-20853.
- (14) Laurier, K. G. M.; Vermoortele, F.; Ameloot, R.; De Vos, D. E.; Hofkens, J.; Roeffaers, M. B. J. J. Am. Chem. Soc. 2013, 135, 14488-14491.
- (15) (a) Zhang, J. -W.; Zhang, H. -T.; Du, Z. -Y.; Wang, X. Q.; Yu, S. -H.; Jiang, H. -L. *Chem. Commun.* 2014, 50, 1092-1094. (b) Ma, J. H.; Song, W. J.; Chen, C. C.; Ma, W. H.; Zhao, J. C.; Tang, Y. L. *Environ. Sci. Technol.* 2005, 39, 5810-5815.
- (16) (a) Horcajada, P.; Surblé, S.; Serre,; Hong, D. -Y.; Seo, Y. -K.; Chang, J. -S.; Grenèche, J. -M.; Margiolaki, I.; Férey, G. *Chem. Commun.* 2007, 2820-2822.
 (b) Seo, Y. -K.; Yoon, J. W.; Lee, J. S.; Lee, U. -H.; Hwang, Y. K.; Jun, C. -H.; Horcajada, P.; Serre, C.; Chang, J. -S. *Micropor. Mesopor. Mater.* 2012, 157, 137-145.
- (17) (a) Zhang, P. F.; Gong, Y. T.; Li, H. R.; Chen, Z. R.; Wang, Y. *RSC Adv.* 2013, 3, 5121-5126. (b) Bianchi, D.; Bortolo, R.; Tassinari, R.; Ricci, M.; Vignola, R. *Angew. Chem. Int. Ed.* 2000, 39, 4321-4323.
- (18) (a) Barbera, D.; Cavani, F.; Alessandro, T. D; Fornasari, G; Guidetti, S.; Aloise, A.; Giordano, G; Piumetti, M.; Bonelli, B.; Zanzottera, C. J. Catal. 2010, 275, 158-169. (b) Neidig, M. L.; Hirsekorn, K. F. Catal. Commun. 2011, 12, 480-484.
- (19) (a) Chen, X. F.; Zhang, J. S.; Fu, X. Z.; Antonietti, M.; Wang, X. C. J. Am. Chem. Soc. 2009, 131, 11658-11659. (b) Ye, X. J.; Cui, Y. J.; Qiu, X. Q.; Wang, X. C. Appl. Catal. B: Environ. 2014, 152-153, 383-389. (c) Devaraji, P.; Sathu, N. K.; Gopinath, C. S. ACS Catal. 2014, 4, 2844-2853.
- (20) Augusti, R.; Dias, A. O.; Rocha, L. L.; Lago, R. M. J. Phys. Chem. A 1998, 102, 10723-10727.
- (21) Fateeva, A.; Horcajada, P.; Devic, T.; Serre, C.; Marrot, J.; Grenèche, J. -M.;

Morcrette, M.; Tarascon, J. -M.; Maurin, G.; Férey, G. *Eur. J. Inorg. Chem.* **2010**, 3789-3794.

- (22) Bilgrien, C.; Davis, S.; Drago, R. S. J. Am. Chem. Soc. 1987, 109, 3786-3787.
- (23) (a) Toma, H. E.; Araki, K.; Alexiou, A. D. P.; Nikolaou, S.; Dovidauskas, S. *Coordin. Chem. Rev.* 2001, 219-221, 187-234. (b) Toma, H. E.; Cipriano, C. J. *Electroanal. Chem.* 1989, 263, 313-322.



Figure 1 (a) Topological view of MIL-100 with MTN-type zeolitic architecture; (b) View of the structure of MIL-68 involving two types (hexagonal and trigonal) of channels running through the c-axis.



Figure 2 (a) XRD patterns of MIL-100(Fe); (b) Uv-vis spectra of MIL-100(Fe) and MIL-68(Fe).







Figure 3 Conversion ratio of benzene as a function of irradiation time in hydroxylation reaction over (a) MIL-100(Fe); (b) reaction system after MIL-100(Fe) was removed after irradiated for 4 h; (c) 1 mL ethanol was added to the reaction system.



Figure 4 The cycling use of MIL-100(Fe) for photocatalytic benzene hydroxylation.

5





0.00 R₂=0.999 benzene- d_6 $(k_{\rm D}=0.012 {\rm min}^{-1})$ -0.05 $ln(C_{t}/C_{0})$ -0.10 R₁=0.997 benzene ($k_{\rm H}$ =0.02 min⁻¹) -0.15 2 i 3 t/h

Figure 5 Kinetics studies for the benzene hydroxylation reaction.



Figure 6 (a) The DMPO spin-trapping ESR spectra for the \cdot OH radical in the presence of MIL-100(Fe) under visible light irradiation ($\lambda \ge 420$ nm); (b) ESR spectra of a mixture of MIL-100(Fe) and benzene in the dark and upon irradiations.

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Entry	Catalyst	Solvent	$H_2O_2/$	Conv./%	Sel./%	Yield/
			benzene			μmol
1	MIL-100(Fe)	CH ₃ CN	1:2	10.3	>99	51.5
2 ^[a]		CH ₃ CN	1:2	_ [d]	-	-
3 ^[b]	MIL-100(Fe)	CH ₃ CN	1:2	-	-	-
4	MIL-100(Fe)	acetone	1:2	2.4	99	11.9
5	MIL-100(Fe)	DMF	1:2	3.3	76	12.5
6	MIL-100(Fe)	H_2O	1:2	8.3	85	35.5
7	MIL-100(Fe)	CH ₃ CN/H ₂ O	1:2	13.6	98	66.5
		(1:1)				
8	MIL-100(Fe)	CH ₃ CN/H ₂ O	3:4	20.1	98	98.5
		(1:1)				
9	MIL-100(Fe)	CH ₃ CN/H ₂ O	2:2	21.7	96	104
		(1:1)				
10	MIL-100(Fe)	CH ₃ CN/H ₂ O	3:2	22.5	92	103.5
		(1:1)				
11 ^[c]	MIL-100(Fe)	CH ₃ CN/H ₂ O	3:4	19.8	98	97
		(1:1)				
12	MIL-68(Fe)	CH ₃ CN/H ₂ O	3:4	14	90	(2)
		(1:1)				63

Table 1 Photocatalytic benzene hydroxylation to form phenol over Fe-based MOFs.

Reaction conditions: benzene (0.5 mmol), H_2O_2 , photocatalyst (10 mg), solvent (4 mL), light irradiation ($\lambda \ge 420$ nm), 8 h. [a] Without photocatalyst. [b] Without light irradiation. [c] The reaction was scaled up by 10 times. [d] "-" refers to no or negligible products were detected.





Scheme 1 Possible reaction mechanism for the photocatalytic benzene hydroxylation over MIL-100(Fe).

Table of Content Graphic

