Efficient photocatalytic one-pot hydrogenation and N-alkylation of nitrobenzenes/benzonitriles with alcohols over Pd/MOFs: effect of the crystal morphology & "quasi-MOF" structure

Hongmei Cheng, Xingyu Long, Fengxia Bian, Chaofen Yang, Xingyan Liu, Heyan Jiang

PII: DOI: Reference:	S0021-9517(20)30214-1 https://doi.org/10.1016/j.jcat.2020.05.033 YJCAT 13763
To appear in:	Journal of Catalysis
Received Date:	13 March 2020
Revised Date:	25 April 2020
Accepted Date:	22 May 2020



Please cite this article as: H. Cheng, X. Long, F. Bian, C. Yang, X. Liu, H. Jiang, Efficient photocatalytic one-pot hydrogenation and N-alkylation of nitrobenzenes/benzonitriles with alcohols over Pd/MOFs: effect of the crystal morphology & "quasi-MOF" structure, *Journal of Catalysis* (2020), doi: https://doi.org/10.1016/j.jcat. 2020.05.033

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Elsevier Inc. All rights reserved.

Efficient photocatalytic one-pot hydrogenation and N-alkylation

of nitrobenzenes/benzonitriles with alcohols over Pd/MOFs:

effect of the crystal morphology & "quasi-MOF" structure

Hongmei Cheng,^[a] Xingyu Long, ^[a] Fengxia Bian,^[a] Chaofen Yang,^[b] Xingyan Liu,^[a] Heyan Jiang *^[a]

[a] Key Laboratory of Catalysis Science and Technology of Chongqing Education Commission, Chongqing Key Laboratory of Catalysis and New Environmental Materials, College of Environmental and Resources, Chongqing Technology and Business University, Chongqing 400067, China. * Corresponding author. E-mail: orgjiang@163.com.

[b] Research Center for Analysis and Measurement, Kunming University of Science and Technology, Kunming 650093, China.

Abstract

One-pot multi-step reactions over visible-light induced catalysis feature the sustainable green process. Here, ligand structure change and 2-MI coordinated modulation were adapted to adjust the crystal size, morphology and crystalline structure of Fe-MOFs; double solvent impregnation was employed for the Pd loading; "quasi-MOF" materials with retained morphology were formed with calcination under N₂. Above modified materials were employed as multifunctional photocatalysts for highly efficient one-pot hydrogenation and N-alkylation of nitrobenzenes or benzonitriles with alcohols after in situ Pd photoreduction. Photocatalytic performance was evidently affected by the Fe-MOFs crystal size, morphology, crystalline structure alteration and "quasi-MOF" construction. One-pot hydrogenation and N-alkylation of benzonitriles with alcohols was achieved with excellent catalytic performance firstly in heteroegeneous catalysis. Reaction mechanism was proposed with the assistance of in situ DRIFTS.

Keywords: Photocatalysis, Pd/quasi-MOF, N-Alkylation, Nitrobenzenes, Benzonitriles.

1. Introduction

N-alkylation products have been widely used in many important fields including pesticides, medicines as well as bioactive molecules [1]. Till now, addition, cycloaddition as well as cross coupling methods have been developed to synthesize such intermediates [2-4]. As a very important branch research in the field of green chemistry, one-pot multi-step reaction is not only

beneficial to avoid intermediates isolating and purifying, but also favorable to improve the atomic economy in practical applications [5-7]. So, different approaches have been explored to avoid harsh reaction conditions, poor atomic economics as well as difficulties in isolating and purifying intermediates in traditional N-alkylation intermediates preparation. Jiang et al. [8] used the multifunctional catalyst PdAg@MIL-101(Cr) to realize a one-pot three-step reaction, which could directly convert nitrobenzene and benzaldehyde to N-benzoaniline in the presence of 2 bar H₂. Using light to drive one-pot multi-step organic transformations under mild conditions is very attractive. Li et al. [9-13] found that N-alkyl amines could be prepared from alcohols and amines with excellent catalytic performance over MIL-100(Fe) or ZnIn₂S₄ loaded Pd nanoparticles with visible light. The N-alkylation of alcohol with amine followed a hydrogen self-transfer mechanism consisting of three continuous catalytic steps.

To achieve one-pot multi-step reaction in a single pot, multifunctional catalyst with different catalytically active sites is typically required to maintain its independent function. Metal organic frameworks (MOFs) have the advantages of diverse highly ordered porous crystalline structure, large specific surface area, easy synthesis and modification as well as good thermal stability and chemical stability [14]. Therefore, MOFs have a broad application prospect in multifunctional catalysis [15]. It is of special interest that catalytic performance could be significantly influenced with the adjustment of the MOFs crystal size, morphology as well as crystalline structure through affect the diffusion pathway of transport guest molecules and active sites exposure in nanocrystal structure [16-18]. Moreover, crystal size, morphology as well as crystalline structure adjustment in MOFs could significantly affect visible light absorption, charge separation efficiency along with charge directional transmission. Commonly used strategies for the crystal size, morphology and crystalline structure adjustment in MOFs mainly include ligand structure and central metal variation [19-21], additive introduction during MOFs synthesis through coordinated modulation strategy [22,23], and chemical etching after MOFs synthesis [24-26].

Metal nanoparticles (NPs)/MOF nanocomposites strategy was commonly applied to light-induced reactions in recent years [27-31]. However, the inorganic nodes in the metal NPs/MOF structure were isolated by coordinated ligands, which weakened the interaction between inorganic nodes and metal NPs [32]. In addition to introducing bridged moieties to improve the interaction, many strategies, such as calcination in air or inert gas to remove the organic ligands [33], have also been developed to improve the interaction between metal NPs and inorganic nodes. Recently, Tsumori et al. [34] addressed the metal/MOF composites controlled deligandation through heat treatment to obtain "quasi-MOF", which enhanced the interaction between Au nanoparticles and Cr^{3+} nodes with retained MOF porous structure. And the catalytic carbon monoxide oxidation performance was obviously improved.

In this study, crystal size, morphology along with crystalline structure adjustment in MIL-101(Fe) was firstly conducted with strategies of ligand structure variation and 2-methylimidazole (2-MI) coordinated modulation. Then Pd nanoparticles embedded in various Fe-MOFs (MIL-101(Fe), NH₂-MIL-101(Fe), MIL-101(Fe)-2MI, NH₂-MIL-101(Fe)-2MI etc.) cavities were prepared by double solvent impregnation method. Thirdly, "quasi-MOF" materials (Pd/MIL-101(Fe)-2MI(300), Pd/NH₂-MIL-101(Fe)-2MI(300), and 300 represented the calcination temperature) were formed through Pd/NH₂-MIL-101(Fe) MOFs calcination under nitrogen. With in situ photoreduction of Pd, above obtained materials were employed for highly efficient photoinduced one-pot hydrogenation and N-alkylation of a broad range of nitrobenzenes or

benzonitriles with alcohols. It is worth mentioning that one-pot hydrogenation and N-alkylation of benzonitriles with alcohols was achieved with excellent catalytic performance for the first time with heteroegeneous catalysis. Accompany with the crystal size, morphology, crystalline structure adjustment and "quasi-MOF" introduction, both photocatalytic activity and chemoselectivity in these four continuous catalytic step reactions was obviously influenced. Such as, in comparison with Pd/NH₂-MIL-101(Fe), 2-MI assisted needle-like Pd/NH₂-MIL-101(Fe)-2MI improved the nitrobenzene conversion from 82% to 100%, and N-alkylation chemoselectivity was promoted from 64% to 86%; with strong interaction formed between Pd NPs and inorganic nodes in "quasi-MOF" (Pd/NH₂-MIL-101(Fe)-2MI(300)), N-alkylation chemoselectivity promotion from 86% to 96% was achieved. In addition, the reaction mechanism was proposed with in situ diffuse reflection infrared Fourier transform spectroscopy (DRIFTS). This investigation not only demonstrated an efficient way to realize N-alkyl amines from nitrobenzenes or benzonitriles and alcohols, but also emphasized the broad application prospect of multifunctional catalysis for the organic compounds preparation in a one-pot multi-step reaction induced by visible light.

2. Results and discussion



Figure 1. The SEM images of (a) MIL-101(Fe); (b) NH₂-MIL-101(Fe); (c) MIL-101(Fe)-2MI; (d) NH₂-MIL-101(Fe)-2MI; (e) NH₂-MIL-101(Fe)-2MI(300). TEM of (f) Pd/NH₂-MIL-101(Fe)-2MI(300).

MOFs have the characteristics of structure flexibility and function adjustable, which provide opportunity to change their size, morphology and crystalline structure. We prepared a series of Fe-MOFs materials, and tried to inspect the relationship between the size, morphology along with crystalline structure change and the photocatalytic performance. The size and morphology of Fe-MOFs was characterized with scanning electron microscopy (SEM). Identical to the classical solvothermally synthesized crystal morphology [35,36], MIL-101(Fe) crystal had a typical octahedral morphology with the size of approximately 7 μ m, and NH₂-MIL-101(Fe) had an irregular polygonal structure with the size of about 3 µm (Figure 1a and 1b). To adjust the size as well as morphology of MIL-101(Fe) and NH₂-MIL-101(Fe), 2-MI was introduced as a modulator during the MIL-101(Fe)-2MI and NH₂-MIL-101(Fe)-2MI synthesis [23]. Uniform shape of grain-like MIL-101(Fe) and needle-like NH₂-MIL-101(Fe) were obtained with 2-MI assistance (Figure 1c and 1d). The size of MIL-101(Fe) as well as NH₂-MIL-101(Fe) crystals was around 11 μ m and 14 μ m, respectively. 2MI could accelerate the deprotonation rate of the carboxyl linker and promote the coordination of the ligand with the metal ion; which result in the formation and growth of different crystal nuclei, change of the crystal size as well as morphology, and increase the crystallinity. As an emerging material, "quasi-MOF" can not only maintain the porosity of the framework to a certain extent, but also promote the interaction between metal NPs and inorganic nodes [34], and the strong interaction might have special influence on the catalytic performance. Therefore, "quasi-MOF" (Pd/NH₂-MIL-101(Fe)-2MI(300)) was prepared by 300 °C calcining under N₂ for 30 min [34,37]. Original size and morphology was maintained during the "quasi-MOF" preparation (Figure 1e). The HRTEM images revealed that Pd NPs were well dispersed on NH₂-MIL-101(Fe)-2MI(300) (Figure 1f). The 0.236 nm lattice fringe matched the Pd (111) face-centered cubic plane (inset in Figure 1f), and the average particle size of Pd NPs was about 4.7 nm (Figure S1 in SI). Energy-dispersive X-ray (EDX) spectra of Pd/NH₂-MIL-101(Fe)-2MI(300) showed the presence of Fe, C, O, N and Pd elements in Pd/NH₂-MIL-101(Fe)-2MI(300) (Figure S2b in SI). Corresponding mapping images showed that Pd was well distributed on NH₂-MIL-101(Fe)-2MI support (Figure S2a in SI).



Figure 2. The XRD patterns of (a) MIL-101(Fe); (b) NH₂-MIL-101(Fe).

X-ray diffraction (XRD) is the most commonly used method to study the crystal structure and crystallinity of materials. Therefore, XRD was used to analyze the change of Fe-MOFs materials in the process of size and morphology change as well as "quasi-MOF" structure formation. According to the XRD pattern (Figure 2), the MIL-101(Fe) and NH₂-MIL-101(Fe) XRD peaks

were consistent with literature [23,35,38]. In addition, the XRD diffraction pattern of MIL-101(Fe)-2MI and NH₂-MIL-101(Fe)-2MI synthesized with the assistance of 2-MI well matched the diffraction pattern of traditional MIL-101(Fe) and NH₂-MIL-101(Fe), which indicated that MIL-101(Fe) and NH₂-MIL-101(Fe) coordination mode was not affected by 2-MI introduction and high pure 2-MI modified MIL-101(Fe)-2MI and NH₂-MIL-101(Fe)-2MI were obtained [17,23]. On the other hand, MIL-101(Fe)-2MI and NH₂-MIL-101(Fe)-2MI displayed stronger diffraction peak intensity than MIL-101(Fe) and NH2-MIL-101(Fe) owing to the crystallinity increase. After Pd loading, the XRD pattern of Pd/MIL-101(Fe)-2MI and Pd/NH₂-MIL-101(Fe)-2MI were similar to parental MIL-101(Fe) and NH₂-MIL-101(Fe), no obvious Pd diffraction was detected, which should be related to small loading as well as well dispersion. Similar to previous report [34], the diffraction peak of "quasi-MOF" Pd/NH₂-MIL-101(Fe)-2MI(300) widened at about 5°-10°, the other diffraction peaks were basically consistent with NH₂-MIL-101(Fe)-2MI. Obviously, NH₂-MIL-101(Fe)-2MI maintained a certain framework structure during the calcination. The diffraction peak intensity decrease in Pd/NH₂-MIL-101(Fe)-2MI(300) should be owing to the MOF crystal structure partly destruction caused by calcining at 300 °C [39]. Such decomposition should be beneficial to enhance the interaction between inorganic nodes and Pd NPs [34]. The Brunauer-Emmett-Teller (BET) surface areas of as-synthesized NH₂-MIL-101(Fe), NH₂-MIL-101(Fe)-2MI, Pd/NH₂-MIL-101(Fe)-2MI and Pd/NH₂-MIL-101(Fe)-2MI(300) were 994.0, 1193.3, 663.8 and 215.5 m²·g⁻¹, respectively (Table S1 in SI). The morphology adjustment with 2-MI increased the specific surface area and pore volume; after Pd NPs loading, the specific surface area and pore volume obviously decreased, implying that the cavities of the host framework were occupied by highly dispersed Pd NPs. Due to the partial organic linker decomposition and/or collapse in Pd/NH₂-MIL-101(Fe)-2MI(300) preparation, further decrease in the surface area and pore volume was detected.



Figure 3. (a) FTIR spectra of MIL-101(Fe), NH₂-MIL-101(Fe), NH₂-MIL-101(Fe)-2MI, Pd/NH₂-MIL-101(Fe)-2MI and Pd/NH₂-MIL-101(Fe)-2MI(300). (b) Raman spectra for Pd/NH₂-MIL-101(Fe), Pd/NH₂-MIL-101(Fe)-2MI(300) and Pd/NH₂-MIL-101(Fe)-2MI. XPS spectra of Fe 2p (c) and Pd 3d (d) of Pd/NH₂-MIL-101(Fe)-2MI and Pd/NH₂-MIL-101(Fe)-2MI(300).

Fourier transform infrared (FTIR), Raman, and X-ray photoelectron spectroscopy (XPS) were employed to study internal structural change during morphology regulation and "quasi-MOF" synthesis. FTIR spectrum of NH2-MIL-101(Fe)-2MI and Pd/NH2-MIL-101(Fe)-2MI were similar to NH₂-MIL-101(Fe) (Figure 3a). Strong bands in 1583 and 1384 cm⁻¹ region were attributed to symmetric and asymmetric telescopic vibration of skeleton O-C-O in MIL-101(Fe) [40]. The peak at 553 cm⁻¹ in MIL-101(Fe) and 523 cm⁻¹ in NH₂-MIL-101(Fe) were Fe-O vibration, and the peak at 1497 cm⁻¹ was related to C=C vibration in aromatic ring [41]. The 1626 and 1262 cm⁻¹ bands were attributed to N-H stretching vibration and C-N deformation vibration [42]. The absorption at 1675 cm⁻¹ in NH₂-MIL-101(Fe)-2MI should be the C=N stretching vibration from 2-MI [43]. Above results illustrated that there had no obvious change in the crystal coordination mode after size and morphology regulation, but some 2-MI may exist in NH₂-MIL-101(Fe)-2MI. After Pd NPs loading, the peak at 1626 cm⁻¹ decreased with a tendency to broaden, indicating Pd NPs should be coordinated with amino groups. For Pd/NH₂-MIL-101(Fe)-2MI(300), 1583 and 1384 cm⁻¹ peaks from 2-aminoterephthalate ligand in NH₂-MIL-101(Fe) became broaden accompany with two peaks distance decrease [23], which further evidenced the partially decompose of the organic ligand in NH₂-MIL-101(Fe). Additionally, the peak belonging to the C=N bond from 2-MI disappeared in Pd/NH₂-MIL-101(Fe)-2MI(300) FTIR spectra, indicating 2-MI had been decomposed during the "quasi-MOF" preparation.

The observation in Raman spectrum (Figure 3b) was in agreement with the FTIR result. In Pd/NH₂-MIL-101(Fe), the band at 1627 cm⁻¹ was the C-O stretching, 1454 cm⁻¹ was the out-of-phase stretching vibration of carboxylate group. The band at 1272 cm⁻¹ was the deformation vibration of the carboxylate group. Three bands at 860, 690 and 630 cm⁻¹ were C-C telescopic vibration and C-H stretching vibration [44-46]. The 1350 cm⁻¹ in Pd/NH₂-MIL-101(Fe)-2MI should be the deformation vibration of C=N bond from 2-MI [47,48]. Peaks at 1400-1700 cm⁻¹ were assigned to characteristic peaks of 2-aminoterephthalate ligand from NH₂-MIL-101(Fe)-2MI. For Pd/NH₂-MIL-101(Fe)-2MI(300), peaks around 1400-1700 cm⁻¹ became broaden and decreased in intensity after the decomposition of NH₂-MIL-101(Fe)-2MI structure during the "quasi-MOF" preparation.

XPS was used to check the chemical valence of Fe and Pd in the catalysts and the change in binding energy during the formation of a "quasi-MOF" structure (Figures 3c, 3d, and Figure S4 in SI). The XPS of Fe 2p in Pd/NH₂-MIL-101(Fe)-2MI showed two peaks at 711.3 and 724.8 eV, which were Fe 2p3/2 and Fe 2p1/2 from Fe(III), respectively. The 716.7 eV satellite peak should also be owing to Fe(III) in Figures 3c [49]. In Pd/NH₂-MIL-101(Fe)-2MI(300), Fe 2p3/2 and Fe 2p1/2 were at 711.5 and 725.0 eV, which indicated that partial decomposition of NH₂-MIL-101(Fe)-2MI framework changed the coordination environment of Fe and increased its binding energy. Pd/NH₂-MIL-101(Fe)-2MI had two peaks at 335.0 and 340.2 eV assigning to Pd⁰ 3d5/2 and Pd⁰ 3d3/2, which demonstrated the existence of Pd NPs in the sample (Figures 3d) [50]. On the other hand, the two peaks of Pd⁰ 3d5/2 and Pd⁰ 3d3/2 in Pd/NH₂-MIL-101(Fe)-2MI(300)

moved to higher binding energy (335.2 and 340.4 eV (Figures 3d) when compared to the Pd/NH_2 -MIL-101(Fe)-2MI. The increase in Pd⁰ 3d5/2 and Pd⁰ 3d3/2 binding energy should be caused by the strong interaction between Pd NPs and inorganic nodes.



Figure 4. TGA of Pd/NH₂-MIL-101(Fe) and Pd/NH₂-MIL-101(Fe)-2MI.

To further confirm the presence of 2-MI in the crystal structure, thermogravimetric analysis (TGA) was performed with Pd/NH₂-MIL-101(Fe) and Pd/NH₂-MIL-101(Fe)-2MI. TGA results (Figure 4) show that Pd/NH₂-MIL-101(Fe) and Pd/NH₂-MIL-101(Fe)-2MI had almost the same thermal behavior. The crystal structure decomposed above 300 °C, and the thermal stability of Pd/NH₂-MIL-101(Fe) was slightly lower than Pd/NH₂-MIL-101(Fe)-2MI, possibly due to the low crystallinity in Pd/NH₂-MIL-101(Fe). The first stage weight loss before 150 °C was the release of solvent molecule (e.g. H₂O and methanol) adsorbed on NH₂-MIL-101(Fe) and NH₂-MIL-101(Fe)-2MI surface [51], weight loss was 7.4%. The second stage weight loss was between 150 and 300 °C, weight loss was 10.7%, which should be the further release of DMF in the pores and the elimination of OH, Cl groups [52], and there was no significant difference in the weight loss of the two crystals at this stage. The third stage weight loss of Pd/NH₂-MIL-101(Fe) after 300 °C was about 42.9% (molecular formula of NH2-MIL-101(Fe) is C24H15ClO13N3Fe3, and the theoretically loss in the third stage should be 44.2%), corresponding to the completely decomposition of 2-aminoterephthalate ligand, and the main residual product was Fe₂O₃ [53]. The third weight loss for Pd/NH₂-MIL-101(Fe)-2MI was about 48.4%. Considering 2-MI would be completely decomposed at about 200 °C, the Pd/NH₂-MIL-101(Fe)-2MI thermal stability improvement above 300 °C should be explained that the existence of 2-MI in NH₂-MIL-101(Fe) channel was beneficial for the overall framework structure stability.



Figure 5. (a) UV-Vis diffuse reflectance spectra, (b) Plots of $(Ahv)^2$ vs photon energy.

The photocatalytic performance is largely depend on the light absorbing ability and the charge carrier separation efficiency, so the light absorbing ability of the catalyst were investigated with UV-Vis diffuse reflectance spectra (DRS). All materials had visible region absorption in UV-vis DRS (Figure 5a) indicating the photocatalysis feasibility. It could be seen from the diagram that the absorption of NH₂-MIL-101(Fe) in visible light region was stronger than MIL-101(Fe), which illustrated the functionalization of amino group in ligand not only regulated the particle size and morphology of MIL-101(Fe) but also greatly enhanced the NH₂-MIL-101(Fe) absorption in the visible region. Strongest absorption band was observed around 350 nm for Fe-MOFs, which was induced by " π - π " transitions between ligands [54]. The NH₂-MIL-101(Fe)-2MI absorption enhancement accompanied with the crystal morphology change and the crystallinity increase in visible light region should be beneficial to the Fe₃- μ_3 - α_5 clusters excitation [55]. It was also found that Pd/NH₂-MIL-101(Fe)-2MI(300) could improve light absorption in compared with Pd/NH₂-MIL-101(Fe)-2MI, but the light absorption in the 500-600 nm was slightly decreased. This decrease should be caused by the partial decomposition in the 2-aminoterephthalate ligand, which reduced the absorption of the ligand in this region [54]. The band gap could be estimated from the Tauc plots of $(Ahv)^2 vs$ photon energy (Figure 5b). Fe-MOFs band gaps were around 2.76, 2.57 and 2.57, 2.39, 2.22 eV for MIL-101(Fe), NH₂-MIL-101(Fe), NH₂-MIL-101(Fe)-2MI, Pd/NH₂-MIL-101(Fe)-2MI and Pd/NH₂-MIL-101(Fe)-2MI(300), respectively. It is worth noting that the addition of 2-MI had no obvious effect on the NH₂-MIL-101(Fe) band gap as well as light absorption and utilization ability. On the other hand, the amine group in ligand, Pd NPs loading and "quasi-MOF" construction had obvious influence on the band gap and light absorption and utilization ability of Fe-MOFs.



Figure 6. (a) Photocurrent responses, and (b) EIS Nyquist plots for MIL-101(Fe), MIL-101(Fe)-2MI, NH₂-MIL-101(Fe)-2MI, NH₂-MIL-101(Fe)-2MI(300) and Pd/NH₂-MIL-101(Fe)-2MI(300).

Photocurrent measurements were employed to determine photogenerated charge separation efficiency, where higher photocurrent usually associated with better photocatalytic performance [56]. The photocurrent response curves (Figure 6a) showed that the introduction of amino and 2MI, the formation of "quasi-MOF" structure, and the loading of Pd NPs were all conducive to the improvement of photocurrent. The study found that Pd/NH2-MIL-101(Fe)-2MI(300) had the highest charge separation efficiency. Electrochemical impedance spectroscopy (EIS) was utilized identify the carrier mobility (Figure 6b). EIS results demonstrated to that Pd/NH₂-MIL-101(Fe)-2MI(300) had the smallest radius, which meant the lowest charge transfer resistance and the highest charge transfer efficiency. At the same time, the introduction of amino group, 2-MI, and the formation of "quasi-MOF" structure were conducive to charge transfer. In short, Pd/NH₂-MIL-101(Fe)-2MI(300) displayed brilliant photoresponsive properties, which should be related to unique structure, matched band gap, efficient charge separation along with electron transfer.

 Table 1. Light-induced one-pot hydrogenation and N-alkylation of nitrobenzene with benzyl alcohol over Pd/Fe-MOFs.

la	NO ₂ + OH catalyst hv, N ₂ 2a	₩ 3a	H 4a	,	ВА	∕NH₂ +	C H
Entry	Catalyst	Base	1a	S	Sel. /%	6	Aldehyde
Entry	Catalyst	Dase	Conv. /%	3a	4a	BA	/µmol
1	Pd/MIL-101(Fe)-2MI	K ₃ PO ₄	100	7	85	8	174
2	MIL-101(Fe)-2MI	K_3PO_4	_a	-	-	-	-
3 ^b	-	K_3PO_4	-	-	-	-	-
4 ^c	Pd/MIL-101(Fe)-2MI	K_3PO_4	-	-	-	-	-
5	Pd/MIL-101(Fe)-2MI	-	-	-	-	-	40
6 ^d	Pd/MIL-101(Fe)-2MI	K_3PO_4	100	10	85	5	169
7	Pd/MIL-101(Fe)-2MI	КОН	74	71	29	-	244

Journal Pre-proofs							
8	Pd/MIL-101(Fe)-2MI	K_2CO_3	92	13	75	12	241
9	Pd/MIL-101(Fe)-2MI	K ₂ HPO ₄	30	12	80	8	202
10	Pd/MIL-101(Fe)-2MI	KHCO ₃	86	10	80	10	191
11	Pd/MIL-101(Fe)-2MI	Et ₃ N	29	34	66	-	293
12	Pd/MIL-101(Fe)	K_3PO_4	73	23	51	26	210
13e	Pd/MIL-101(Fe)	K ₃ PO ₄	72	22	50	28	213
14	Pd/NH ₂ -MIL-101(Fe)	K ₃ PO ₄	82	16	64	20	198
15	Pd/NH ₂ -MIL-101(Fe)-2MI	K ₃ PO ₄	100	4	86	10	166
16	Pd/MIL-101(Fe)-2MI(300)	K ₃ PO ₄	100	5	91	3	146
17	Pd/NH ₂ -MIL-101(Fe)-2MI(300)	K ₃ PO ₄	100	4	96	-	139
18	Pd/NH ₂ -MIL-101(Fe)-2MI(350)	K ₃ PO ₄	94	11	83	1	153

Reaction conditions unless otherwise noted: 1a (0.1 mmol), 2a (3 mmol), 0.1 mmol% catalyst (based on Pd), base additive (0.2 mmol), CH₃CN (2 mL), N₂, 0.75 W cm⁻² blue LED, irradiated for 24 h, conversion and chemoselectivity were analyzed by GC and GC-MS. ^a "-" referred to no products or negligible products were detected. ^b No catalyst. ^c Without light irradiation, 80 °C. ^d NaBH₄ reduced Pd. ^e Add the 2-MI(0.02 mmol).

N-alkylamines have broad application prospects in the synthesis of fine chemicals, pharmaceuticals and agrochemicals [1]. In most catalytic studies, N-alkylamines were synthesized through halobenzenes and benzylamines [57-59]. Interestingly, anilines and alcohols were employed for N-alkylamines synthesis under visible light in recent years [9-13]. However, the use of more challenging starting materials like nitrobenzenes or benzonitriles for the clean one-pot, multi-step and highly chemoselectivie N-alkylamines synthesis is still rather attractive and challenging. In table 1, the as-prepared Pd/Fe-MOF nanocomposites were employed to catalyze N-alkylation reactions with nitrobenzene (1a) and benzyl alcohol (2a) with visible light in CH₃CN. Reaction was initially carried out with the Pd/MIL-101(Fe)-2MI nanocomposite as the photocatalyst and K₃PO₄ as the base additive. Nitrobenzene was completely converted in 24 h, with 85% chemoselectivity to N-benzylaniline (4a). N-benzylideneaniline (3a) and aniline (BA) were the byproducts (Table 1, entry 1). The combination of Pd with MIL-101(Fe)-2MI was necessary, no catalyst or just MIL-101(Fe)-2MI as the catalyst had no photocatalytic activity (Table 1, entries 2-3). In the absence of visible-light, no nitrobenzene conversion was detected with 80 °C for 24 h, which indicated that catalytic activity was induced by visible-light (Table 1, entry 4). Base additives were reported to have promotion effect on the catalytic hydrogenation and dehydrogenation [60,61], similar phenomenon was observed in our photocatalytic system and nitrobenzene hydrogenation could not be initiated in the absence of K_3PO_4 (Table 1, entry 5). For comparison, the Pd/MIL-101-2MI prepared by NaBH₄ reduction was also used as the photocatalyst in the one-pot hydrogenation and N-alkylation, and both the conversion of nitrobenzene and the chemoselectivity to N-benzylaniline (4a) were nearly identical to Pd/MIL-101(Fe)-2MI prepared by photoreduction (Table 1, entries 1 vs 6). The results indicated that the Pd NPs should reasonably be the catalytic center during the photocatalytic N-benzylaniline. In short, above results indicated the N-alkylation of nitrobenzene with benzyl alcohol over Pd/MIL-101(Fe)-2MI nanocomposites was truly visible light induced photocatalysis, while base additive introduction was an essential factor.

In order to clarify the effect of base, N-alkylation reaction was carried out with K₃PO₄, KOH, K₂CO₃, K₂HPO₄, KHCO₃ and Et₃N base additives (Table 1, entries 7-11). K₃PO₄ was found to be

the best base additive. It was obvious that base additive K_3PO_4 played the key role in the nitrobenzene photocatalytic hydrogenation initiation (Table 1, entries 1 vs 5). Considering the role of base additives on heterogeneous photocatalytic organic reactions was rarely studied, some other experiment was carried out to clarify the effect of the base additive. Such as, when aniline was used to replace nitrobenzene without or with base additive K₃PO₄ under the same reaction conditions for 12 h, the conversion of aniline was increased from 39% to 60% accompany with the 4a chemoselectivity increase from 36% to 82% (Table S2 in SI). As we all know, the formation of imine from benzaldehyde and aniline is very fast, therefore, the improvement of aniline conversion indicated that base additive K_3PO_4 had a significant promotion effect on the benzyl alcohol oxidation to benzaldehyde. The increase in 4a chemoselectivity indicated that the base additive K₃PO₄ also accelerated the C=N group hydrogenation. Effect of light color on the catalytic performance was further investigated. Pd/MIL-101(Fe)-2MI was utilized as the photocatalyst to test one-pot hydrogenation and N-alkylation reaction with different lights including white, blue, green, cyan and red LED (0.75 W cm⁻²), respectively. The influence of the light source on the nitrobenzene conversion and the 4a chemoselectivity was obvious, and the blue LED was the best light source (Figure 7). 450-600 nm light absorption should be related to the excitation of Fe₃- μ_3 -oxo clusters in the MIL-101(Fe) frame, which belonged to the Fe³⁺ d-d transition [62]. The blue LED wavelength was 460-465 nm, and $Fe_3-\mu_3$ -oxo clusters could be excited more easily under this blue light radiation.



Figure 7. Pd/NH₂-MIL-101(Fe)-2MI photocatalyzed one-pot hydrogenation and N-alkylation of nitrobenzene with benzyl alcohol under different light sources.

The morphology and crystallinity change in MOF materials would affect the charge separation, charge transport along with photocatalytic performance [63,64]. In this study, we modified the morphology and crystallinity characteristics of Fe-MOFs by introducing the amino group in the organic linker ligand or applying 2-MI coordination modulator during the growth of Fe-MOF. The relationship between morphology along with crystallinity of Fe-MOFs and one-pot hydrogenation and N-alkylation catalytic reaction performance was evaluated with Pd/Fe-MOFs as the catalyst. Only 73% nitrobenzene was hydrogenated with 51% chemoselectivity to **4a** over Pd/MIL-101(Fe) catalyst (Table 1, entry 12). This result indicated that the introduction of 2-MI in the material synthesis process not only adjusted the morphology and crystallinity of the material, but also improved the photocatalytic activity and chemoselectivity (Table 1, entries 1 *vs* 12). In order to clarify whether the photocatalytic performance improvement was owing to the presence of 2-MI or not, an appropriate amount of 2-MI was introduced to the Pd/MIL-101(Fe) catalyzed

reaction and almost no change in photocatalytic performance was observed (Table 1, entries 12 vs 13), which suggested the improvement of catalytic capability should be caused by the morphology and crystallinity change. With the amino group introduced in the organic linker ligand and the 2-MI added to assist NH₂-MIL-101(Fe)-2MI synthesis, further catalytic performance improvement was observed with the Pd/NH₂-MIL-101(Fe)-2MI morphology and crystallinity change (Table 1, entries 14-15). Compared with the 82% conversion and 64% chemoselectivity to 4a with Pd/NH₂-MIL-101(Fe), the conversion of nitrobenzene could reach 100% with 86% chemoselectivity to 4a over Pd/NH₂-MIL-101(Fe)-2MI (Table 1, entry 15). The catalytic performance improvement with the amino group in organic linker ligand should be ascribed to the improved metal stabilization and dispersion in the presence of amino group along with the elevated light absorption ability accompany with the morphology change (Table 1, entries 12 vs 14 and entries 1 vs 15). Furthermore, the catalytic property optimization with the 2-MI addition should be reasonably related to the light absorption enhancement accompany with crystallinity and morphology adjustment (Table 1, entries 1 vs 12 and entries 14 vs 15). It was reported that "quasi-MOF" could promote the interaction between metal NPs and inorganic nodes, and the influence of "quasi-MOF" structure on photocatalytic performance was further investigated. After the "quasi-MOF" treatment, 100% conversion and 91% chemoselectivity to 4a was attained with Pd/MIL-101(Fe)-2MI(300) with nitrobenzene and benzyl alcohol (Table 1, entry 16), in addition, up to 96% chemoselectivity to 4a was achieved with completely conversion over "quasi-MOF" based material Pd/NH₂-MIL-101(Fe)-2MI(300) (Table 1, entry 17). In combination with XPS, above catalytic result indicated that the strong interaction between metal Pd and inorganic nodes was successfully formed with the partially remove of the organic ligand to fabricate "quasi-MOF" and this strong interaction was favorable to the one-pot hydrogenation and N-alkylation catalytic performance promotion. Further increase the material calcination temperature, Pd/NH₂-MIL-101(Fe)-2MI(350) showed 94% conversion with 83% chemoselectivity to 4a (Table 1, entry 18). The catalytic activity decrease should be owing to the serious decomposition of the MOF structure, which was also observed in TGA. In addition, the stability of the catalyst was determined with Pd/NH₂-MIL-101(Fe)-2MI(300) in light-induced one-pot hydrogenation and N-alkylation reaction. Pd/NH₂-MIL-101(Fe)-2MI(300) showed high stability and recyclability, and no catalytic activity and chemoselectivity loss was detected in five cycling tests (Figure 8), and the XRD pattern of the catalyst is similar before and after five tests (Figure S5 in SI).



Figure 8. Cycling of Pd/NH2-MIL-101(Fe)-2MI(300) for the one-pot hydrogenation and N-alkylation of nitrobenzene with benzyl alcohol under visible light irradiation.

The one-pot hydrogenation and N-alkylation of nitrobenzenes with alcohols to generate N-alkylated amines over Pd/NH₂-MIL-101(Fe)-2MI(300) nanocomposite was also explored in Table 2. Different substituted nitrobenzenes and alcohols could be converted to N-alkyl anilines with good to excellent activity and chemoselectivity. Nitrobenzenes with electron-withdrawing substituents exhibited significantly conversion decrease (Table 2, entries 2-7). For contrast, the conversion for nitrobenzenes with electron-donating groups was much better owing to the electronic effect (Table 2, entries 8-12). Meanwhile, the steric effect also had obvious influence on the catalytic performance, such as, ortho-substituted substrates and meta-substituted substrates exhibited obviously lower catalytic activity and chemoselectivity than para-substituted substrates (Table 2, entries 6 vs 7, 8 vs 9, 10 vs 11). Similarly, the hydrogenation and N-alkylation reactions between different alcohols and nitrobenzene proceeded with good to excellent activity and chemoselectivity after 24 h with Pd/NH₂-MIL-101(Fe)-2MI(300) nanocomposite (Table 2, entries 13-15). The substrates could also be extended to nitrobenzene and alkyl alcohol, and the conversion of nitrobenzene was 28%, and the chemoselectivity to N-alkylamine was 56% (Table 2, entry 16).

Table 2. Light-induced one-pot hydrogenation and N-alkylation of nitrobenzenes with benzyl alcohol over Pd/NH₂-MIL-101(Fe)-2MI(300)

R_1 + R_2 OH hv, N_2 R + R_1 4							
Entry	Sut	ostrate	1	4 9 -1 /0/	Aldehyde		
	R ₁	R ₂	Conv./%	4 Sel. /%	/µmol		
1	Н	Phenyl	100	96	139		
2	o-Cl	Phenyl	75	86	126		
3	p-Cl	Phenyl	76	84	124		
4	<i>p-</i> F	Phenyl	71	88	133		
5	р-СНО	Phenyl	80	87	156		
6	o-COCH ₃	Phenyl	37	86	199		
7	<i>m</i> -COCH ₃	Phenyl	82	95	128		
8	o-OCH ₃	Phenyl	89	90	174		
9	<i>p</i> - OCH ₃	Phenyl	96	92	151		
10	<i>о</i> -СН ₃	Phenyl	91	90	112		
11	<i>p</i> -CH ₃	Phenyl	96	94	142		
12	<i>р</i> -ОН	Phenyl	91	93	159		
13	Н	<i>p</i> -Methoxyphenyl	76	88	67		
14	Н	<i>p</i> -Methylphenyl	90	93	119		
15	Н	o-Methylphenyl	70	85	45		
16	Н	Propyl	28	56	24		

	+ R ₂	$H \xrightarrow{\text{catalyst}}_{\text{hv},\text{N}_2} \longrightarrow \prod_{i=1}^{i}$	^H R ₂
1	2	К ₁	4

Reaction conditions unless otherwise noted: 1 (0.1 mmol), 2 (3 mmol), 0.1 mmol% Pd/NH₂-MIL-101(Fe)-2MI(300) (based on Pd), K_3PO_4 (0.2mmol), CH₃CN (2 mL), N₂, 0.75 W cm⁻² blue LED, irradiated for 24 h, conversion and chemoselectivity were analyzed by GC and GC-MS.

Benzonitriles and their derivatives are wildly used in synthetic organic chemistry, chemical industry and biological applications [65,66]. The one-pot hydrogenation and N-alkylation of benzonitriles with alcohols was also attempted over Pd/NH₂-MIL-101(Fe)-2MI(300) nanocomposite, and the reaction between the benzyl alcohol and benzonitrile (5) was adopted as the model reaction (Table 3, entries 1-3). It was found that the one-pot hydrogenation and N-alkylation product dibenzylamine (7) could be achieved with 57% conversion and 88% chemoselectivity after irradiated for 24 h under N₂. Considering the reduction of nitrile group was more difficult than nitro group, 1 atm H₂ was introduced and the N-alkylation product dibenzylamine (7) could be synthesized with 85% conversion and 94% chemoselectivity in 24 h, when the reaction time was extended to 30 h, the benzonitrile conversion could reach 91% with 95% chemoselectivity to N-alkylamine (Table 3, entry 2). To the best of our knowledge, this is the first N-alkylation report between benzonitriles and alcohols with heterogeneous catalysis. When pure benzyl alcohol was used as the solvent, both the conversion of benzonitrile and the chemoselectivity to N-alkylamine were decreased (Table 3, entry 3). Pd/NH₂-MIL-101(Fe)-2MI was also used as the catalyst for the reaction under the same conditions, and the conversion rate of benzonitrile was only 44% (Table 3, entry 4). The conversion decrease further proved that calcination to form "quasi-MOF" could improve the photocatalytic performance. The reaction could not be carried out in the dark at 80 °C (Table 3, entry 5). Different substituted benzyl alcohols and benzonitriles could also be converted to the corresponding N-alkyl anilines with good activity and excellent chemoselectivity (Table 3, entries 6-12). Introduction of both strong electron-withdrawing group (- CF_3) and strong electron-donating group (-OMe) to the benzonitriles obviously decreased the photocatalytic activity, however, the chemoselectivity was almost maintained (Table 3, entries 6, 9). When the reaction time was extended to 48 h, the p-Trifluoromethylbenonitrile conversion could reach 85% with 92% chemoselectivity to N-alkylamine (Table 3, entry 6). When moderate electron-donating group substituted tolunitriles were the substrates, slightly increase in photocatalytic activity along with almost maintained chemoselectivity to N-alkylamines was observed (Table 3, entries 7-8 vs 2). The N-alkylation reaction between different substituted benzyl alcohols and benzonitrile was also carried out, and both the benzonitrile conversion and the chemoselectivity to N-alkylamines was decreased (Table 3, entries 10-12). Both the steric bulk and the electronic nature of substrate influenced the photocatalytic performance.

Table 3. Light-induced one-pot hydrogenation and N-alkylation of different benzonitriles with alcohols over Pd/NH₂-MIL-101(Fe)-2MI(300).

R₁—CN	I + R ₂ ОН_	catalyst hv,H ₂ R ₁ N R ₂		R ₂ +	.R1	► _{NH2} +	R ₂ —CHO
5	2	6	7		Bi	A	
Entre	5	2	5		Sel. /	V ₀	Aldehyde
Entry	5	2	Conv. /%	6	7	BiA	/µmol
1ª	Benzonitrile	Benzyl alcohol	57	12	88	_b	179

2	Benzonitrile	Benzyl alcohol	85(91) ^c	6	94(95) ^c	-	126
3 ^d	Benzonitrile	Benzyl alcohol	42	15	85	-	214
4 ^e	Benzonitrile	Benzyl alcohol	44	12	86	2	209
5 ^f	Benzonitrile	Benzyl alcohol	-	-	-	-	-
6	p-Trifluoromethylbenonitrile	Benzyl alcohol	45(85) ^g	9	91(92) ^g	-	189
7	o-Tolunitrile	Benzyl alcohol	85	6	91	3	130
8	<i>p</i> -Tolunitrile	Benzyl alcohol	89(93) ^c	8	92(92) ^c	-	121
9	<i>m</i> -Anisonitrile	Benzyl alcohol	39(56) ^g	5	87(91) ^g	10	206
10	Benzonitrile	p-Methoxybenzyl alcohol	65	8	85	7	67
11	Benzonitrile	p-Methylbenzyl alcohol	68	5	87	8	119
12	Benzonitrile	o-Methylbenzyl alcohol	31	10	84	6	45

(0.1)Reaction conditions unless otherwise noted: 5 mmol), 2 (6 mmol), 0.1 mmol% Pd/NH₂-MIL-101(Fe)-2MI(300) (based on Pd), K₂CO₃ (0.2mmol), CH₃CN (2 mL), 1 atm H₂, 0.75 W cm⁻² blue LED, irradiated for 24 h, conversion and selectivity were analyzed by GC and GC-MS. ^a N₂ instead of H₂. ^b "-" referred to no products or negligible products were detected. c Irradiated for 30 h. d Benzyl alcohol (2 mL) was used as a solvent. e Pd/NH2-MIL-101(Fe)-2MI was used as catalyst. f Without light irradiation, 80 °C. g Irradiated for 48 h.

With above catalytic system characterization and one-pot hydrogenation along with N-alkylation reaction exploration, it is reasonable to clearly clarify the effect of "quasi-MOF" structure on the photocatalytic performance in the Pd/MOFs photocatalytic system. The XPS of Pd/NH₂-MIL-101(Fe)-2MI(300) confirmed that calcination to form a "quasi-MOF" structure could promote the interaction between Pd NPs and organic nodes. This improved interaction could reduce the band gap and improve the light absorption, charge separation, electron transfer along with utilization in one-pot hydrogenation and N-alkylation reactions. Therefore, Pd/NH₂-MIL-101(Fe)-2MI(300) exhibited better photocatalytic performance in comparison with Pd/NH₂-MIL-101(Fe)-2MI.

In order to study the visible light induced activation of substrates in the Pd/NH₂-MIL-101(Fe)-2MI(300) photocatalytic system, in situ DRIFTS test was conducted to analyze the difference in nitro and alcohol activation in the dark at 50 °C or under light irradiation at room temperature with simulated photocatalytic conditions. Nitrobenzene and p-methylbenzyl alcohol were used as the substrates, and in situ DRIFTS showed the relative changes in the catalytic system (Figure 9). The baseline spectrum was tested before light irradiation or heating. The following characteristic peaks decreasing or increasing were obviously observed in the in situ DRIFTS during light irradiation or heating, such as the decrease in tensile vibration of O-H bond in p-methylbenzyl alcohol between 3300 and 3700 cm⁻¹; the decrease in asymmetric tensile vibration of N-O bond in nitrobenzene between 1500 and 1600 cm⁻¹; the decrease in the O-H in-plane deformation vibration and C-O tensile vibration in p-methylbenzyl alcohol around 1200 and 1100 cm⁻¹ [67,68]; meanwhile, the increase in the aldehyde group C-H bond stretching vibration around 3200 cm⁻¹; the increase in C-N stretching vibration in product N-(4-methylbenzyl) aniline at about 850 cm⁻¹[69]. With Pd/NH₂-MIL-101(Fe)-2MI(300) catalyst in the dark at 50 °C, the O-H tensile vibration, the N-O asymmetric tensile vibration, the O-H in-plane deformation vibration and the C-O tensile vibration gradually decreased with heating time increase, which should be related to the substrate catalytic activation with heating. For

comparison, the decrease in the O-H tensile vibration, the N-O asymmetric tensile vibration, the O-H in-plane deformation vibration as well as the C-O tensile vibration with visible light irradiation at 25 °C was much faster than heating. Additionally, the increase in the aldehyde group C-H bond stretching vibration and the N-alkylation product N-(4-methylbenzyl) aniline C-N bond stretching vibration was evidently observed with visible light irradiation at 25 °C. Obviously, the activation efficiency promotion with visible light irradiation was much faster than that of heating in the benzyl alcohol dehydrogenation, the nitro group reduction was well as the N-alkylation product formation, which should be the key reason for the evident one-pot hydrogenation and N-alkylation catalytic efficiency improvement with visible light.



Figure 9. In situ DRIFTS of the one-pot hydrogenation and N-alkylation of nitrobenzene with *p*-methylbenzyl alcohol over Pd/NH₂-MIL-101(Fe)-2MI(300).

Mechanism for the light induced one-pot hydrogenation and N-alkylation of nitrobenzene with benzyl alcohol over Pd/NH₂-MIL-101(Fe)-2MI(300) could therefore be proposed (Scheme1). When NH₂-MIL-101(Fe)-2MI(300) was irradiated with light, Fe₃- μ_3 -oxo clusters were excited to generate electrons and holes (step i). Photogenerated electrons on NH₂-MIL-101(Fe)-2MI(300) would reduce the adsorbed of Pd²⁺ to Pd NPs, and then other photogenerated electrons were transferred from NH₂-MIL-101(Fe)-2MI(300) to Pd NPs to form electron-rich Pd species (step ii). Meanwhile, benzyl alcohol adsorbed on the surface reacted with photogenerated holes to create alkoxide intermediate (step iii). Subsequently, the alkoxide intermediate was further oxidized by photogenerated holes, and C-H was cleaved to form benzaldehyde, accompany with the hydrogen transferred to the electron-rich Pd to generate Pd-H hydride (step iv). Part of Pd-H hydride was utilized to reduce nitrobenzene to aniline (step V). The Lewis acidic Fe^{3+} in NH₂-MIL-101(Fe)-2MI(300) promoted the condensation between the benzaldehyde and aniline to form an imine (step vi). Finally, another part of the hydride of Pd-H was used to reduce the imine to a secondary amine (step vii). N-Alkylation of benzonitriles with alcohols should be preceded through a similar hydrogen auto-transfer mechanism. In addition, the photocatalytic performance improvement with morphology change and "quasi-MOF" structure construction should mainly be related to the promotion in photoelectrons and holes separation efficiency, along with the electrons transformation capability, which was confirmed by the change in photocurrent and electrochemical impedance.



Scheme1. Plausible reaction mechanism for the visible-light induced one-pot synthesis of N-alkylamine.

3. Conclusion

In conclusion, Fe-MOFs with different crystal size, morphology and crystalline structure were constructed with strategies of ligand structure change and 2-MI coordinated modulation. XRD revealed that the presence of 2-MI did not change the coordination mode of MIL-101(Fe) and NH₂-MIL-101(Fe). After Pd loading with double solvent impregnation method, "quasi-MOF" materials formation with retained morphology and Pd in situ photoreduction with visible light, highly efficient one-pot photocatalytic hydrogenation and N-alkylation of a broad range of nitrobenzenes and benzonitriles with alcohols were carried out with above constructed multifunctional catalytic materials. The Fe-MOFs crystal size, morphology, crystalline structure alteration and "quasi-MOF" structure construction were demonstrated to have obvious influence on the photocatalytic performance of one-pot multi-step continuous catalytic step hydrogenation and N-alkylation reactions. With strong interaction formed between Pd NPs and inorganic nodes "quasi-MOF" Pd/NH₂-MIL-101(Fe)-2MI(300), nitrobenzene photocatalytic one-pot hydrogenation and N-alkylation chemoselectivity promotion from 86% to 96% was achieved. This work established a highly efficient way to realize N-alkyl amines from nitrobenzenes or benzonitriles and alcohols via a successful coupling of the ligand structure and 2-MI based crystal size, morphology and crystalline structure optimization in Fe-MOFs, double solvent impregnation method based Pd loading into Fe-MOFs, "quasi-MOF" based strong interaction between Pd NPs and inorganic nodes, as well as Pd NPs based one-pot multi-step hydrogenation. In situ DRIFTS spectra verified that substrates activation with visible light irradiation at 25 °C was much faster than heating in one-pot hydrogenation and N-alkylation reaction. This work highlights the great potential of multifunctional photocatalysis in light-induced one-pot multi-step organic transformation.

Acknowledgements

This work was financially supported by Natural Science Foundation Project of CQ (No. cstc2018jcyjAX0735, cstc2019jcyj-msxmX0641), National Natural Science Foundation of China (No. 21201184), Ministry of Education of Chongqing (No. KJQN201900811), Chongqing Technology and Business University (950119090) and Chongqing Key Laboratory of Catalysis and New Environmental Materials (KFJJ2019082).

References

- [1] J.R. Cabrero-Antonino, R. Adam, M. Beller, Angew. Chem. Int. Ed., 58 (2019) 12820-12838. <u>https://doi.org/10.1002/anie.201810121</u>
- [2] X.H. Yang, L.L. Zhao, T. Fox, Z.H. Wang, H. Berke, Angew. Chem. Int. Ed., 49 (2010) 2058-2062. <u>https://doi.org/10.1002/anie.200906302</u>
- [3] B, Basu, S. Paul, A.K. Nanda, Green Chem., 11 (2009) 1115–1120. https://doi.org/10.1039/B905878H
- [4] P. Zhou, Z.H. Zhang, L. Jiang, C.L. Yu, K.L. Lv, J. Sun, S.G. Wang, Appl. Catal. B-Environ., 210 (2017) 522-532. <u>https://doi.org/10.1016/j.apcatb.2017.04.026</u>
- [5] Y.J. Song, H. Wang, S.J. Liang, Y. Yu, L.Y. Li, L. Wu, J. Catal. 361 (2018) 105-115. <u>https://doi.org/10.1016/j.jcat.2018.02.005</u>
- [6] W.W. Yu, X.W. Guo, C.S. Song, Z.K. Zhao, J. Catal., 370 (2019) 97-106. <u>https://doi.org/10.1016/j.jcat.2018.12.011</u>
- [7] Y.R. Zhang, Y.J. Gao, S.Y. Yao, S.W. Li, H. Asakura, K. Teramura, H.J. Wang, D. Ma, ACS Catal., 9 (2019) 7967-7975. <u>https://doi.org/10.1021/acscatal.9b01429</u>
- [8] Y.Z. Chen, Y.X. Zhou, H.W. Wang, J.L. Lu, T. Uchida, Q. Xu, S.H. Yu, H.L. Jiang, ACS Catal., 5 (2015) 2062–2069. <u>https://doi.org/10.1021/cs501953d</u>
- [9] D.K. Wang, Z.H. Li, J. Catal., 342 (2016) 151-157. https://doi.org/10.1016/j.jcat.2016.07.021
- [10] D.K. Wang, Y.T. Pan, L.Z. Xu, Z.H. Li, J. Catal., 361 (2018) 248-254. https://doi.org/10.1016/j.jcat.2018.02.033
- [11] B.Q. Wang, Z.R. Deng, X.Z. Fu, C. Xu, Z.H. Li, Appl. Catal. B-Eenviron., 237 (2018) 970-975. <u>https://doi.org/10.1016/j.apcatb.2018.06.067</u>
- [12] B.Q. Wang, G.S. Liu, X.Y. Deng, Z.R. Deng, W. Lin, Z.H. Li, J. Catal., 383 (2020) 304-310. <u>https://doi.org/10.1016/j.jcat.2020.01.021</u>
- [13] D.K. Wang, J. Albero, H. Garcia, Z.H. Li, J. Catal., 349 (2017) 156-162. <u>https://doi.org/10.1016/j.jcat.2017.01.014</u>
- [14] J.H. Wang, Y. Zhang, M. Li, S. Yan, D. Li, X.M. Zhang, Angew. Chem. Int. Ed., 56 (2017) 6478-6482. <u>https://doi.org/10.1002/anie.201701217</u>
- [15] A. Dhakshinamoorthy, Z.H. Li, H. Garcia, Chem. Soc. Rev., 47 (2018) 8134-8172. <u>https://doi.org/10.1039/C8CS00256H</u>
- [16] J.M. Yang, Q. Liu, W.Y. Sun, Microporous Mesoporous Mater., 190 (2014) 26–31. <u>https://doi.org/10.1016/j.micromeso.2014.01.020</u>
- [17] C.Y. Guo, Y.H. Zhang, L. Zhang, Y. Zhang, J.D. Wang, CrystEngComm., 20 (2018) 5327-5331. <u>https://doi.org/10.1039/C8CE00954F</u>
- [18] N. Shi, D. Xu, X. Zhou, L. Song, L. Li, L. Xie, L. Wang, M. Yi, W. Huang, CrystEngComm., 18 (2016) 4830–4835. <u>https://doi.org/10.1039/C6CE00818F</u>

- [19] R. Anderson, J. Rodgers, E. Argueta, A. Biong, D.A. Gomez-Gualdron, Chem. Mater., 30 (2018) 6325-6337. <u>https://doi.org/10.1021/acs.chemmater.8b02257</u>
- [20] Y.J. Sun, L.X. Sun, D.W. Feng, H.C. Zhou, Angew. Chem. Int. Ed., 55 (2016) 6471-6475. <u>https://doi.org/10.1002/anie.201602274</u>
- [21] F.C. Leng, H. Liu, M.L. Ding, Q.P. Lin, H.L. Jiang, ACS Catal., 8 (2018) 4583–4590. <u>https://doi.org/10.1021/acscatal.8b00764</u>
- [22] C. Avci, J. Ariñez-Soriano, A. Carné-Sánchez, V. Guillerm, C. Carbonell, I. Imaz, D. Maspoch, Angew. Chem., Int. Ed., 54 (2015) 14417-14421. https://doi.org/10.1002/anie.201507588
- [23] C.Y. Guo, Y.H. Zhang,Y. Guo, L.G. Zhang,Y. Zhang, J.D. Wang, Chem. Commun., 54 (2018) 252-255. <u>https://doi.org/10.1039/C7CC07698C</u>
- [24] J. Koo, I.C Hwang, X. Yu, S. Saha, Y. Kim, K. Kim, Chem. Sci., 8 (2017) 6799-6803. <u>https://doi.org/10.1039/C7SC02886E</u>
- [25] Z.J. Zhang, M.J. Zaworotko, Chem. Soc. Rev., 43 (2014) 5444-5455. https://doi.org/10.1039/C4CS00075G
- [26] R.C. Arbulu, Y.B. Jiang, E.J. Peterson, Y. Qin, Angew. Chem., Int. Ed., 57 (2018) 5813-5817. <u>https://doi.org/10.1002/anie.201802694</u>
- [27] Q.H. Yang, Q. Xu, H.L. Jiang, Chem. Soc. Rev., 46(2017) 4774-4808. https://doi.org/10.1039/C6CS00724D
- [28] D.R. Sun, Z.H. Li, J. Phys. Chem. C., 120 (2016) 19744–19750. https://doi.org/10.1021/acs.jpcc.6b06710
- [29] X.Y. Deng, Z.H. Li, H. Garcia, Chem. Eur. J., 23 (2017) 11189-11209. <u>https://doi.org/10.1002/chem.201701460</u>
- [30] X.Y. Deng, M.M. Hao, Z.H. Li, Current Org. Chem., 22 (2018) 1825-1835. https://doi.org/10.2174/1385272822666180419161532.
- [31] D.R. Sun, M.P. Xu, Y.T. Jiang, J.L. Long, Z.H. Li, Small Methods., 2 (2018) 1800164. https://doi.org/10.1002/smtd.201800164
- [32] G.W. Zhan, H.C. Zeng, Coordin. Chem. Rev., 320 (2016) 181–192. https://doi.org/10.1016/j.ccr.2016.03.003
- [33] W.T. Koo, S.J. Choi, S.J. Kim, J.S. Jang, H.L. Tuller, I.D. Kim, J. Am. Chem. Soc., 138 (2016) 13431–13437. <u>https://doi.org/10.1021/jacs.6b09167</u>
- [34] N. Tsumori, L.Y. Chen, Q.J. Wang, Q.L. Zhu, M. Kitta, Q. Xu, Chem., 4 (2018) 845–856. <u>https://doi.org/10.1016/j.chempr.2018.03.009</u>
- [35] A.D.S. Barbosa, J.D. Fernandes, A.F. Peixoto, C. Freire, B. de Castro, C.M. Granadeiro, S.S. Balula, L. Cunha-Silva, Polyhedron., 127 (2017) 464–470. https://doi.org/10.1016/j.poly.2016.10.032
- [36] X.H. L, A.K. Tjiptoputro, J. Ding, J.M. Xu, Y.H. Zhu, Catal. Today, 279 (2017) 77-83. https://doi.org/10.1016/j.cattod.2016.03.044
- [37] L.L. Fan, F.G. Zhao, Z.L. Huang, B. Chen, S.F. Zhou, G.W. Appl Catal A-Gen. 572 (2019) 34-43. <u>https://doi.org/10.1016/j.apcata.2018.12.021</u>
- [38] Z.G. Zhang, X.Y. Li, B.J. Liu, Q.D. Zhao, G.H. Chen, RSC Adv., 6 (2016) 4289-4295. <u>https://doi.org/10.1039/C5RA23154J</u>
- [39] Y. Shen, L.W. Bao, F.Z. Sun, T.L. Hu, Mater. Chem. Front., 3 (2019) 2363-2373. https://doi.org/10.1039/C9QM00277D

- [40] J. Sun, G. Yu, Q. Huo, Q. Kan and J. Guan, RSC Adv., 4 (2014) 38048–38054. <u>https://doi.org/10.1039/C4RA05402D</u>
- [41] T.A. Vu, G.H. Le, C. D. Dao, L.Q. Dang, K.T. Nguyen, P.T. Dang, H.T. Tran, Q.T. Duong, T.V. Nguyen, G.D. Lee, RSC Adv., 4 (2014) 41185–41194. <u>https://doi.org/10.1039/C4RA06522K</u>
- [42] A. Modrow, D. Zargarani, R. Herges, N. Stock, Dalton Trans., 41 (2012) 8690–8696. <u>https://doi.org/10.1039/C2DT30672G</u>
- [43] C.Y. Guo, Y.H. Zhang, L. Zhang, Y. Zhang, Naeem Akram, J.D. Wang, ACS Appl. Nano Mater. 1 (2018) 5289–5296. <u>https://doi.org/10.1021/acsanm.8b01283</u>
- [44] L. Shen, S. Liang, W. Wu, R. Liang, L. Wu, Dalton Trans., 42 (2013) 13649–13657. https://doi.org/10.1039/C3DT51479J
- [45] O.V. Zalomaeva, K.A. Kovalenko, Y.A. Chesalov, M.S. Mel'gunov, V.I. Zaikovskii, V.V. Kaichev, A. B. Sorokin, O. A. Kholdeeva, V. P. Fedin, Dalton Trans., 40 (2011) 1441–1444. <u>https://doi.org/10.1039/C0DT01474E</u>
- [46] S. S. Balula, C. M. Granadeiro, A. D. S. Barbosa, I. C. M. S. Santos, L. Cunha-Silva, Catal. Today., 210 (2013) 142–148. <u>https://doi.org/10.1016/j.cattod.2012.12.003</u>
- [47] D.A. Carter, J.E. Pemberton, K.J. Woelfel, J. Phys. Chem. B, 102 (1998) 9870–9880. <u>https://doi.org/10.1021/jp982741g</u>
- [48] D.A. Carter, J.E. Pemberton, Raman Spectrosc. 28 (1997) 939-946.
- [49] S.H. Dong, Z. Liu, R.H. Liu, L.M. Chen, J.Z. Chen, Y.S. Xu, ACS Appl. Nano Mater., 8 (2018) 4247-4257. <u>https://doi.org/10.1021/acsanm.8b01039</u>
- [50] S. Xu, M. Wang, B. Feng, X.C. Han, H.J. Gu, H.X. Li, J. Catal. 363 (2018) 9-17. <u>https://doi.org/10.1016/j.jcat.2018.04.006</u>
- [51] Y.L. Hu, Z.L. Huang, L.J. Zhou, D.M. Wang, G.K. Li, J. Sep. Sci., 37 (2014) 1482–1488. <u>https://doi.org/10.1002/jssc.201400100</u>
- [52] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, Science, 309 (2005) 2040–2042. <u>https://doi.org/10.1126/science.1116275</u>.
- [53] M. Almášia, V. Zeleňáka, P. Palotaia, E. Beňováa, A. Zeleňákováb, Inorg Chem Commun., 93 (2018) 115-120. <u>https://doi.org/10.1016/j.inoche.2018.05.007</u>
- [54] D. Wang, R. Huang, W. Liu, D. Sun, Z. Li, ACS Catal., 4 (2014) 4254–4260. <u>https://doi.org/10.1021/cs501169t</u>
- [55] S. Bordiga, C. Lamberti,G. Ricchiardi, L.Regli, F. Bonino, A. Damin, K.P. Lillerud, M. Bjorgen, A. Zecchina, Chem. Commun., 20 (2004) 2300–2301. https://doi.org/10.1039/B407246D
- [56] X.Y. Dao, J.H. Guo, JH Y.P. Wei, F. Guo, Y. Liu, W.Y. Sun, Inorg. Chem., 58 (2019) 8517-8524. <u>https://doi.org/10.1021/acs.inorgchem.9b00824</u>
- [57] C.T. Yang, Y. Fu, Y.B. Huang, J. Yi, Q.X. Guo, L. Liu, Angew. Chem. Int. Ed., 48 (2009) 7398-7401. <u>https://doi.org/10.1002/anie.200903158</u>
- [58] M.N. Pahalagedara, L.R. Pahalagedara, D. Kriz, S.Y. Chen, F. Beaulieu, W. Thalgaspitiya, S.L. Suib, Appl. Catal. B-Environ., 188 (2016) 227-234. <u>https://doi.org/10.1016/j.apcatb.2016.02.007</u>
- [59] M. Ousmane, G. Perrussel, Z. Yan, J.-M. Clacens, F. De Campo, M. Pera-Titus, J. Catal. 309 (2014) 439-452. <u>https://doi.org/10.1016/j.jcat.2013.10.003</u>

- [60] S. Elangovan, C. Topf, H.J. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge, M. Beller, J. Am. Chem. Soc., 138 (2016) 8809–8814. <u>https://doi.org/10.1021/jacs.6b03709</u>
- [61] Y.Y. Zhang, J.X. Li, L.L. Ding, L. Liu, S.M. Wang, Z.B. Han, Inorg. Chem., 57 (2018) 13586–13593. <u>https://doi.org/10.1021/acs.inorgchem.8b02206</u>
- [62] D.K. Wang, M.T. Wang, Z.H. Li, ACS Catal., 5 (2015) 6852–6857. https://doi.org/10.1021/acscatal.5b01949
- [63] K.H. Li, D.H. Olson, J. Seidel, T.J. Emge, H.W. Gong, H.P. Zeng, J. Li, J. Am. Chem. Soc., 131 (2009) 10368-10369. <u>https://doi.org/10.1021/ja9039983</u>
- [64] F. Wang, X.X. He, L.M. Sun, J.Q, Chen, X.J. Wang, J.H. Xu, X.G. Han, J. Mater. Chem. A., 5 (2018) 2091-2099. <u>https://doi.org/10.1039/C7TA09166D</u>
- [65] Y.Y. Cao, L.B. Niu, X. Wen, W.H. Feng, L. Huo, G.Y. Bai, J. Catal., 339 (2016) 9-13. <u>https://doi.org/10.1021/ja102759z</u>
- [66] J. Neumann, C. Bornschein, H.J. Jiao, K. Junge, M. Beller, Eur. J. Org. Chem., 27 (2015) 5944–5948. <u>https://doi.org/10.1002/ejoc.201501007</u>
- [67] G. Richner, J.A. van Bokhoven, Y.M. Neuhold, M. Makosch, K. Hungerbuhler, Chem. Phys., 13 (2011) 12463–12471. <u>https://doi.org/10.1039/C1CP20238C</u>
- [68] L.C. Liu, P. Concepcion, A. Corma, J. Catal., 369 (2019) 312–323. https://doi.org/10.1016/j.jcat.2018.11.011
- [69] K.A Kumar, T.S. Sreelekha, K.N. Shivakumara, K.C. Prakasha, D.C. Gowda, Synthetic Commun., 39 (2009) 1332-1341. <u>https://doi.org/10.1002/chin.200938067</u>

Declaration of interests

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:





Highlights

1. MOF morphology, crystalline structure alteration and "quasi-MOF" construction affect photocatalytic performance.

2. Efficient photocatalytic one-pot hydrogenation and N-alkylation of nitrobenzenes and benzonitriles.

3. N-alkylation of benzonitriles with alcohols was achieved firstly in heteroegeneous catalysis.

4. Reaction mechanism was proposed with the assistance of in situ DRIFTS.