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# Nickel–alkyne–functionalized metal–organic frameworks: An efficient and reusable catalyst

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#### ABSTRACT

Electron-donating groups in the robust MOF motif are able to provide an excellent catalytic platform, therefore obtaining site-isolated metal sites. In this study, the terminal alkyne is firstly introduced into UiO-66-type metal-organic frameworks (UiO-66-alkyne). Herein, to further study the application potential of this material, a covalently bonded nickel catalyst based on the alkynyl-tagged UiO-66-alkyne has been prepared and afforded us unprecedented highly dispersed and highly efficient catalytic active species. Meanwhile, this nickel-contained catalyst method for joining metals provided an alternative pathway regarding catalyst designing. With UiO-66-alkyne-Ni, the heterogeneous transformation of homogeneous catalysts is realized. Using benzaldehyde and malononitrile as starting materials, we were able to catalyze the Knoevenagel condensation within 45 min under room temperature with yield (> 99 %). Moreover, the recovery rate of the UiO-66-alkyne-Ni also outperformed previous MOFs in both small-scale and gram-level reactions, which shows UiO-66-alkyne-Ni is a potential contributor to the subsequent industrialization.

#### 1. Introduction

With an increasing emphasis on environmental protection and green chemistry [1], it is urgent to eliminate the pollution of industrial catalysts effectively. The Knoevenagel condensation is a fundamental reaction to form carbon-carbon bonds [2–4], which can be used for the preparation of substituted olefins and coumarin derivatives. In the industrial field [5,6], Knoevenagel condensation is widely used for the synthesis of cosmetics, perfumes, polymers, and pharmaceuticals [7,8]. However, basic organic compounds such as amine, pyridine, urea and piperidine, are used as catalysts for this reaction in the traditional industrial production process [9]. All of the aforementioned homogeneous catalysts are not recoverable and are likely to cause serious environmental pollution due to the product separation issues [10,11]. The heterogeneous transformation of homogeneous catalysts may solve these problems, because heterogeneous catalysts not only improve the stability of catalysts that accompanied without any product separation issue, but also be able to reduce environmental pollutions [12]. As such, developing the supported catalysts for Knoevenagel condensation has become a research hotspot [13,14], and many researches were focused on finding novel catalytic carriers such as zeolite [15], carbon nanotubes [16], silica gel [17], graphene [18] and metal – organic frameworks (MOFs) [19], etc..

MOFs, as novel porous organic-inorganic hybrid materials, have great application potential in catalytic-related programs [20–23]. Dhakshinamoorthy and co-workers reported two Al-MOFs with CAU-1

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Fig. 1. Alkynyl as a liner to connect MOF and metal.

and CAU-10-type structures and successfully catalyzed the Knoevenagel condensation reaction under mild conditions (40  $^{\circ}$ C, in ethanol) [24]. In 2019, Gong and co-workers reported a MOF catalyst that based on UiO-66 (UiO-67-BPY@UiO-66), which could achieve an efficient conversion of Knoevenagel condensation at room temperature, indicating the catalytic potential of this types of structure in the Knoevenagel condensation reaction [25].

Functionalization is the distinctive property of MOF materials. Postsynthesis modification (PSM) represents an attractive functionalization strategy for modifying pores of MOFs through introducing catalytic active sites that endows MOFs a huge contribution in the field of catalysts [26–31]. For UiO-66 [32], several organic tagged-groups have been introduced into UiO-66 including aldehydes [33], amino [34], or nitro groups [35]. Among them, the introduction of amino groups was considered able to improve the catalytic performance of UiO-66 significantly [36,37], whereas other functional groups were not helpful. Therefore, it is necessary to introduce new functional groups into UiO-66 to meet the needs of the catalyst field.

As a common functional group, the alkyne has good chemical activity. On one hand, terminal alkyne, as a weak acid, can react with alkali metals or heavy metal ions to form metal alkyne. On the other hand, terminal alkyne can act as two-electron donors to coordinate with transition metals [38,39]. As such, we considered the terminal alkynyl groups as a "linker" to connect metallic active sites and MOF material therefore making the metallic active sites distributed on the surface of the MOF material evenly (Fig. 1). The introduction of the terminal alkynyl groups onto the network of MOFs will pave us a new promising way to obtain site-isolated and coordinatively unsaturated metal sites for catalytic application [40,41]. In 2015, Li et al. reported an alkyne-tagged MOF (UiO-68-alkyne) and developed a new MOF material with an azido functional group [27]. To the best of our knowledge, very few alkynyl functionalized MOFs have been reported, potentially due to the difficulties of the synthesis thereof. Metallic platinum (Pt) [38] and metallic palladium (Pd) [39], as well as non-precious metals such as copper (Cu) [42] and metallic nickel (Ni) [43] can bond with terminal alkynes. Among them, nickel is widely used in industry due to its low cost and high catalytic activity, however, it is the main source of heavy metal pollutions [44–46]. Therefore, if nickel can be introduced into the MOF material through bonding reactions, the usage amount of nickel-metal can be reduced, and therefore reducing the environmental nickel-metal pollutions.

In this work, the synthesis of alkynyl-tagged UiO-66 MOFs is reported for the first time. To be specific, a stable alkynyl-tagged Zr(IV)based MOF (UiO-66-alkyne) in water and acidic media was synthesized by utilizing BDC-alkynyl (2-Alkynyl-1,4-benzene dicarboxylic acid) as the ligand under relatively mild hydrothermal or solvothermal conditions. Based on the new functionalized MOF motif, the catalytic active site of nickel is firstly incorporated into UiO-alkyne by bonding with terminal alkynyl groups (UiO-66-alkyne-Ni). As a heterogeneous catalyst, UiO-66-alkyne-Ni shows excellent catalytic activity, stability, and industrialization prospects for catalyzing Knoevenagel condensation.

#### 2. Experimental section

#### 2.1. Materials and instruments

**Chemicals:** 2-Bromoterephthalic acid, trimethylsilyl acetylene, benzaldehyde, malononitrile, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, PPh<sub>3</sub>, other aldehyde derivatives were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), Acros or other suppliers and were used without any further purifications. All solvents and chemicals used in this work are analytical grade.

**Characterizations:** Powder X-ray diffraction (PXRD) were measured on a D2 PHASER. diffractometer (CuK $\alpha$ ,  $\lambda =$ 1.54056 Å). The morphology of MOF materials in this work was obtained by transmission electron microscope 120 kV (TEM: HT7700 Exalens) and scanning electron microscope (SEM: MERLIN Compact 6164, ZEISS). X-ray photoelectron spectra (XPS) related tests such as element content and valence analysis were all tested by X-ray photoelectron spectroscopy instrument (PHI 5000 C&PHI 5300) with a dual X-ray anode (Mg and Al). Fourier transform infrared (FTIR) spectra were obtained on a Bruker Alpha FTIR spectrometer using potassium bromide as a reference. The N<sub>2</sub> adsorption-desorption isotherm of the catalysts was measured by fully automatic specific surface and micropore analyser (AUTOSORB-IQ). NMR data were recorded with a Mercury plus 400 MHz (Varian, Inc., Palo Alto, CA, USA) or Bruker ASCEND 600 MHz NMR system.

#### 2.2. Synthesis of a MOF-ligand

As shown in Scheme 1, MOF-ligand (see the Fig.S5 for the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the *MOF-ligand*) and UiO-66-C $\equiv$ CH could be synthesized by following a similar published procedure [28].



Scheme 1. Synthesis routes of the MOF-ligand, UiO-66-alkyne and UiO-66-alkyne-Ni.

**Compound 1** To a solution of 2-bromoterephthalic acid (7.5 g, 40 mmol) in 250 mL methanol, conc.  $H_2SO_4$  (15 mL) was added slowly. Then being stirred at 65 °C overnight. After methanol was removed by evaporation, 300 mL ethyl acetate (EA) was added. The mixture was washed with K<sub>2</sub>CO<sub>3</sub> solution (1 M) and dried with Na<sub>2</sub>SO<sub>4</sub>. Finally, the crude product **1** was purified by flask silica gel column chromatography (white solid 7.7 g, yield 92.2 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d, *J* = 1.8 Hz, 1 H), 8.12 - 7.93 (m, 1 H), 7.81 (t, *J* =6.7 Hz, 1 H), 4.00–3.93 (m, 6 H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  167.96, 164.36, 137.47, 134.56, 132.18, 129.76, 126.96, 122.04, 47.07.

**Compound 2** 2-bromoterephthalate (7.7 g, 28.2 mmol), trimethylsilyl acetylene (3.1 g, 31.0 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (790 mg, 1.2 mmol), CuI (110 mg, 0.56 mmol) and PPh<sub>3</sub> (180 mg, 1.2 mmol) were dissolved in Et<sub>3</sub>N, then stirred at 90 °C under N<sub>2</sub> atmosphere. After reacting for 9 h, the mixture was filtered with EA and the solvent was removed. The crude product was purified by flask silica gel column chromatography to give desired compound **2** (white solid 5.3 g, yield 64.6 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 – 8.20 (m, 1 H), 7.96 (ddd, J = 12.5, 8.4, 4.1 Hz, 2 H), 3.97 – 3.91 (m, 6 H), 0.28 (q, J = 4.8, 3.8 Hz, 9 H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  166.90, 164.40, 136.41, 134.30, 132.16, 130.13, 128.21, 123.78, 101.55, 100.35, 50.62, 1.22.

**Compound 3** To the solution of dimethyl 2-((trimethylsilyl)ethynyl) terephthalate (5.3 g, 17.2 mmol) in 50 mL THF, tetra-*n*-butylammonium fluoride THF solution (15 mL, 1 M) was added. Then the mixture was quenched with H<sub>2</sub>O and extracted with EA. The mixture was dried with NaOH and EA was removed by reduced pressure. The crude product was purified by column chromatography to give the pale red product **3** (solid 3.5 g, yield 90 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.27 (d, *J* =1.9 Hz, 1 H), 8.06 – 7.94 (m, 2 H), 3.95 (d, *J* =2.8 Hz, 6 H), 3.46 (d, *J* =1.6 Hz, 1 H). <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  166.53, 164.81, 141.23, 134.41, 132.39, 129.71, 128.23, 122.28, 84.00, 79.60, 50.69.

**Compound 4** To the solution of compound **3** (3.5 g, 16.1 mmol) in THF (50 mL), aqueous KOH solution (4 %, 50 mL) was added. Then stirred at room temperature overnight, the THF was removed and the reaction mixture was acidified with 1.0 M HCl aqueous solution. The crude product was collected by filtration and washed with water (2 × 50 mL). Then the compound **4** was obtained by reduced pressure (solid 2.7 g, yield 90 %). <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  13.50 (s, 2 H), 8.04 (s, 1 H), 8.00 (d, *J* =8.1 Hz, 1 H), 7.93 (d, *J* =7.8 Hz, 1 H), 4.50 (s, 1 H). <sup>13</sup>C NMR (600 MHz, DMSO)  $\delta$  167.28, 166.48, 138.98, 135.30, 134.00, 130.72, 129.33, 122.25, 86.73, 81.23.

#### 2.3. Preparation of UiO-66-alkyne and UiO-66-alkyne-Ni

**UiO-66-alkyne** To a solution of compound 4 (300 mg, 1.57 mmol),  $ZrCl_4$  (262.8 mg, 1.12 mmol) in DMF (30 mL) and HCl (2 mL) was added, the mixture was placed in a 50 mL vial. After all solids were dissolved by ultrasound, the mixture was heated to 80 °C and kept at this temperature for 12 h. The crude product was isolated by centrifugation and washed three times with DMF and MeOH, respectively. The residual solvents in the centrifuged microcrystalline powders were removed under vacuum. The as-obtained powder was dried to give the white solid (solid 424.5 mg, yield 89 %).

**UiO-66-alkyne-Ni** UiO-66-alkyne-Ni was synthesized with the similar published procedure used to synthesize small molecule [43]. UiO-66-alkynyl (100 mg) was added into the solution of Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (300 mg), and CuI (13 mg) in a 10 mL mixed solvent (CH<sub>2</sub>Cl<sub>2</sub>: TEA = 1:1), then stirred for about 12 h. The catalyst powders were collected through being filtered and washed DCM ( $3 \times 50$  mL) and TEA ( $3 \times 50$  mL). Then the solid was dried under reduced pressure to give the product (solid 245 mg, yield 80 %).

#### 2.4. Catalytic reaction

Knoevenagel condensations were all carried out in 5 mL small round bottom flasks. Put benzaldehyde (1 mmol), malononitrile (1.1 mmol),



Fig. 2. XRD patterns of the UiO-66, MOF-ligand, UiO-66-alkyne at different temperature, UiO-66-alkyne-Ni and UiO-66-alkyne-Ni-recycle.

catalyst, and methanol (0.3 mL) into the flask. The reaction was carried out at room temperature. After the reaction was completed, 100  $\mu$ L dibromomethane was added, and the yield was determined by <sup>1</sup>H NMR.

#### 2.5. Recycling test

In order to determine the stability of the catalyst UiO-66-alkyne-Ni after reuse, the catalyst was separated by centrifugation, washed with DCM and TEA, and then the catalyst was dried for the next use, and the reaction was catalyzed under the same conditions. Then the yield was determined by  $^{1}$ H NMR.

#### 3. Results and discussion

## 3.1. Preparation and characterization of the UiO-66-alkyne and UiO-66-alkyne-Ni

Previous work showed that the formation process of tagged UiO-66 can be modulated through varying reaction temperature [33]. Therefore, the influence of temperature on the formation of MOF in the synthesis of UiO-66-alkyne was explored. It can be seen from Table S1 that the UiO-66-alkyne cannot be formed normally at 60 °C, and MOF appeared at 80 °C. Compared with entries under 100 °C (83 %) or 120 °C (72 %), the yield of UiO-66-alkyne at 80 °C (89 %) was the highest under the premise of the same feeding amount. The PXRD patterns suggested that the as-synthesized UiO-66-alkyne and UiO-66 were isomorphic. The diffraction peaks of UiO-66-alkyne synthesized at different temperatures (Fig. 2) were overlapped, showing the synthesis temperature that ranged from 80 °C to 120 °C could afford us UiO-66-alkyne with pure phase. The SEM images of the UiO-66-alkyne synthesized at 80 °C and 120 °C exhibited that UiO-66-alkyne under lower temperature had more uniform particle size and morphology (Fig. 3 and Fig S1 in Supporting Information). Therefore, 80 °C was chosen as the best synthesis temperature according to the analysis results.

Metallic nickel is non-precious therefore is widely used in industrial catalysis. In view of the mild reaction of terminal acetylene with nickel chloride [43], a facile chemical method has been developed to incorporated the nickel centers into the network of UiO-66 through bonding reactions between the terminal alkynyl groups and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in a weakly basic solvent under the catalysis of CuI (Scheme 1). Here, it is expected to synthesize highly stable non-noble metal heterogeneous catalysts with active site separation using the stable chemical bond.



Fig. 3. SEM images: UiO-66-alkyne synthesized at 80 °C (a-b); UiO-66-alkyne-Ni (c-d); UiO-66-alkyne-Ni-recycle (e-f).

#### 3.2. Characterization UiO-66-alkyne and UiO-66-alkyne-Ni

The morphology and crystal size of MOF materials can be determined via field-emission scanning electron microscopy (FE-SEM) (Fig. 3). The HRSEM images of UiO-66-alkyne illustrated an octahedral shape morphology with particle size ~140 nm and its particle size uniform (Fig. 3(a) and (b)). Compared with UiO-66-alkyne, UiO-66-alkyne-Ni is slightly changed regarding morphology, however, overall morphology and particle size were still well-maintained after the introduce of nickel into the frameworks (Fig. 3(c) and (d)). A same conclusion could be drawn from the TEM images too (Fig. 4). Similar to UiO-66-alkyne (Fig. 4(a) and (b)), the TEM images of UiO-66-alkyne-Ni (Fig. 4(c) and (d)) show that the novel catalyst has a uniform structure, indicating that the introduction of nickel did not cause UiO-66-alkyne to collapse. The uniformly distribution of Ni elements in the material can also be seen from Fig. 5.

PXRD was used to evaluate the crystal structure of the materials. Fig. 2 presented the XRD patterns of MOF-ligand, UiO-66-alkyne, UiO-66-alkyne-Ni, and recycled UiO-66-alkyne-Ni. The XRD patterns of UiO-66-alkyne and UiO-66-alkyne-Ni matched perfectly with the simulated patterns of UiO-66 from the crystallographic data, therefore suggesting that the as-synthesized UiO-66-alkyne and UiO-66 are isomorphic, which means that, the introduction of nickel doesn't destroy the crystal structure of MOF. Meanwhile, the diffraction peaks of UiO-66-alkyne synthesized at different temperatures (Fig. 2) were overlapped and the results, showed the synthesis temperature ranging from 80 °C to120 °C could afford us UiO-66-alkyne with pure phase. In addition, FT-IR spectra analysis was very important that could be used to confirm the chemical bonding effect between the MOF materials and metallic nickel. In the FT-IR spectra of UiO-66-alkyne and the ligand, the absorption peak at 3301 cm<sup>-1</sup> could be assigned to the C—H stretching band of the alkynyl group (Fig. 6). However, no absorption peak of the C—H alkynyl group was observed from the spectrum of UiO-66-alkyne. Ni, indicating that the terminal alkyne was reacted with Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.

The N<sub>2</sub> adsorption and desorption isotherms of that UiO-66-alkyne, UiO-66-alkyne-Ni and UiO-66 at 77 K were both isotherms of type I, indicating that the MOF materials were microporous (Fig. 7). The BET surface area of UiO-66 was 1097.230 m<sup>2</sup> g<sup>-1</sup>, larger than UiO-66-alkyne which is attributed to increased overall weight and reduced free space available of UiO-66-alkyne [35]. However, the BET surface area of



Fig. 4. TEM images: UiO-66-alkyne (a-b); UiO-66-alkyne-Ni (c-d); UiO-66-alkyne-Ni-recycle (e-f).



Fig. 5. Elemental mapping: UiO-66-alkyne-Ni (a-c); UiO-66-alkyne-Ni-recycle (d-f).

UiO-66-alkyne (852.618 m<sup>2</sup> g<sup>-1</sup>) was larger than UiO-66-alkyne-Ni (438.849 m<sup>2</sup> g<sup>-1</sup>), potentially due to the gap shrinkage when metal was introduced. In order to validate the hypothesis, non-local density functional theory analysis of the N<sub>2</sub> sorption isotherm was used to study

the pore size distributions of the two MOF materials. As is shown in the Fig. 7, two mode diameters for UiO-66-alkyne (9 and 11 Å) and UiO-66 also have two mode diameters (4 and 5 Å). In addition, only one significant peak was observed in UiO-66-alkyne-Ni, indicating that the



Fig. 6. The FT-IR spectra of the MOF-ligand, UiO-66-alkyne at different temperature, UiO-66-alkyne-Ni and UiO-66-alkyne-Ni-recycle.



Fig. 7. (a-b) N<sub>2</sub> sorption isotherm of UiO-66-alkyne and UiO-66-alkyne-Ni obtained at 77 K. (c-d) Pore size distribution of UiO-66-alkyne and UiO-66-alkyne-Ni.



Scheme 2. Knoevenagel condensation of the benzaldehyde and malononitrile.

introduction of metal had further caused the reduction of the pore size.

#### 3.3. Catalytic performance

The Knoevenagel condensation reaction was selected as a template reaction to evaluate the catalytic activity of UiO-66-alkyne-Ni, and benzaldehyde and malononitrile were used as reaction substrates (Scheme 2). As a heterogeneous catalyst, UiO-66-alkyne-Ni showed excellent catalytic activity that could catalyze the Knoevenagel condensation reaction at room temperature. The catalytic performance

of UiO-66-alkyne-Ni depended on the reaction time and catalyst amount in Fig. 8 (a) and (b), and the yield of the reaction was measured by <sup>1</sup>H-NMR. UiO-66-alkyne-Ni showed superior catalytic activity. The conversion could reach 93.5 % using 10 mg UiO-66-alkyne-Ni after 15 min and when the reaction time was prolonged to 45 min, the yield was up to more than 99 %. In order to confirm whether the metal Ni leaches, a leaching test was done and shown in Fig. S2. We removed the catalyst at 5 min, the reaction the reaction almost stopped. As a comparison, a blank test without any catalysts was performed to investigate the reactivity of the substrates themselves. It was found that the conversion distributions were 6.5 %, 11.2 %, and 16 % after 15, 30 and 45 min respectively, indicating that there was a lower conversion rate between reaction substrates without catalysts. In addition, in order to clarify the real active species, UiO-66-alkyne, NiCl<sub>2</sub>, PPh<sub>3</sub>, and Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> were used as catalysts. The results showed that UiO-66-alkyne not only not promote the reaction but also shows a certain inhibitory effect on the reactions (Fig. 8 (a)). To explore the reason, the experiment that UiO-66 catalyzed the Knoevenagel condensation reaction was added and got a



Fig. 8. (a) The conversions of benzaldehyde after 15, 30, 45 min ((UiO-66-alkyne-Ni (10 mg), UiO-66-alkyne (10 mg), Ni(PPh<sub>3</sub>)Cl<sub>2</sub> (7 mg), PPh<sub>3</sub> (7 mg), NiCl<sub>2</sub> (7 mg)). (b) The effect of the amounts of UiO-66-alkyne-Ni (0, 4, 7, 10 mg) on the conversions of benzaldehyde (reaction time: 45 min).

#### Table 1

Reported MOFs for the Knoevenagel condensation of benzaldehyde and malononitrile (RT).

Entry	Catalyst (Amount)	Solvent	Substrate (mmol)	t / min	Yield	Ref.
1	ZIF-9 (15 mol%)	Water	0.75	240	99 %	[47]
2	ZIF-8 (5 mol%)	$PhCH_3$	1.9	180	100%	[8]
3	DETA-MIL-101	$PhCH_3$	1.9	60	97%	[48]
	(50 mg)					
4	Zn@ZIF-67	DMSO	3.8	90	50%	[3]
	(2.5 mol%)					
5	UiO-66-NH-	$PhCH_3$	1.9	120	97%	[2]
	RNH2 (50 mg)					
6	UiO-66-NH-	EtOH	1.9	120	53%	[2]
	RNH2 (50 mg)					
7	UiO-67-	DMSO	1	60	98 %	[25]
	BPY@UiO-66					
	(18 mg)					
8	UiO-66-alkyne	EtOH	1	45	12.9%	This
	(10 mg)					work
9	UiO-66-alkyne-	EtOH	1	45	>99	This
	Ni (10 mg)				%	work

yield between UiO-66-alkyne and blank test. It indicated that the inhibitory effect of Knoevenagel condensation may be attributed to the acidic property of both terminal alkyne and UiO-66 itself. Furthermore, NiCl<sub>2</sub>, PPh<sub>3</sub> and Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> also showed limited catalytic activity in the Knoevenagel condensation reaction. Among them, Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> could afford 82 % yield after 45 min, so the synergistic effect between PPh<sub>3</sub> and NiCl<sub>2</sub> may be responsible for the excellent performance of UiO-66-alkyne-Ni.

The amount of catalyst was another key factor that affected the reaction. As shown in Fig. 8(b), with increased amounts of catalyst, the yield per unit time constantly turned better. But the amount of catalysts showed less significant impact on the yield.

For Knoevenagel condensation, most MOF catalysts require high temperature or harsh condition [7,36,49–52]. The catalytic performance of UiO-66-alkyne-Ni for the Knoevenagel condensation reaction using benzaldehyde and malononitrile as substrates was compared with the other MOF-based catalysts (Table 1). Though most of Knoevenagel condensation reactions can be carried out at room temperature, more equivalents of catalyst or longer reaction time (more than or equal to 1 h) were required, whereas, benzaldehyde was completely converted within a very short time with a very small amounts of UiO-66-alkyne-Ni (10 mg) under mild reaction conditions. Such results indicated that UiO-66-alkyne-Ni outperforms other reported MOF-based catalysts in

Table 2
The catalytic activity of UiO-66-alkyne-Ni using different aldehydes. <sup>a</sup>

Entry	Substrate	Product	Yield <sup>b</sup>	Time (min)
1	$\bigcirc$		>99 %	45
2	F C C C C C C C C C C C C C C C C C C C	CN CN	>99 %	30
3			>99 %	45
4			>99 %	30
5	$\bigcirc$		>99 %	30
6	Br		>99 %	45
7			>99 %	45
8			>99 %	45
9	$\bigcirc$	CN CN	>99 %	45
10		CN	> 99 %	30
11	<b>⟨</b> ⟩∠⁰		>99 %	45
12	$\sqrt[n]{}$		>99 %	45
13	$\bigcirc \widehat{}$		>99 %	60

<sup>a</sup> Reaction conditions: aldehyde (1 mmol), malononitrile (1.1 mmol), UiO-66alkyne-Ni (10 mg) EtOH (0.3 mL), room temperature (RT).

 $^{\rm b}$  The conversions of aldehydes were determined by  $^{\rm 1}{\rm H}$  NMR analysis using the dibromoethane as the internal standard (see the Fig.S6 for the  $^{\rm 1}{\rm H}$  and  $^{\rm 13}{\rm C}$  NMR spectra).

terms of catalytic performance.

The adaptability of the substrate is an important performance index of catalyst. The scope of the substrates was further expanded with UiO-66-alkyne-Ni as the catalyst (Table 2). The structure information of the corresponding product was characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra (Supporting Information). It was found the catalytic performance of UiO-66-alkyne-Ni towards Knoevenagel condensation of the benzalde-hydes with different substituents such as steric, electron-withdrawing or electron-donating were all good (Table 2, Entries 1–9). In addition, the



Fig. 9. The recycling performance of UiO-66-alkyne-Ni.

benzaldehyde substrate with the electron-withdrawing group (Entries 2, 3, and 5) showed better reactivity (30 min). Other aromatic aldehydes could also be converted completely under mild conditions (Table 2, Entries 10–12). When the substrate was replaced by cyclohexane carboxaldehyde, the reaction time of the product was slightly increased (60 min). In addition, the substitution positions of the substituents on the benzene ring showed no effect on the yield (Table 2, Entries 3 and 4,

or 6 and 7, or 8 and 9).

In order to study the reusability, a loop experiment has been performed and the results were shown in Fig. 9. The yield was slightly dropped after 5 cycles. Subsequently, the properties of the recycled catalyst were characterized by PXRD, XPS, SEM, TEM, and IR. The PXRD patterns showed that the crystal structure of UiO-66-alkyne-Ni after 5 cycles was still intact, whose diffraction peaks was completely consistent with the fresh UiO-66-alkyne-Ni (Fig. 2). In addition, TEM and SEM images showed that the morphology and size of the catalyst kept almost unchanged before and after recycling (Figs. 3 and 4).

The element distribution pictures of the catalyst before and after the reaction were shown in Fig. 5. It was found that the content of Ni elements maintained a very high level and dispersed uniformly on the catalyst after the catalytic reaction, which was mainly due to the coexistence of acetylene and metal. The bonding effect endowed the good stability of the catalyst. The extra evidence for this conclusion was the analysis results of XPS data (Fig. S3 in Supporting Information). The elemental analysis of XPS showed that the Ni metal content before and after cycling was 11.2 % and 9.17 %, respectively. This result also verified the Ni metal content on the surface of the MOF remained almost unchanged after cycle. The hypothesis that the alkynyl group acts as a "linker" to connect Ni and MOF through bonding effect was further supported by the aforementioned results.

The analysis of XPS spectra of fresh and used UiO-66-alkyne-Ni was shown in Fig. 10. The best-fitted peaks of fresh UiO-66-alkyne-Ni (857.4 eV, 874.9 eV) and UiO-66-alkyne-Ni-recycle (857.2 eV,



Fig. 10. XPS spectra of UiO-66-alkyne: (a) fresh UiO-66-alkyne; (b) used UiO-66-alkyne.



Fig. 11. Proposed mechanisms for the Knoevenagel condensation of benzaldehyde with malononitrile over UiO-66-alkyne-Ni.



Fig. 12. The recycling performance of UiO-66-alkyne-Ni (10 mmol).

874.6 eV) should be assigned as the binding energy of Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (Ni2p<sub>3/2</sub> and Ni2p<sub>1/2</sub>) [53], which demonstrated the existence form of Ni is Ni(II). This conclusion further confirmed that the valence state of nickel does not change in the process of bonding with terminal alkyne and the catalytic reaction.

A possible reaction mechanism for Knoevenagel condensation with UiO-66-alkyne-Ni as catalyst is proposed (Fig. 11). Firstly, benzaldehyde is activated by the catalytic center Ni(II) at the alkynyl end of the MOF material [54]. Triphenylphosphine acts as a Lewis base to promote the deprotonation of malononitrile, thereby generating carbanion intermediates [36]. The formed carbanion intermediate attacks the activated the carbonyl carbon to generate the intermediate (III), which is converted to the product (2-benzylidene malononitrile) through dehydration, and the catalyst returns to the initial state in order to enter the next cycle. This reaction mechanism can be further proved by the resolved compounds of the synthetic catalyst raw material Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> As shown in Fig. 8(a), both PPh3 and NiCl2 increase the yield of Knoevenagel condensation, which coincides with the activation of aldehyde groups by metals in the reaction mechanism [54] and the activation of malononitrile by Lewis bases. Meanwhile, using Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, to catalyze the reaction could further improve the yield, potentially because the two substrates are activated at the same time. Furthermore, the use of MOF as the carrier maximizes the performance of the catalyst.

In order to explore the potential application of the as-synthesized catalyst in the industry, 10-fold (10 mmol) and 500-fold (500 mmol) scale reaction were studied (Fig. S4 in Supporting Information). In the two amplification experiments, the amount of benzaldehyde was 10 mmol (1.06 g) and 500 mmol (53.00 g), and the amount of catalyst was 100.00 mg and 5.00 g, respectively. Without increasing the catalyst equivalent and extending the time, both reactions can be completed under the regulated conditions (RT) that selected from pilot experiments, and the yields of the 10 mmol experiment (1.50 g, 98 %) and 500 mmol experiment (76.50 g, 99 %) are almost unchanged. Cyclicity of the 10 mmol experiment reaction was further analysed. The results showed that the gram-level reaction still maintains a good cyclicity (Fig. 12), which indicates UiO-66-alkyne-Ni is a promising industrialization prospect catalyst.

#### 4. Conclusion

To sum up, a novel alkynyl-tagged UiO-66 material (UiO-66-alkyne) was designed and synthesized in this study. Thanks to the characteristics of alkynyl groups, a new non-noble metal catalyst (UiO-66-alkyne-Ni) was prepared using alkynyl groups as the linker. In addition, introducing Ni into MOF through a bonding reaction between terminal alkyne and Ni (II) was firstly attempted in the literature. UiO-66-alkyne-Ni shows excellent catalytic performance in the Knoevenagel condensation

reaction, in which a yield of 99 % in 45 min at room temperature was obtained, and the high yield value remains even after 5 cycles. In addition, UiO-66-alkyne-Ni also shows the promising industrialization characteristics. To be more specific, it maintains high catalytic activity after the reaction being amplified 10 times and 500 times and showed strong reusability stability when being magnified by 10 times. The developed efficiently and environmentally friendly nickel-alkyne-functionalized catalyst provides valuable insights into the usage of the functional MOF materials with alkyne as a linker.

#### CRediT authorship contribution statement

L.M. Shao, S.Y. Liao, and X. Liu conceived the conceptualization. L. M. Ning and H. Cheng did the data curation and formal analysis. J.L. Li, S.Y. Tang and H.X. Chen did the data curation and formal analysis. S.Y. Liao and X. Liu carried out the investigation of XPS measurements. H.X. Chen and W. Li performed the investigation of HRTEM and HRSEM analyses. The manuscript was primarily written by H. Cheng and L.M. Ning, and revised by L.M. Shao, S.Y. Liao, and X. Liu. S.Y. Tang helped improve the language and corrected minor language errors in the article. All authors discussed the results of the manuscript.

#### **Declaration of Competing Interest**

The authors report no declarations of interest.

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#### 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.apcata.2021.118216.

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