Journal of Catalysis 374 (2019) 110-117

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Zr and Hf-metal-organic frameworks: Efficient and recyclable heterogeneous catalysts for the synthesis of 2-arylbenzoxazole via ring open pathway acylation reaction



JOURNAL OF CATALYSIS

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ARTICLE INFO

Article history: Received 28 January 2019 Revised 12 April 2019 Accepted 15 April 2019

Keywords: Acylation Metal-organic framework Benzoxazoles Ring-opening mechanism Heterogeneous catalysis

1. Introduction

2-Aryl substituted benzoxazoles are an important class of heterocyclic organic molecules in various fields including pharmaceutical research, natural products chemistry, and agrochemical industry [1–4]. There are several reported strategies for the synthesis of these substances. Among them, two typical approaches are the condensation of 2-aminophenols with carboxylic acid derivatives [5] or aldehydes [6–8], and the transition-metal-catalyzed direct C-H functionalization of benzoxazoles with acylating agents [9–11]. Yet, they have some drawbacks such as the use of expensive catalysts and organic ligands which cannot be reused and recovered [11-13], exhibit long reaction times [6,14], volatile organic solvents [7,12], or requirement of prefunctional substrates [9,15]. Recently, the ring-opening and ring-closing reaction between benzoxazoles and benzoyl chlorides [16] or aldehydes [17] has been emerged as a potential pathway for the construction of benzoxazoles. Though this method shows noticeable advantage of high yield and mild reaction conditions, its application remains challenging due to high loading of catalysts, difficulty in recovery

ABSTRACT

Zirconium- and hafnium-based metal-organic frameworks which constructed by 12-coordinated clusters and 6-coodinated clusters were shown to be highly effective heterogeneous catalysts for the ring opening acylation of benzoxazole to 2-arylbenzoxazole under solvent free conditions. Owning the wide opening spaces structures and inherent formate sites, MOFs based on 6-connected Zr₆/Hf₆ node were able to identify a significantly enhanced yield in Brønsted acid catalyzed reactions under conventional heating and microwave irradiation. In addition, the detailed mechanism of active sites of the ring opening acylation reaction was confirmed by employing of density functional theory (DFT) calculations.

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of the catalysts [16], and the use of oxidizing agents or strong base with halogenated solvents [17]. Consequently, the development and exploration of effective systems for acylation of benzoxazole are highly desired.

Metal-organic frameworks (MOFs), a class of porous materials constructed from inorganic metal cluster as nodes and organic linkers, have attracted enormous attention for catalysis [18-21]. Among MOF materials, Zr(IV)- and Hf(IV)-based MOFs have been emerged as promising heterogeneous catalysts for organic reactions because of their structural efficiency [22–24]. These materials have highly active sites including Zr^{4+} or Hf^{4+} (Lewis acid) [25,26] and metal-bound hydroxides/water (Brønsted acid) on the Zr(IV) or Hf(IV)-oxo clusters within the frameworks [27-29]. Due to strong affinity of the Zr⁴⁺ or Hf⁴⁺ ions with carboxylate groups of organic linkers, their structures achieve high chemical stability leading to the ease of recycling and possibility for microwaveassisted reactions [23,30]. We have recently studied the efficiently heterogeneous catalytic activity of Zr- and Hf- MOFs in various organic transformations including 2-arylbenzoxazole synthesis [31]. Adopting knowledge from the previous works, herein, we describe unprecedented ring-opening and ring-closing 2arylbenzoxazole synthesis from benzoxazole and benzoyl chlorides catalyzed by Zr- and Hf-MOFs. In this research, we focused on the reactivity of MOFs built from 12-connected and 6-connected Zr₆/



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Hf₆ clusters coordinated with ditopic and tritopic carboxylate linkers, respectively (Fig. 1). According to the reaction studies, Zr- and Hf-MOFs exhibited high catalytic activity in the solvent-free 2-arylbenzoxazole synthesis under conventional heating and microwave irradiation. It should be noted that the efficiency of VNU-11 (Hf), 6-connected Hf-cluster-based MOF, was significantly higher in comparison to the other MOFs and catalysts. In addition, theoretical calculations were employed to determine role of the metal cluster in the proposed reaction mechanism.

2. Results and discussion

2.1. Catalysts characterization

All Zr- and Hf-MOFs were synthesized via solvothermal reaction with slight modifications to the methods reported in the literature [31–34]. The detailed synthesis and activation procedures were described in the Supporting Information (SI). In general, microcrystal powder of the MOFs were obtained through the reaction between ZrOCl₂·8H₂O or HfOCl₂·8H₂O and organic linkers in *N*,*N*dimethylformamide (DMF) with monocarboxylic acid added as a modulator. The reaction was heated at 120 °C for 1 day in an isothermal oven. As-synthesized sample was washed with DMF to remove guest molecules and solvent-exchanged. The solventexchanged sample was activated by heating under reduced pressure for 24 h. The activated samples were confirmed by various techniques including Powder X-ray Diffraction (PXRD) patterns and N₂ sorption isotherms to confirm successful activation and pure phase of the materials.

2.2. Catalytic performance

Following the material preparation, the catalytic activity of the materials was initially studied through the optimization of the exemplary reaction between benzoxazole (1) and benzoyl chloride (2) under catalysis of VNU-11(Hf) (Table 1 and Section S6). Specifically, the effect of solvent on the reaction was investigated by screening various solvents and under solvent-free conditions. The investigation indicated that the best result obtained at 170 °C for 3 h using 1 mol% catalyst under solvent-free conditions could afford the desired compound **3** (2- phenylbenzoxazole) with an excellent yield of 98% (Table 1, Entry 7). Whereas reasonable yields could achieve in dichloromethane and toluene (60 vs 59%, Table 1, Entries 4 and 5), 1,4-dioxane used as reaction solvent reached 96% yield after 3 h (Table 1, Entry 6). However, the reaction in the polar solvents gave low yields (less than 25%, Table 1, Entries 1–3).

After screening the optimized conditions for the reaction, the catalytic behavior of Zr- and Hf-MOFs was compared by adopting the arylation of benzoxazole as model reaction. As shown in Table 2, the catalytic activity of MOF-808(Zr) and VNU-11(Hf) in the reaction was superior to that of UiO-type MOFs, VNU-1(Zr), and VNU-2(Hf) (Table 2, Entries 2–9). Under the reaction conditions without a solvent, the performance of Hf-MOFs was more efficient than that of the Zr analogues due to higher oxophilic character and stronger acidity of the Hf-oxo clusters, as described in Section S5 [27,29,35]. The higher catalytic activity of the MOFs with larger pore size revealed that the reaction proceeded not only on the surface on the surface but also within the pores. Also, the best catalytic performance was obtained using MOF-808(Zr) or



Fig. 1. Zr₆/Hf₆ cluster (a) is connected with organic linkers to form MOFs. UiO-type MOF structures of Zr/Hf-UiO-66 (b) and Zr-, Hf-UiO-67 (b) are built by 12-connected cluster and ditopic linkers, H₂BDC and H₂BPDC, respectively. Interpenetrated structure (d) of VNU-1(Zr) and VNU-2(Hf) is constructed from 12-connected cluster and slim, linear H₂CPEB linker. Structures (e) of MOF-808(Zr) and VNU-11(Hf) are based on 6-connected cluster and tritopic linkers H₃BTC. Color code: C, black; O, red; Zr or Hf, blue polyhedra. The yellow and purple balls represent the cages of the structures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Screening of the reaction conditions.

• +	$\begin{array}{c} O \\ \hline \\$	+ HCI + CO		
1 Entry	Z Type of solvent	Solvents	Cat. (mol%)	Isolated yield (%)
1	Polar protic	Ethanol	1	23
2		n-Buthanol	1	17
3	Polar aprotic	DMF	1	2
4	Nonpolar	Dichloromethane	1	60
5		Toluene	1	59
6		1,4-Dioxane	1	96
7	Free-solvent	-	1	98
			0.5	53
			0.1	31
			0	0

A mixture of VNU-11(Hf), benzoyl chloride (0.140 g, 1 mmol) and benzoxazole (0.119 g, 1 mmol) in a flask bottom was stirred under solvent condition at 170 °C for 3 h. Yield of compound **3** was isolated by column chromatography (acetone/petroleum).

Table 2 Comparative study of catalysts used in the synthesis of 2-phenylbenzoxazole^a.

Entry	Туре	Catalyst	$A_{BET}^{b} (m^2 g^{-1})$	PSD ^c (Å)	Yield ^d (%)	TOF (h^{-1})
1	Free catalyst	-	-	-	4	-
2	MOFs	Hf-UiO-66	800	11.2	56	18.7
3		Zr-UiO-66	1150	11.2	48	16.0
4		Hf-UiO-67	1720	14.5	76	25.3
5		Zr-UiO-67	2105	14.5	60	20.0
6		VNU-2(Hf)	1700	20.0	85	28.3
7		VNU-1(Zr)	2100	20.0	74	24.7
8		VNU-11(Hf)	1530	15.0	98	32.7
9		MOF-808(Zr)	2060	15.0	89	29.7
10	Metal salts	ZrO ₂	_	_	27	9.0
11		TiO ₂	_	_	32	10.7
12		AlCl ₃	_	_	46	15.3
13		FeCl ₃	_	_	40	13.3
14		ZnCl ₂	_	_	43	14.3
15		HfOCl ₂ ·8H ₂ O	-	_	23	7.7
16		ZrOCl ₂ ·8H ₂ O	-	-	20	6.7

^a Reaction conditions: benzoxazole (5 mmol) and benzoyl chloride (5 mmol) were stirred under free solvent at 170 °C for 3 h in the presence of catalyst (1 mol%).

^b Calculated Brunauer–Emmett–Teller surface areas.

^c Pore size distribution.

 $^{\rm d}\,$ Yield of compound 3 was isolated by column chromatography (acetone/petroleum).

VNU-11(Hf). This mainly results from the Zr-OH/Zr-OH₂ or Hf-OH/ Hf-OH₂ facing the pores in the structure, which makes the catalytically active sites more accessible for the substrates to react. However, the traditional Lewis acids including metal salts and metal oxides were not well reactive with the yields obtained from 20% to 46% (Table 2, Entries 10–16). In order to highlight role of acid sites in the acylation, the control experiment was performed without the presence of any catalysts. From the result in Table 2, it was clear that the reaction did not proceed by heating alone (Table 2, Entry 1).

In order to broaden the results of this study, we carried out the acylation reaction of various functional groups in the aromatic ring of acyl chloride, including 4-methoxybenzoyl chloride (**4**), 4-fluorobenzoyl chloride, 4-nitrobenzoyl chloride (**8**). The influence of substituted aromatic chloride such as electron-donating (*p*-OMe) and halo substituents (*p*-F) substituents on the aromatic ring was investigated (Table 3). The synthesis of 2-(4-methoxyphenyl) benzoxazole (**5**), 2-(4-fluorophenyl)benzoxazole (**7**), and 2-(4-nitrophenyl)benzoxazole (Table 3, Entry 2-4) in the presence of the VNU-11(Hf) catalyst were obtained in 97%, 92%, and 11% yields, respectively. In the next series, these optimized conditions were then applied to benzoxazole derivatives, and the reactions were found to be successful for all benzoxazole derivatives. The use of

5-methylbenzoxazole (**10**) and 5-nitrobenzoxazole (**14**) proceeded more smoothly with benzoyl chloride (**2**) giving 97 to 86% isolated yields (Table 3, Entries 8–15). However, the reaction between benzoxazole derivatives and several aromatic acyl chlorides showed lower efficiency than the others with the expected products 5-m ethyl-2-(4-methoxyphenyl)benzoxazole (**12**) (84% yield, Table 3, Entry 6) and 5-methyl-2-(4-fluorophenyl)benzoxazole (**13**) (65% yield, Table 3, Entry 7). Finally, the reaction of (**14**) with aromatic acyl chloride led to 5-nitro-2-(4-fluorophenyl)benzoxazole (**17**) with a moderate yield of 36% after 7 h (Table 3, Entry 10). This result could be explained due to the weak nucleophilic characteristics of aromatic acyl chloride.

Moreover, we studied the effect of heating methods such as conventional heating and microwave irradiation on the reaction between 5-nitrobenzoxazole (**14**) and various aromatic acyl chlorides under VNU-11(Hf) catalyst. The reaction was carried out at 170 °C for 7 h under conventional heating or for 40 min under microwave irradiation. The desired products were isolated by column chromatography and weighted to calculate the yields. As the results shown in Fig. 2, microwave irradiation exhibited as a powerful tool to enhance catalytic activity of VNU-11(Hf) in the reaction with high yield and short reaction times. For example, the reaction under microwave irradiation for 40 min could obtain 5-



R1 N	+ R2	VNU-11(Hf) 170 °C solvent-free		R2 + HCI + CO		
R1: H (1) R1: CH ₃ (10) R1: NO ₂ (14)	R2: H (2 R2: OM R2: F (6 R2: NO	2) e (4)) 5 (8)				
Entry	R1	R2	Time (h)	Product	Yield (%)	TOF (h^{-1})
1	Н	Н	3		98	32.7
2	Н	ОМе	6		97	16.2
3	Н	F	6		92	15.3
4	Н	NO ₂	6		11	1.83
5	CH ₃	Н	6		97	16.7
6	CH ₃	OMe	6		84	14.0
7	CH ₃	F	6		65	10.8
8	NO ₂	Н	7		86	12.3
9	NO ₂	ОМе	7		48	6.85
10	NO ₂	F	7		36	5.14

nitro-2-phenylbenzoxazole **(15**) or 5-nitro-2-(4-methoxyphenyl)b enzoxazole (**16**), and 5-nitro-2-(4-fluorophenyl)benzoxazole (**17**),

0

CI



Fig. 2. Effect of conditional heating and microwave radiation method in yields (column) and TOF (line) of (14) 5-nitrobenzoxazole (14) with aromatic acyl chloride (2), or (4), and catalyzed by VNU-11(Hf).

whereas using conventional heating required 7 h for obtaining the same yield of these products (Fig. 2). We calculated the maximum catalyst TOF (Turn-Over Frequency) for the acylation of benzoxazole derivatives with different aromatic acyl chlorides. In the conventional heating condition, the reaction between (1) and (2) using VNU-11(Hf) catalyst, 1 mol% and 0.5 mol%, achieved the maximum values of TOF as 32.7 and 35 h⁻¹, respectively. Remarkably, TOF increases 8.5 and 10 times by using microwave irradiation (Fig. 2) at 170 and 180 °C, respectively, for 40 min.

To investigate the recyclability of the catalysts, the reaction between benzoxazole and benzoyl chloride with catalysis of VNU-11(Hf) under microwave was chosen. After the reaction, the catalyst was collected via centrifugation, washed with acetone and ethanol, reactivated under reduced pressure, and analyzed by X-Ray Diffraction, scanning electron microscopy, transmission electron microscopy, and infrared spectroscopy (Section S7). PXRD patterns corresponding to the fresh and used VNU-11(Hf) for five times, which were observed with no considerable change in structure despite lower intensity (Fig. 3). The leaching test was also determined by ICP-OES and the Hafnium content in ethyl acetate was less than 5 ppb, indicating a little leaching of the metal from the catalyst during the reaction. The recovered VNU-11(Hf) was



Fig. 3. PXRD analysis of VNU-11(Hf) before (blue) and after (red) the symthesis 2phenylbenzoxazole in comparison to the simulated pattern. Inset: The recycling experiments of the reaction over five cycles (the numbers on the top represent the yield of reaction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reused in the reaction of (1) and (2) for 5 times with slightly fall of reactivity and insignificant decrease of yield by about 5%. This should be able to imply the recyclability of VNU-11(Hf) as an important feature for industrial application.

2.3. Mechanistic considerations

A study mechanism for the ring open path way acylation reaction has been also investigated computationally using benzoxazole and benzoyl chloride. Initially, we allowed benzoxazole to interact with the Hf cluster without the presence of benzoyl chloride. It was confirmed experimentally by ¹³C NMR that upon the use of benzaldehyde, there must be a C substitution in the five-membered ring, and it was not possible to undergo C—H activation [36]. More specifically, there must be a ring opening at first, then C from the carbonyl group in benzoyl chloride would come in and replace the C in the five-membered ring. Therefore, while exploring the reaction mechanism, we strictly followed the pathway involving C substitution.

Since N possessed one pair of electrons, it was highly attracted by one Hf site. In the initial step, the Hf-N bond could be established easily. Since the reactant came to bind with Hf, the nearby Hf-formate bond could be released with a low energy barrier of 0.36 eV (8.3 kcal/mol). Such dissociated formate residue will involve in a later stage of the catalyzing process. According to our optimization, it is interestingly observed that the resultant product in this step was more energetically stable than the initial product by an amount of 2.64 kcal/mol. After accomplishing those benchmarking calculations, we introduced benzoyl chloride to the system and started to explore the reaction mechanism. This structure is denoted as complex 1 in our reaction mechanism in Scheme 1. For the ease of discussion, we denote the C atom in the five-membered ring of benzoxazole as $C^{(1)}$, while the C of benzoyl chloride is denoted as $C^{(2)}$. Those two C atoms played a significant role in the overall reaction mechanism. The attachment of N to Hf was important, because it would help to reduce the $C^{(1)} = N$ bond. As a result, $C^{(1)}$ became more attractive and subsequently established a bond to O from benzovl chloride. On the other hand, upon the consideration of O from benzyol chloride attaching to Hf, it would be more difficult for this O atom to form a bond with $C^{(1)}$ from the unattached benzoxazole. More importantly, the bonding interaction between N and Hf helps to weaken the C-N bond, thus leads to its rupture later on.

Electron-rich $C^{(2)}$ attacked the N site of the initial reactant, and attempted to establish a new σ bond. Almost at the same time, Cl

was released from benzoyl chloride, and hosted by the free formate residue released earlier. Surprisingly, it did not combine with O, but indeed formed a σ bond with C in the formate residue. The O atom of such a formate residue, on the other hand, attempted to establish bonding to $C^{(2)}$ of benzoyl chloride. Therefore, there are three elementary steps occurring in the first primary process, as shown in transition state 1 (TS1). In terms of free energy, TS1 is 22.22 kcal/mol (0.96 eV) above the initial state 1. Upon performing vibrational analysis for TS1, we observe one imaginary wavenumber of -97 cm^{-1} , which is associated with the bond breaking process. After this process, we obtained complex 2, which was 16.21 kcal/mol (0.70 eV) above **1** in terms of free energy. In complex **2**, the benzoyl residue was successfully attached to N with electron transfer from N to benzoyl chloride as confirmed by Mulliken charge analysis. More importantly, the C–N bond in the five member ring was reduced from π to σ . This is important for a complete dissociation of C–N, so that C⁽²⁾ from benzoyl could come in to substitute the old $C^{(1)}$ site from the five member ring. At this point, the C⁽¹⁾—N single bond distance was 1.46 Å. To investigate the C⁽¹⁾—N bond dissociation, we performed partial optimization for the cleavage of the bond. When reaching a distance of 2.79 Å, the C–N bond underwent a transition state for dissociation (TS2), and the reaction free energy barrier was 31.21 kcal/mol (1.35 eV). Executing vibrational analysis for TS2, we obtained a negative wavenumber of -85 cm^{-1} . In fact, this free energy barrier is the highest barrier in the entire reaction scheme, and plays the decisive role in the chemical reaction. Fortunately, this reaction was actually carried out under the activation of microwave; therefore, that high reaction barrier could be overcome. One other reason for the high reaction barrier is that, during this process, not only the $N-C^{(1)}$ bond was broken. Indeed, we observed the formation of chloro-formaldehyde. In a previous paper [17], the C–O bond was weakened under the influence of OH⁻, and subsequently suffered dissociation to achieve ring opening. Our reaction was carried out under the acidic condition, and our DFT calculations verified that it was not possible to break the C–O bond. Indeed, the rupture of C-N bond was the most sensible strategy so that the reaction would come to the C substitution in a later stage.

At this point, N already connected to benzoyl, while still remained bonding with the original six-membered phenyl ring. Moreover, there was a formate residue attached to the aromatic phenyl ring. The subsequent process concerned the release of chloro-formaldehyde. In complex 3, the C from chloroformaldehyde still linked with N through a weak bond with a distance of 1.50 Å. In this case, the C–O bond was not a π bond, and O had to complete its electron configuration with a linkage with Hf. To release chloro-formaldehyde, the N-C bond had to be broken, and we found a transition barrier of 14.81 kcal/mol (0.64 eV) with an imaginary vibrational wavenumber of -56 cm^{-1} (TS3). Chloroformaldehyde was formed in this stage (complex 4), and it is soon broken into HCl and CO. The presence of HCl can be confirmed experimentally by the decrease of pH (2.542 before reaction and 1.567 after reaction). For simplicity of calculations, we eliminate chloro-formadehyde from the entire structure from this point. After eliminating chloro-formaldehyde, we optimized complex 5, as shown in Scheme 1. It should be noticed that after the departure of chloro-formaldehyde, the structure was unstable due to the lack of bonding on the $C^{(1)}$ site.

This problem was soon taken care of by an internal rearrangement, and an intermediate seven-membered ring was established, as seen in complex **5**. It should be noticed, however, that $C^{(1)}$ connected to three surrounding O sites. This bonding behavior was indicative of structural instability. Therefore, the intermediate complex **5** would soon suffer from bond dissociation; one of the three O—C bond was broken very easily (to **TS4** as a matter of structural re-arrangement). The total energy barrier for this



Scheme 1. Ring opening acylation reaction between benzoxazole (1) and benzoyl chloride (2)-reaction path starting with capping VNU-11(Hf) step.

process was only 0.78 kcal/mol (0.04 eV). More surprisingly, the free energy barrier was observed to be quite negative (-2.95 kcal/mol), while implied the rapid conversion at this step. Moreover, the $C^{(2)}$ —O bond suffered cleavage at the same time: consequently, C^{1} was accompanied by two O- to form a formate residue and released from the seven-membered ring during the process. After this stage, complex **6** was produced with $C^{(2)}$ connected to N via a triple bond (the bond length was 1.19 Å with a partial positive charge on N), while the O atom from the initial reactant connected to the phenyl ring and one Hf site. In the last process, such an O atom and $\tilde{C}^{(2)}$ approached each other to make a new bond, and established a new five-membered ring in the last process. To achieve TS5, the structure overcame an energy barrier of 4.71 kcal/mol (0.20 eV). For TS5, an imaginary wavenumber of -127 cm^{-1} was observed. In the final product (complex 7), the $C^{(2)}\!\!-\!\!N$ bond distance changed to 1.31 Å, which was more or less descriptive of a π bond. The final product was found to be 7.25 kcal/mol below TS5.

We then performed a new set of calculations for the reactants, transition states, and final product with Zr instead of Hf. The results showed that the new free energy barriers catalyzed by Zr were higher than those catalyzed by Hf. Especially, to arrive at TS1, the complex was predicted to overcome a free energy barrier of 32.23 kcal/mol. The key step, which involves C—N rupture through TS2, occurred with a remarkably high barrier of 41.65 kcal/mol. As illustrated in Fig. 4, the other reaction barriers (shown in bracket) were also predicted to be higher than the previous case.

3. Experimental

3.1. Materials

All chemicals for synthesized MOF were obtained from Sigma-Aldrich Chemical Company, Merck, and Alfa Aesar. All reagents and solvents for catalytic studies were obtained from Acros Organics. Deuterated solvents, $CDCl_3$, acetone d_6 and DMSO d_6 , were purchased from Cambridge Isotope Laboratories (Andover, MA). The detailed preparation of all MOF catalysts was described in Section S2.

3.2. General methods

Powder X-ray diffraction patterns were recorded using a D8 Advance diffractometer equipped with a LYNXEYE detector (Bragg-Brentano geometry, Cu K α radiation λ = 1.54056 Å. Fourier transform infrared (FT-IR) spectra were measured on a Bruker E400 FT-IR spectrometer using potassium bromide pellets. Solution NMR spectra were acquired on a Bruker Advance-500 MHz NMR spectrometer. ICP-MS analyses were performed on a PerkinElmer NexION 350X. Microwave irradiation was performed on a CEM Discover BenchMate apparatus, which is offered for microwave synthesis with safe pressure regulation using a 10 mL pressurized glass tube with Teflon-coated septum and vertically focused IR temperature sensor controlling reaction temperature.

3.3. Procedure of 2-arylbenzoxazoles derivatives

A mixture of VNU-11(Hf) (0.018 g, 0.01 mmol), aromatic acyl chloride (0.140 g, 1 mmol) and benzoxazole (0.119 g, 1 mmol) was heated at 170 °C under conventional heating for a few hours or microwave irradiation of a CEM Discover apparatus for a few minutes. After completion of reaction, the catalyst was filtered from the reaction mixture. The filtrate was diluted with ethyl acetate (50 mL), washed with H_2O (3 × 20 mL), aqueous NaHCO₃ (2 × 20 mL), and dried over Na₂SO₄. The solvent was removed in a rotary evaporator. The crude product was purified by flash chromatography (90:10 acetone/petroleum ether to give corresponding product. The purity and identity of the products were confirmed by GC–MS spectra, which were compared with the spectra in the NIST library, and by ¹H and ¹³C NMR spectroscopy.

3.4. Theoretical calculations

In this section, density functional theory [37,38] (DFT) calculations were employed to explore the stepwise reaction mechanism.



Fig. 4. Energy profile of ring open acylation between benzoxazole (1) and benzoyl chloride (2) following the reaction path starting with the capping metal-organic framework step (Scheme 1) B3LYP energies calculated for MOF-808(Zr) and VNU-11(Hf) are reported.

The Perdew-Burke-Ernzerhof functional [39–41] was used in conjunction with the split-valence 6–31 g basis set [42,43] for C, H, O, N, Cl, while the effective core potential method [44] with the LANL2dz basis set [45–47] was employed to describe the valence wave functions of Hf. To account for long-range van der Waals interaction, we used the well-established D3 empirical correction terms developed by Grimme [48]. All calculations were executed using the Gaussian 16 package. First, the core cluster consisting of six Hf (or Zr) cations, which was the main recipe to constitute VNU-11(Hf), was optimized. For computational feasibility, all linkers connected to the metal cluster were simplified by formate (COO–) residues as shown in Fig. 4.

4. Conclusions

The heterogeneously catalytic capability of Zr- and Hf-MOFs in the solvents-free acylation of benzoxazole derivative with different aromatic acyl chloride was investigated under conventional heating and microwave irradiation. As a result, the MOF catalysis in the reaction showed the good efficiency with high yield and ease of recycling. Moreover, the catalytic activity of MOF-808(Zr) and VNU-11(Hf) were significantly higher in comparison to UiO-type MOFs, VNU-1(Zr), and VNU-2(Hf) catalysts. Experimental investigation was accompanied by the DFT-modeling of the reaction mechanism catalyzed by formate, Brønsted and Lewis acid sites. The mechanism involves two important key steps: the broken of a C=N double bond under the activation of the formate residue and Hf site, and the combination of N-C (from benzoyl chloride). In the final product, it was clearly observed that C from benzoyl chloride successfully came in and made a replacement to establish a new five-membered ring. Finally, the reaction was shown to occur more easily under the influence of Hf in comparison with Zr.

Acknowledgements

This work was funded by Vietnam National University, Ho Chi Minh city (no. VNU-C2018-50-2 and TX-2019-50-01). We gratefully acknowledge the support of Center for Innovative Materials & Architectures (INOMAR), Vietnam National University, Ho Chi Minh City for instrument use. We thank Ha L. Nguyen at UC Berkeley and Hung. A. T. Hang at the University of Science for their valuable discussions.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.04.023.

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