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Introduction

Highly efficient Meerwein–Ponndorf–Verley reductions over a robust zirconium-organoboronic acid hybrid⁺

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The Meerwein–Ponndorf–Verley (MPV) reaction is an attractive approach to selectively reduce carbonyl groups, and the design of advanced catalysts is the key for these kinds of interesting reactions. Herein, we fabricated a novel zirconium organoborate using 1,4-benzenediboronic acid (BDB) as the precursor for MPV reduction. The prepared Zr-BDB had excellent catalytic performance for the MPV reduction of various biomass-derived carbonyl compounds (*i.e.*, levulinate esters, aldehydes and ketones). More importantly, the number of borate groups on the ligands significantly affected the catalytic activity of the Zr-organic ligand hybrids, owing to the activation role of borate groups on hydroxyl groups in the hydrogen source. Detailed investigations revealed that the excellent performance of Zr-BDB was contributed by the synergetic effect of Zr^{4+} and borate. Notably, this is the first work to enhance the activity of Zr-based catalysts in MPV reactions using borate groups.

To relieve the excessive reliance on the depleting fossil resources, utilization of the renewable and abundantly available biomass to produce valuable chemicals has gained significant attention.¹ In the past decades, many carbonyl compounds have been obtained through biomass conversion or direct extraction from plants. Thus, further upgrading of these biomass-based carbonyl compounds is highly attractive.² In this regard, selective hydrogenation of the carbonyl groups to generate hydroxyl compounds has been recognized as a highly promising strategy to convert these biomass-based carbonyl compounds,³ considering that the hydrogenation products can be widely applied as fine chemicals and valuable synthetic intermediates. However, the biomass-derived carbonyl compounds often contain other reducible moieties (e.g., C=C, phenolic hydroxyl group, and aromatic ethers), resulting in the difficulty for selective hydrogenation of the carbonyl groups.

A convenient strategy to realize selective hydrogenation of carbonyl groups is Meerwein-Ponndorf-Verley (MPV) reductions,⁴ which employ secondary alcohols as the hydrogen resource. For MPV reduction, Zr-containing catalysts (e.g., ZrO₂,⁵ zirconium alkoxides,⁶ Zr-containing zeolites,⁷ and Zr-organic ligand hybrids⁸) are widely used. The easily tunable activity affords Zr-organic ligand hybrids being highly attractive among the developed Zr-containing catalysts. Currently, several Zr-organic ligand hybrids have been fabricated from the coordination of Zr with various organic ligands (e.g., dicarboxylic acids,^{8d,e,9} phytic acid,^{8b} tannic acid,^{8a} and cyanuric acid¹⁰) for the MPV reaction of biomass-derived furfural and levulinic acid/levulinate esters. However, these developed Zrorganic ligand hybrids often required high reaction temperature or long reaction time, especially for the MPV reaction of levulinate esters. Thus, novel and robust Zr-organic ligand hybrids are still highly desired to afford MPV reductions being conducted under mild reaction conditions.

Improving the ability of the catalysts to activate the hydroxyl group in the hydrogen donor (secondary alcohols) is a general strategy to achieve high reactivity of the MPV reaction. The catalytic activity of the reported Zr-organic ligand hybrids for the MPV reaction was usually enhanced by involving basic groups (*e.g.*, phosphate^{8b} and phenate^{8a,11}). However, to overcome the above limitations of the current Zr-organic ligand hybrids, it is still of crucial importance to develop innovative approaches to activate the hydroxyl groups in the hydrogen donor.

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As reported, boric acid (H₃BO₃) as a Lewis acid can coordinate with the hydroxyl group in alcohols,¹² and could activate the hydroxyl group. We assume that there is great potential to design efficient Zr-based catalysts for the MPV reaction by combining the catalytic role of Zr (to activate the carbonyl group) and H₃BO₃/borate (to activate the hydroxyl groups). As far as we know, no attention has been paid to the role of H₃BO₃ (or borate) in the MPV reaction. Herein, we designed a porous zirconium organoborate simply by the reaction of ZrOCl₂ and 1,4-benzenediboronic acid (BDB, Scheme S1[†]), denoted as Zr-BDB. The prepared Zr-BDB could efficiently catalyze the MPV reactions of various biomass-based carbonyl compounds with high selectivity (>97%) owing to the synergetic effect of Zr and borate. As far as we know, this is the first work on the employment of borate groups to boost the catalytic activity of Zr-organic ligand hybrids in MPV reactions.

Results and discussion

Preparation and characterization of the Zr-BDB

The Zr-BDB was synthesized from ZrOCl_2 and BDB in *N*,*N*-dimethylformamide (DMF) *via* a solvothermal process, and the detailed procedure is provided in the ESI.[†] The fabricated Zr-BDB consisted of small particles with a diameter of approximately 100 nm (Fig. 1A), and there were plenty of mesopores in the Zr-BDB as shown in the TEM image (Fig. 1B). Elemental distribution mappings suggested that the four elements, including Zr, C, O, and B, uniformly dispersed in the Zr-BDB (Fig. S1[†]). Moreover, the N₂ adsorption–desorption isotherm (Fig. 1C) further indicated that the Zr-BDB was a porous material with a surface area of 271 m² g⁻¹ (Table S1[†]), and the size of the mesopores was centered around 3.4 nm. In FT-IR spectra (Fig. 1D), the characteristic vibration (800–1200 cm⁻¹,¹³ the shadow area) of boric-acid groups in the



Fig. 1 Characterization of the prepared Zr-BDB. (A) SEM image, (B) TEM image (the inserted image was achieved from the high resolution TEM), (C) N_2 adsorption–desorption isotherm, and (D) FT-IR spectra.

Zr-BDB was significantly weakened in comparison with that in BDB, implying the coordination between Zr^{4+} and the BDB. Meanwhile, there was only one broad diffraction peak in the XRD pattern of the Zr-BDB (Fig. S2[†]), indicating the amorphous nature of the Zr-BDB. Additionally, one Zr⁴⁺ could theoretically coordinate with two borate groups, and thus, the molar ratio of Zr and BDB should be 1:1. However, as determined by ICP-AES and element analysis, the molar ratio of Zr and BDB in the obtained Zr-BDB was about 1.2:1. Considering that the rigid structure of BDB, the most possible connectivity pattern of Zr⁴⁺ and BDB is shown in Scheme S2,† but there should be much irregular connectivity or defects in Zr-BDB deduced from the XRD result (Fig. S2[†]) and element analysis. For comparison, Zr-CPB (using 4-carboxyphenylboronic acid, denoted as CPB, Scheme S1[†]), Zr-BDC (using 1,4-benzenedicarboxylate acid, denoted as BDC, Scheme S1[†]) and Zr-B (using boric acid, denoted as B) were prepared by a similar route to synthesize Zr-BDB, and these three catalysts were characterized by TEM (Fig. S3[†]), SEM (Fig. S4[†]), and N₂ adsorption-desorption examinations (Table S1†).

Activity of various catalysts on the MPV reaction of ethyl levulinate

Levulinate esters, a typical class of biomass-derived carbonyl chemicals, can be converted into γ -valerolactone (GVL), which is an important reaction for biomass transformation.¹⁴ As is well known, the reaction process involves the hydrogenation of carbonyl groups. Thus, MPV reduction of levulinate esters to synthesize GVL was selected as a model reaction to evaluate the catalytic performance of the prepared Zr-BDB. Initially, we used ethyl levulinate (EL) as the reactant to investigate the effect of various reaction parameters (Table 1). No reaction occurred in the absence of catalysts (Table 1, entry 1). The reac-

 Table 1
 Activity of various catalysts for the MPV reaction of levulinate esters^a

Entry	Catalyst	$T^{b}(^{\circ}\mathrm{C})$	$t^{b}(\mathbf{h})$	$C^{b}(\%)$	$Y^{b}(\%)$	S ^b (%)
1	None	130	6	0	0	0
2	Zr-BDB	130	6	99.5	98.7	99.2
3	ZrO_2	130	6	10.1	8.5	84.2
4	Zr-CPB	130	6	70.2	62.4	88.9
5	Zr-BDC	130	6	98.1	34.9	35.6
6	UiO-66	130	6	85.1	46.9	55.1
7	Zr-B	130	6	93.9	80.3	85.5
8	Zr-BDB	100	12	88.9	84.3	94.8
9 ^c	Zr-BDB	130	12	85.7	77.6	90.5
10^d	Zr-BDB	130	12	99.4	95.3	95.9
11^e	Zr-BDB	130	4	99.7	98.4	98.7
12^{f}	Zr-BDB	130	6	89.9	86.7	96.4
13^g	Zr-BDB	130	6	81.4	77.2	94.8
14^h	Zr-BDB	130	3	99.7	97.2	97.5
15^h	Zr-BDB	120	6	99.4	96.6	97.2

^{*a*} Reaction conditions: EL, 1 mmol; catalyst, 0.2 g; isopropyl alcohol, 5 g. ^{*b*} The conversion and yield were determined by GC using cyclohexanol as the internal standard. T = temperature, t = time, C = conversion, Y = yield, and S = selectivity. ^{*c*} The amount of Zr-BDB was 25 mg. ^{*d*} The amount of Zr-BDB was 50 mg. ^{*e*} The reactant was ML. ^{*f*} The reactant was PL. ^{*g*} The reactant was BL. ^{*h*} The reactant was LA.

tion could be efficiently proceeded over Zr-BDB at 130 °C (Table 1, entry 2), and the GVL yield could reach 98.7% with a reaction time of 6 h. In contrast, commercial ZrO₂ only provided very low activity for the reaction (Table 1, entry 3). Furthermore, it was found that the number of borate groups on the benzene ring significantly affected the catalytic activity of the prepared three Zr-organic ligand hybrids (Table 1, entries 2, 4, and 5). The GVL yields were 62.4% and 34.9% over Zr-CPB and Zr-BDC (Table 1, entries 4 and 5), respectively. The commercial metal-organic framework UiO-66 only provided a moderate GVL yield of 46.9% (Table 1, entry 6) although it had a much higher BET surface area than the Zr-BDB (Table S1[†]). Additionally, Zr-B showed a good activity for the GVL formation with a yield of 80.3% (Table 1, entry 7), further indicating the promoting effect of the borate group. The results above indicated that the prepared Zr-BDB was a superior catalyst for the MPV reaction owing to the synergistic effect of Zr and the borate, as will be discussed below.

Optimization of reaction parameters

In general, reaction temperature and catalyst usage are two important parameters that affect reaction efficiency. As expected, both the EL conversion and the yield of GVL increased with increasing reaction temperature over Zr-BDB (Fig. 2A), and the reaction was completed at 130 °C with a GVL yield of 98.7%. Importantly, the GVL yield could reach 84.3% at 100 °C over Zr-BDB with a prolonged reaction time of 12 h (Table 1, entry 8), while no GVL was formed over ZrO_2 or Zr-BDC. Similarly, more catalyst usage was beneficial for the reaction (Fig. 2B), and the optimal amount of Zr-BDB was 0.2 g. To our delight, Zr-BDC maintained its high activity in the MPV reaction of EL at lower usage of Zr. The GVL yields could reach 77.6% and 95.3% (Table 1, entries 9 and 10) at 130 °C when the amount of Zr-BDB was 0.025 or 0.05 g with a reaction time of 12 h. These investigations verified that Zr-BDC could cata-



Fig. 2 (A) Effect of reaction temperature, (B) influence of reaction time, (C) effect of reaction time, and (D) reusability of Zr-BDB. Reaction conditions: EL, 1 mmol; isopropyl alcohol, 5 g; the amount of Zr-BDB, 0.2 g for A, C and D; reaction temperature, 130 °C for B–D; reaction time, 6 h for A and B or 2 h for D.

lyze the MPV reaction under lower reaction temperature and catalyst usage, further indicating its excellent catalytic activity. Moreover, the reactivity of levulinate esters decreased as follows (Table 1, entries 2 and 11–13): methyl levulinate (ML) > EL > propyl levulinate (PL) > butyl levulinate (BL), which probably resulted from the increasing steric hindrance from methyl to butyl. Meanwhile, Zr-BDB could also efficiently catalyze the MPV reaction of levulinic acid (LA), and a GVL yield of 97.2% was obtained at 130 °C with a reaction time of 3 h (Table 1, entry 14). In addition, the catalytic activity of Zr-BDC was still high for LA at 120 °C, and the GVL yield reached 96.6% with a reaction time of 6 h (Table 1, entry 15).

The influence of different alcohols as hydrogen donors on the MPV reaction of EL was further studied (Table S2†). It was found that secondary alcohols (isopropyl alcohol and *sec*-butyl alcohol) showed better performance than the primary alcohols (methanol, ethanol, and *n*-propanol) owing to the lower reduction potential of secondary alcohols (Table S2,† entries 1-2 vs 3-5).¹⁵ The poor performance of methanol as the hydrogen donor was caused by its much higher reduction potential than other alcohols (Table S2,† entry 3).^{15b} Moreover, the yield of GVL was low when using *tert*-butanol as the hydrogen donor (Table S2,† entry 6) because the structure of *tert*-butanol resulted in great difficulty for the hydrogen-transfer step in MPV reduction.^{15a,b}

Reusability of Zr-BDB

For heterogeneous catalysts, easy reusability is the main superiority in comparison with the homogeneous ones. First, the heterogeneous nature of Zr-BDB was evaluated. After the reaction was performed for 2 h at 130 °C, the Zr-BDB was removed from the reaction system via hot filtration. No further reaction was observed after the removal of Zr-BDB (Fig. 2C), verifying that Zr-BDB was heterogeneous in the reaction process. Meanwhile, as determined by ICP-AES, the concentration of Zr in the reaction mixture was very low (<0.8 ppm), indicating the negligible leaching of active species. Second, it was found that Zr-BDB could be reused for at least five catalytic cycles without obvious decrease in activity and product selectivity (Fig. 2D and S5[†]). The recovered Zr-BDB was characterized by several techniques (Fig. S6 and Table S1[†]), including XRD, FT-IR, HR-TEM, and N₂ adsorption-desorption method, which showed that there was no obvious change in the properties of the recovered Zr-BDB, implying that Zr-BDB was stable.

Scope of substrates

Encouraged by the excellent performance regarding the conversion of levulinate esters, we further investigated the catalytic activity of Zr-BDB for the MPV reaction of other biomassderived carbonyl compounds (Table 2). To our delight, the Zr-BDB could efficiently catalyze the MPV reaction of various biomass-based aldehydes and ketones. From the results in Table 2, it was obvious that aldehydes were generally more reactive than ketones, resulting from the lower steric hindrance of the aldehyde group. More importantly, the reactivity of the substituted substrates decreased in comparison with the

Table 2MPV reaction of various biomass-based carbonyl compoundsover Zr-BDB^a

Entry	Reactant	Product	T^b (°C)	t ^b (h)	C^b (%)	<i>Y^b</i> Y (%)
1	0	но	100	2	99.4	98.7
	\bigcirc	\bigcirc				
2	\sim	Он	100	2	99.6	98.5
3	0	но	100	6	98.4	98.2
4	°	но	100	6	97.2	96.7
5	°	но	100	4	98.7	98.2
		NO ₂				
6	°	но	120	6	99.1	96.6
	OH	OH				
7	°	HO	130	6	97.2	95.8
	ОН	ОН				
8	°	HO	130	8	97.3	95.7
	OH	OH				
9		ОН	100	6	96.9	94.2
10	$\bigcirc \bigcirc \bigcirc \bigcirc$	ОН	100	2	96.2	95.7
11	\downarrow	\downarrow	100	4	97.9	93.8
		ОН				
12	Ļ	ОН	100	6	98.7	98.3
		\bigcup				
13	Let 5	OH M5	100	6	97.5	96.1
14		ОН	150	10	96.7	96.2
15 ^c	, Î	OH	160	12	90.4	88.1
16 ^{<i>c</i>}		OH O	160	12	88.7	87.3
17 ^c	~~^	OH OH	160	12	87.5	86.4

Table 2 (Contd.)

Entry	Reactant	Product	T^{b} (°C)	<i>t</i> ^{<i>b</i>} (h)	C^{b} (%)	<i>Y^b</i> Y (%)
18 ^c	O H	OH OH OH	150	12	94.6	92.2
19 ^c		OH	160	12	88.1	86.8
20		OH OH	130	6	99.2	98.3

^{*a*} Reaction conditions: reactant, 1 mmol; Zr-BDB, 50 mg; isopropyl alcohol, 5 g. ^{*b*} The conversion and yield were determined by GC. T = temperature, t = time, C = conversion, and Y = yield. ^{*c*} The amount of Zr-BDC was 0.1 g.

unsubstituted ones, and the substrate with electron donating groups showed low reactivity. For example, benzaldehyde could be completely converted into benzyl alcohol with a reaction time of 2 h at 100 °C (Table 2, entry 1), while other substituted benzaldehydes required longer reaction time (Table 2, entries 3-5) and/or higher reaction temperature (Table 2, entries 6-8). This phenomenon was more obvious for acetophenone (Table 2, entry 14) and the substituted ones (Table 2, entries 15-17). 4-Nitrobenzaldehyde (Table 2, entry 5) had higher reactivity than 4-methoxybenzaldehyde (Table 2, entry 3), indicating the less negative effect of the electron withdrawing group than the electron donating group. Cinnamaldehyde (Table 2, entry 9) showed lower reactivity than 3-phenylpropionaldehvde (Table 2, entry 10) owing to the conjugative effect of the C=C bond. Moreover, the reactivity decreased for the reactants with the phenolic hydroxyl group because its interaction with the borate group was too strong (Table 2, entries 6-8), and thereby, higher reaction temperature was needed to break this interaction to release the borate, which was one of the catalytic sites in Zr-BDB. Moreover, aliphatic ketones (Table 2, entries 12 and 13) showed much higher reactivity than aromatic ketones (Table 2, entries 14-19). In addition, Zr-BDB could efficiently catalyze the MPV reaction of 2-phenoxyacetophenone (Table 2, entry 20), a lignin model compound. These results further verified the superior catalytic activity of Zr-BDB in MPV reactions.

Discussions on the high activity of the Zr-BDB

As discussed above, the prepared Zr-BDB had superior catalytic activity for the MPV reaction of various biomass-derived carbonyl compounds, which was much better than ZrO_2 , Zr-BDC, and UiO-66. Generally, for the Zr-catalyzed MPV reaction, the catalytic activity mainly depends on the oxophilicity of Zr,^{8b,9,11} which was the active site to activate the carbonyl group in the reactant, and the basicity of the catalyst, which affects the activation of the hydroxyl group in the hydrogen donor (the alcohol).^{8b,11}

In one aspect, a much higher catalytic activity was achieved over Zr-BDB in comparison with ZrO_2 (Table 1, entries 1 and

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Fig. 3 XPS spectra of Zr 3d in Zr-BDB, Zr-BDC, UiO-66, and ZrO₂.

2). As determined by XPS spectra (Fig. 3), the binding energies of Zr 3d in Zr-BDB were much higher than those in ZrO_2 , indicating the higher positive charge on the Zr atoms in the Zr-BDB, which afforded the Zr in Zr-BDB having a stronger oxophilicity than that in ZrO_2 . The stronger oxophilicity was beneficial for the activation of the carbonyl group in the reactant, and thus, Zr-BDB showed higher activity than ZrO_2 . Meanwhile, as determined from CO_2 -TPD examinations (Table S3†), Zr-BDB showed much higher basicity than ZrO_2 . Higher basicity was favorable to activate the hydroxy group in the synergistic effect of Zr with stronger oxophilicity and higher basicity resulted in Zr-BDB having much higher catalytic activity than ZrO_2 .

In another aspect, Zr-BDB showed much higher catalytic activity for the MPV reaction than both Zr-BDC and UiO-66. However, Zr-BDB, Zr-BDC, and UiO-66 had similar binding energies of Zr 3d as well as similar basicity (Fig. 3 and Table S3[†]). Thereby, the difference in these three catalysts did not originate from the oxophilicity of Zr and the basicity. On the basis of the above discussion, the catalytic activity of the Zr-organic ligand hybrids increased with the number of borate groups on the benzene ring of the organic ligands (Table 1, entries 2, 4, and 5). From these results, we could deduce that the difference in catalytic activity of Zr-BDB, Zr-BDC, and UiO-66 resulted from the borate groups. As reported, the B atom in the borate groups, acting as the Lewis acidic sites, could activate the hydroxyl groups in the isopropyl alcohol via the interaction between the B atom and the O atom of the hydroxyl group,12 and thus, H was much easier to be released to attend the MPV reaction. ¹H NMR spectra (Fig. 4 and S7-9[†]) clearly showed new peaks centered at 1.21, 4.65, and 8.71 ppm in the mixture of isopropyl alcohol and 1,4-benzenediboronic acid, which corresponded to the H signals in the activated isopropyl alcohol (Scheme S3[†]). Meanwhile, the signal for the hydroxyl group became broader in the mixture of isopropyl alcohol and 1,4-benzenediboronic acid compared to that in isopropyl alcohol (Fig. 4). In contrast, no new signals were



Fig. 4 1 H NMR spectra of isopropyl alcohol, 1,4-benzenediboronic acid, and their mixture in DMSO- d_{6} .

found in the mixture of isopropyl alcohol and BDC (Figs. S7 and S10–12[†]), and the difference between the isopropyl alcohol and the mixture of isopropyl alcohol and BDC was that the signal for the hydroxyl group became broader in the mixture, which may be caused by the hydrogen bonding between BDC and isopropyl alcohol. These results implied the stronger activation role of borate groups on isopropyl alcohols than carboxylate groups, and also confirmed the strong interaction between the hydroxyl group and the borate group, thereby significantly improving the reactivity of the hydroxyl group. Thus, higher catalytic activity was achieved when using Zr-BDB as the catalyst.

Mechanism

Based on the obtained results and some reported knowledge,^{8b,10,11} we can deduce that both Zr and borate groups, playing the role of activating the carbonyl and hydroxyl groups respectively, were crucial to achieve high catalytic activity for the MPV reaction. Thus, we proposed a possible mechanism for the Zr-BDB-catalyzed MPV reaction (Scheme 1). In each catalytic cycle, the carbonyl group in the reactant was activated by the interaction between the O atom in the C=O group and the Zr^{4+} in Zr-BDB. Meanwhile, the O atom in the hydroxyl group of the isopropyl alcohol interacted with the B atom in the Zr-BDB, which could promote the dissociation of



Scheme 1 Possible mechanism for the Zr-BDB-catalyzed MPV reaction of biomass-derived carbonyl compounds.

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the hydroxyl group to attend the MPV reactions. Subsequently, hydrogen transfer occurred from the activated hydroxyl group to the activated carbonyl group *via* the formation of a six-link intermediate. Finally, the carbonyl compounds were reduced to the desired alcohols, and isopropyl alcohol was transformed into acetone. For the MPV reaction of levulinate esters, an intramolecular transesterification was essential to generate the desired GVL (Scheme S4[†]).

Conclusions

In summary, porous zirconium-organic borate (Zr-BDB) was fabricated by the coordination between ZrOCl₂ and 1,4-benzenediboronic acid. The synthesized Zr-BDB could efficiently and selectively catalyze the MPV reduction of various biomassderived carbonyl compounds, including levulinate esters, aldehydes and ketones. Moreover, the Zr-BDB showed much better catalytic performance than ZrO₂ and the common Zr-based metal organic framework (UiO-66). Systematic studies indicated that the excellent performance of Zr-BDB originated from the synergetic effect of Zr⁴⁺ and borate groups, which activated the carbonyl groups in the substrates and the hydroxyl groups in isopropyl alcohol, respectively. We believe that zirconium-organic borates have great potential applications in MPV reductions, and they could be potentially applied in other important transformations involving alcohols as the reactants.

Experimental

Preparation of the Zr-BDB

In a typical process, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (5 mmol) and BDB (5 mmol) were dissolved in DMF (100 mL). The solution was stirred at room temperature for 4 h. Then, the solution was transferred into a reactor of 150 mL volume. After being sealed, the reactor was placed into an oven with a temperature of 150 °C for 48 h. When the reactor was cooled down to room temperature, a white solid (Zr-BDB) was obtained by centrifugation, and the white solid was washed with DMF (3 × 8 mL), ethanol (3 × 8 mL), and diethyl ether (3 × 5 mL). Finally, the solid was dried at 80 °C under vacuum for 12 h. Anal. Found: 39.14% Zr, 26.35% C, 4.85% H, and 7.82% B.

Other catalysts, including Zr-CPB, Zr-BDC, and Zr-B, were synthesized with a similar route except for using the different organic ligands.

Characterization

Scanning electron microscopy (SEM) measurements were conducted on a Hitachi S-4800 Scanning Electron Microscope operating at 15 kV. Transmission electron microscopy (TEM) measurements were performed on a TEM JEOL-1011 with an accelerating voltage of 120 kV. The HR-TEM and corresponding elemental mappings were recorded on a HR-TEM JEOL-2100F. FT-IR spectra were obtained using the Bruker Tensor 27 IR spectrometer via the KBr pellet method. X-ray diffraction (XRD) measurements were carried out on an X-ray diffractometer (D/MAX-RC, Japan) operating at 40 kV and 200 mA with Cu Ka (λ = 0.154 nm) radiation. XPS measurements were performed on an ESCALab 220i-XL spectrometer at a pressure of $\sim 3 \times 10^{-9}$ mbar (1 mbar = 100 Pa) using Al K α as the excitation source ($h\nu$ = 1486.6 eV) and operating at 15 kV and 20 mA. The contents of Zr and B in Zr-BDB were determined with ICP-AES (VISTA-MPX), and the contents of C and H in Zr-BDB were measured by elemental analysis using the FLASH EA1112 analyzer. N2 adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2020 V3.00 H (USA) surface area analyser at 77 K. Temperatureprogrammed desorption of carbon dioxide (CO2-TPD) was performed on a Micromeritics' AutoChem 2950 HP Chemisorption Analyzer. ¹H NMR spectra were recorded on a Bruker Avance NMR spectrometer (400 MHz) with DMSO- d_6 as the solvent.

MPV reactions

In a typical experiment, reactant (1 mmol), isopropyl alcohol (5 g) and suitable amounts of catalyst were charged into a stainless reactor of 15 mL. After being sealed, the reactor was placed into an air oven at a desired temperature. After the reaction was conducted for a desired reaction time, the reactor was cooled down quickly with ice water. Finally, the conversion of the reactant and the yield of the product were analyzed quantitatively using gas chromatography (GC, Agilent 7890, using cyclohexanol as the internal standard) equipped with the flame-ionized detector (FID) and the HP-5MS capillary column (0.25 mm in diameter, 30 m in length), and the product was also confirmed by GC-MS (Agilent 5977A).

Reusability of Zr-BDB

To determine the reusability of the Zr-BDB, the used Zr-BDB was recovered by centrifugation, and washed with ethyl ether (3 \times 5 mL). After being dried at 80 °C under vacuum for 12 h, the recovered Zr-BDB was reused for the next cycle.

Conflicts of interest

There are no conflicts to declare.

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