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Ligand plays a key role in modern catalysis research area and occasionally determines whether a reaction will take place under specific condition, such as in water. In this experiment, ligands containing indole-based diacid moiety were employed to prepare the corresponding cobalt coordination polymer material (Co-CIA) and porous oval polymer material (Co-NCIA) tuned. Interestingly, it was observed that Co-CIA could promote the alkylation of ketones with alcohols, alcohols with alcohols, while Co-NCIA was effective for the synthesis of 1-benzyl-2-aryl-1*H*-benzo[d]imidazoles from various phenylenediamine and benzyl alcohols through borrowing hydrogen and dehydrogenation strategy. Other mechanism explorations, such as the deuterium labeling experiments and the kinetic study, were conducted to better understand Co-CIA and Co-NCIA systems, and the related transformations. Our studies provided an efficient method for the development of high active cobalt coordination polymer materials with excellent recovery performance for the dehydrogenation and borrowing hydrogen reactions under water and base-free conditions.

Keywords: cobalt; borrowing hydrogen; ligand; dehydrogenation; water

Introduction

During the past several years, borrowing hydrogen and dehydrogenation reactions have gained tremendous interests and became one of the most promising areas in organic chemistry and material science research.^{1,2} Traditionally, noble metals, such as Rh, Ru, Ir, Au and Pd have been used in the catalysts for C-C, C-N, and C-O bonds formations through borrowing hydrogen and dehydrogenation pathways.^{3,4} In order to achieve the goal of sustainable and economical chemistry, it is urgent to develop novel catalysts employing earth-abundant and inexpensive metals instead of noble metals for these reactions, especially for large-scale productions.⁵ Recently, earth-abundant and inexpensive

metals, for example Fe,⁶ Co,⁷ Ni,⁸ Mn,⁹ have been used in the catalysts for hydrogenation, dehydrogenation,, dehydrogenation cyclization and borrowing hydrogen reactions.¹⁰ As one of the typical inexpensive and earthabundant metals, Cobalt has attracted considerable attentions in the past. For example, Kirchner group developed a novel cobalt complex and successfully applied it as an efficient catalyst to achieve alkylations of amines in the presence of alcohols.^{11a} In 2015, Kempe et al demonstrated another Cocatalyzed alkylation reaction of amines with alcohols in which the novel Co complex was stabilized by a PN₅P ligand under mild conditions.^{12a} Later, they reported Co-catalyzed Calkylation of unactivated amides and esters with alcohols which was catalyzed by PN5P-stabilized Co complexes.^{12b} Zheng and Zhang described Co-catalyzed synthesis of aromatic, aliphatic, and cyclic sec-amines through alkylation of amines with amines by using a cobalt pincer complex [(PNHPCy)Co(CH₂SiMe₃)][BArF₄].^{13a} In 2018, Madhu and Balaraman developed a phosphine-free Co-NNN pincer complex which showed high activity in catalyzing direct Nalkylation of amines with alcohols through borrowing hydrogen pathway and This novel catalyst was also employed in the synthesis of imines through dehydrogenative coupling of benzylamines with secondary alcohols.^{14a} Zhang group

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reported direct and selective C-H alkylation of 2alkylquinolines catalyzed by a reusable doped TiO₂-supported nanocobalt oxides.^{15a} Sundararaju et al reported the aalkylation of ketones with alcohols employing a phosphinefree and well-defined cobalt catalyst.¹⁶ Very recently, Kundu group reported the synthesis of a variety of methyl-substituted N-heteroarenes through alkylation of various methylsubstituted N-heteroarene derivatives in the presence of a phosphine-free and stable Co(NNN) catalyst.¹⁷ Quintard and Rodriguez also indicated that well-defined Co is a valuable alternative to expensive noble metals for the development of sustainable and economic catalyst and its application in borrowing hydrogen reactions could lead to a great number of innovative transformations.¹⁸ Xu and coworkers developed transition-metal free alkylation reactions of ketones with alcohols to selectively afford ketone or alcohol products under KOH or NaOH conditions, which is an excellent base metal catalyzed systems for borrowing hydrogen reactions.4k Based on the aforementioned discoveries, it is undoubtable that the development of recyclable cobalt catalytic system for borrowing hydrogen reactions is in urgent needs to achieve sustainable and economic chemistry goals.¹⁹

Recently, we have developed several triazole-skeleted ligands²⁰ and successfully applied them in borrowing hydrogen and dehydrogenation transformations,²¹ However, noble metals were commonly used in most of the catalysts and the resulting metal composites usually demonstrated poor reactivity, stability and reusability. Furthermore, it is also challenging to apply these catalysts in water or solvent-free conditions at high temperature. Herein, indole-skeleteddiacids based cobalt coordinationed polymer material (Co-CIA) and porous oval polymer material (Co-NCIA) were developed. Interestingly, it was observed that Co-CIA could realize the alkylation of ketones with alcohols, alcohols with alcohols through borrowing hydrogen strategy, while Co-NCIA was effective for the synthesis of 1-benzyl-2-aryl-1Hbenzo[d]imidazoles from various phenylenediamine and benzyl alcohols through dehydrogenative cyclization reaction in water.

Results and discussion

Synthesis of Co-CIA and Co-NCIA catalysts.

Two indole- based diacids (L₁) and (L₂) were prepared according to the similar experimental procedures used in our triazole acids synthesis (For details, see supporting information).²² Co-CIA and Co-NCIA catalysts were obtained by using different substituted diacids and auxiliary ligand 1,4-bisimidazole through hydrothermal method (Scheme 1). For the synthesis of material **1a** (Co-CIA): a mixture of the dissolved diacid (1-(carboxymethyl)-1Hindole-3-carboxylic acid, L₁, 0.1 mmol) and CoCl₂·6H₂O (0.05 mmol) in 8 mL DMF-ethanol-water (5: 2: 1, v/v/v) was stirred for 30 minutes at room temperature. Then, the mixture was placed in a 15 mL autoclave lined with a Teflon stopper and heated for 72 hours $a_{tw} 4 \pm 0.0$ $^{\circ}Ce$ Subsequently, the resulting mixture was cooled to wooth temperature and the obtained solid was washed three times with anhydrous ethanol, centrifuged three times, and dried to gain the material Co-CIA (1a) in 85% yield. Using the same hydrothermal synthesis method, under the condition of a high temperature 140 °C for 72 hours, then material Co-NCIA (1b) was gained in 77% yield from diacids (L₂) (For details, please see SI).



Scheme 1. The synthesis of Co-CIA and Co-NCIA catalysts.

Characterization of composite Co-CIA and Co-NCIA.

The materials Co-CIA and Co-NCIA were both carefully characterized through scanning electron microscope (SEM), energy dispersive X-ray (EDX), X-ray power diffraction (XRD), and X-ray photoelectron spectrometry (XPS).



Fig. 1. (a) (b): SEM images of Co-CIA; (c) (d): SEM images of Co-NCIA.

In Figure 1 (a) and (b) shows the SEM images of the material Co-CIA, which indicate a regular square structure on the surface of the coordination polymer. Fig. (a) shows the overall morphology of the prepared material, while Fig. (b) shows more direct and clear material map formed by the self-assembly of the ligand and metal. Figure (c) and (d) shows the full and partial enlarged the scanning electron microscopes images of Co-NCIA, respectively. The Co-NICA processes a porous and elliptical structure as shown in Fig. (c).

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Furthermore, this porous and elliptical structure is composed of sheet-like agglomerate as shown in Fig (d) From the SEM images, it can be seen that the morphology of these two materials differs greatly from one to the other due to the change of ligands which enables controllable material synthesis.



Fig. 2. (a) EDX pattern of Co-CIA; (b) EDX pattern of Co-NCIA.

In Figure 2, images of (a) and (b) shows the EDX pattern of Co-CIA and Co-NCIA, respectively. The spatial distribution of different elements was studied through elemental analysis. From Fig. (a), it was observed that C, O and Co elements of Co-CIA are evenly distributed in the material from Fig. (a). The characteristic peaks of Co were found at 1.0 keV and 1.5 keV in EDS spectrum, which further proved the existence of cobalt in the prepared material. The distribution of C, N, O and Co elements in the material Co-NCIA could be determined from figure (b). The characteristic peaks of Co were found at 0.7 keV and 1.7 keV in EDS spectrum, which proved the existence of Co-NCIA. EDS images revealed that the element assignments of these two materials are different, making them two kinds of materials.



Fig. 3. (a) XRD spectrum of Co-CIA; (b) XRD spectrum of Co-NCIA.

X-ray diffraction (XRD) was performed to determine the position at which the metal degree, thereby, appeared to prove the crystallinity of the materials (Fig. 3). The XRD pattern (a) shows two diffraction peaks of cobalt at $2\theta = 44.2^{\circ}$ and 51.5° , respectively. The diffraction peak of C in the ligand (L₁) is also shown in Figure 3(a). Obviously, the diffraction peak at $2\theta = 10^{\circ}$ of the XRD pattern (a) is the characteristic peak of the ligand (L₁). The results were shown in the XRD pattern (a) indicated the existence form of metal Co in Co-CIA. Figure (b) shows a more distinct characteristic peak of Cobalt





Fig. 4. (a) XPS spectrum of Co-CIA, (b) high-resolution Co 2p spectrum, (c) high-resolution C 1s spectrum, (d) high-resolution O 1s.



Fig. 5. (a) XPS spectrum of Co-NCIA, (b) high-resolution Co 2p spectrum, (c) high-resolution C 1s spectrum, (d) high-resolution O 1s.

The chemical state and element composition on the surface of Co-CIA and Co-NCIA coordination polymer materials were also tested by XPS (Figs. 4-5). The full spectrum of Co-CIA and Co-NCIA showed that the materials are composed of C, N, O and Co, respectively. Fig. 4b and Fig. 5b revealed the presence of Co $2P_{3/2}$ and Co $2P_{1/2}$ peaks. The binding energies of Co-CIA were 781.06, 785.68, 796.74 and 802.25 eV, while binding energies of Co-NCIA were 781.32, 785.64, 797.20

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and 802.13 eV, respectively. The binding energies of Co-CIA at 785.68 and 802.25 eV were attributed to metal Co, while the binding energies of 781.06 and 796.74 eV were attributed to Co^{2+} , Similar results were observed for Co-NCIA. Four major peaks were seen from C 1s spectrum (Fig 4c), which are assigned to C=C (284.7 eV), C-N (285.8 eV), C=O (287.8 eV), and O-C=O (288.7 eV). The O 1s spectrum (Fig. 4d) showed two peaks, which are attributed to C=O (530.7 eV), C-OH (532.1 eV). The surface element composition of Co-CIA and Co-NCIA proved the successful synthesis of cobalt-containing coordination polymers synthesis.

Catalytic activity

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With Co-CIA and Co-NCIA in hand, the classic borrowing hydrogen reaction of ketone with benzyl alcohol was selected as a model reaction to examine catalytic activities of these two materials. The reaction of acetophenone and benzyl alcohol was attempted with Co-CIA as a catalyst in water. As can be seen from Table 1, it was found that the reaction could take place in water without extra base, however, an additive was needed to promote the reaction. After screening a series of conditions, it was found that the combination of AgNTf₂ and KF as additives produced a better result. Further conditions screening revealed that phase transfer catalyst TBAB greatly promoted this reaction and the reaction yield reached 93%.. Meanwhile, it was found that Co-NCIA could also promote this reaction with a slightly lower yield. Therefore, the optimal reaction condition was established to have AgNTf₂ and KF as additives, Co-CIA/TBAB as catalyst and stirring in water at 90°C for 16h, which realizes the goal of sustainable development in green chemistry.

Table 1. Optimization of reaction conditions.^{*a,b*}

2a	+ 3a	OH [Co], additives	S→ Ph Ph 4a	+ Ph 5a
entry	cat	additives	ratio(4a/5a)	yield(4a)[%]
1	-	-	-	<5
2	Co-CIA	-	-	23
3	Co-CIA	LiCl	-	<5
5	Co-CIA	KF	-	11
6	Co-CIA	I_2	-	<5
7	Co-CIA	AgOTf	-	27
8	Co-CIA	$AgBF_4$	-	31
9	Co-CIA	$AgSbF_6$	13:1	48
10	Co-CIA	$AgNTf_2$	>20:1	54
11	Co-CIA	$AgNTf_2/KF$	>20:1	73
12	Co-CIA	$AgNTf_2/KF$	>20:1	90 ^c
13	Co-CIA	$AgNTf_2/KF$	>20:1	93 ^d
14	Co-CIA	$AgNTf_2/KF$	>20:1	81 ^e

15	-	$AgNTf_2/KF$	- DOI: 10 1	View Argcle Online
16	Co-CIA	TBAB	-	38
17	-	TBAB	-	<5
18	Co-NCIA	AgNTf2/KF	>20.1	86^d

^{*a*}Conditions: **2a** (1.0 mmol), **3a** (1.2 mmol), cat.(10 mg), additive (1.0 mmol), H_2O (3 mL), 16 h, 90 °C. ^{*b*}Isolated yields. ^{*c*} TBAF (0.2 mmol). ^{*d*} TBAB (0.2 mmol). ^{*e*} TBAI (0.2 mmol).

In the optimization of conditions, $AgNTf_2$ is an auxiliary agent, which converts its coordination complex (Co-CIA) from neutral to cationic form, and the reaction is much smooth. Through screening, it was found that the combined additive of $AgNTf_2$ and KF can achieve a higher yield.

After optimizing the reaction conditions, the substrate scope of borrowing hydrogen reaction between ketones and benzyl alcohols were investigated and the results were shown in Table 2. From this study, it was found showed that the substrate with an electron-withdrawing group is less reactive than that with electron-donating group. For example, substrate 1-(*p*-tolyl)ethan-1-one and 1-(4methoxyphenyl)ethan-1-one gave the desired products in 84% and 87% yields, respectively. However, the substrates with halogen group resulted in slightly lower yields, such as 41, 4q, 4r. Generally, the catalyst Co-CIA demonstrated good selectivity for cross-coupling reaction of ketones with alcohols though moderate yields were commonly seen.

Table 2. Substrate expansion of borrowing hydrogen reaction.^{a,b}



^{*a*} Reagents and conditions: **2** (1.0 mmol), **3** (1.2 mmol), Co-CIA (10 mg), AgNTf₂ (1.0 mmol), KF (1.0 mmol), TBAB (0.2 mmol), H₂O (3 mL), 16 h. ^{*b*} Yields of isolated product.

Next, alkylation between alcohols was studied to further evaluate the activities of Co-CIA and Co-NCIA catalysts.. The results showed that most of the alcohol substrates reacted Published on 30 October 2020. Downloaded by University of New England on 10/30/2020 12:28:39 PM.

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smoothly and the corresponding substituted ketones were obtained in moderate to good yields with Co-CIA as catalyst (Table 3). When substrate with *para*-methoxy group was employed in this reaction, the highest yield of the desired product was 90%. It should be noted that only moderate yield was achieved when Co-NCIA was used as catalyst in this reaction.

Table 3. Substrate expansion.^{a,b}



^{*a*} Reagents and conditions: **6** (1.0 mmol), **3** (1.2 mmol), Co-CIA (10 mg), AgNTf₂ (1.0 mmol), KF (1.0 mmol), TBAB (0.2 mmol), H₂O (3 mL), 24 h. ^{*b*} Yields of isolated product.

1H-benzo[d]imidazole derivatives were known as valuable building blocks due to their antidiabetic, antiviral, antimalarial, antibiotic and inhibitory activities.²³ For example, our group recently found that 2-aryl-1H-benzo[d]imidazoles and 1-benzyl-2-aryl-1H-benzo[d] imidazoles display certain fungicidal activities against Rhizoctonia solani, Fusaium graminearum, Penicillium digitatum, Magnaporthe grisea and Penicillium italicum.24 Research on the synthesis of 1Hbenzo[d]imidazoles has attracted considerable attentions during the past four years. However, synthesis of these derivatives under water or solvent-free conditions is still challenging.^{25,26}. Based on our previous synthesis of 1-benzyl-2-aryl-1*H*-benzo[d] imidazole derivatives,²⁴ herein, we employed the Co-CIA and Co-NCIA catalysts in the base-free reactions of phenylenediamines and substituted benzyl water achieve 1-benzyl-2-aryl-1Halcohols in to benzo[d]imidazole derivatives. To our delight, the Co-NCIA was found to be an effective catalyst in this reaction leading to high product yields (Table 4). It should be noted that this reaction couldn't happen without this catalyst under strong base conditions. However, the Co-CIA was inactive in promoting this transformation, which indicated that the ligand impact on the activity of the catalysts is dominant.

Table 4. Substrate expansion.^{*a,b*}



^{*a*} Reagents and conditions: 7 (1.0 mmol), **2** (3.0 mmol), Co-NCIA (10 mg), AgNTf₂ (1.0 mmol), KF (1.0 mmol), TBAB (0.2 mmol), H₂O (3 mL), 36 h. ^{*b*} Yields of isolated product. ^{*c*} Conditions: NaOH (1 mmol), toluene, 110 °C, 24 h.

Electrocatalytic water decomposition is known as be an efficient and simple hydrogen production method, which is widely used for hydrogen production.. The efficiency of water decomposition is often determined by oxygen evolution. This is mainly because the oxygen evolution reaction occurs undergo a 4e transformation process, which usually accompanied by the cleavage of the O-H bond and the formation of the O-O bond. Therefore, the oxygen evolution reaction requires a larger overpotential. IrO₂ and RuO₂ are generally recognized as the most efficient catalysts for oxygen evolution reaction, however, these noble metals are relatively expensive. Therefore, designing and developing an efficient and inexpensive oxygen evolution catalyst is in urgent need to further improve the oxygen evolution reaction. To better understand the feasibility and advantages of Co-CIA and Co-NCIA catalysts in oxygen evolution reaction, the electrochemistry properties of these two catalysts were investigated and the results were concluded in Fig. 5.

The electrocatalytic activities of Co-CIA and Co-NCIA for water oxidation reaction were studied in alkaline solution (1.0 M, KOH) using linear sweep voltammetry (LSV) with standard three-electrode system in which rotating disk electrode (RDE) acted as a working electrode. The detailed procedure of electrochemical experiments and calculations

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were presented in the supporting information. Figure 5a showed the linear sweep voltammetry (LSV) polarization curves of Co-CIA, Co-NCIA, IrO_2 and $CoCl_2 \cdot 6H_2O$ catalysts with a scan rate of 5 mV/s. Furthermore, the LSV curve for these catalysts revealed that the overpotential of 320, 309, 303, and 334 mV was required to produce an anodic current density of 10 mA/cm², respectively.

The reaction kinetics of water oxidation catalyzed by Co-CIA and Co-NCIA were determined by Tafel plot which correlates the catalytic current density with overpotential. In the alkaline solution (1.0 M, KOH), the Tafel plot exhibited linear behavior within a broad range of potential values. The slope of the Tafel plot for Co-CIA and Co-NCIA was found to be 74.8 mV dec⁻¹ and 69.1 mV dec⁻¹ respectively (Figure 5b), indicating the high efficiency of these two catalysts. Meanwhile, these results were comparable to the values of some Co-based water oxidation catalysts reported recently. Furthermore, the Tafel plot of the costly water oxidation catalyst IrO₂ was also studied in the alkaline solution (1.0 M, KOH) for comparison. The Tafel slope for IrO₂ was found to be 69.1 mV dec⁻¹. Therefore, the Tafel plot studies show that the catalyst Co-CIA and Co-NCIA could serve as an efficient electrocatalyst for the water oxidation reaction.



Fig.5. (a) LSV curves of IrO_2 , $CoCl_2 \cdot 6H_2O$, $Co-NCIA_{icand}$, $Co-CIA_{icand}$ in electrolyte solution of 1M KOH. (b) The corresponding 2Bafel fitting plots of IrO_2 , Co-NCIA and Co-CIA.

As indicated above, the Co-CIA and Co-NCIA could be utilized for efficient electrocatalytic oxygen evolution reactions. Compared with IrO₂, Co-CIA and Co-NCIA have very similar potentials and Tafel slopes compared to the precious metal IrO₂. Meanwhile, it was observed that Co-NCIA showed better catalytic oxidation performance than Co-CIA, which provided another clue to explain the different catalytic activities of these two catalysts found in the dehydrogenation and borrowing hydrogen transformations.

Based on the literature reports, the driving force of catalytic reaction was caused by the morphology, surface functional groups, active sites, and/or surface structures of a catalytic material.²⁷ The morphology of catalytic the cobalt coordination polymers Co-CIA and Co-NCIA with two different organic ligands lead to different catalytic active sites. The indole-skeletoned diacid ligand is acidic and cobalt ions could easy diffuse in the solution area near the surface of the ligand, and some cobalt ions are adsorbed on the surface. Cobalt acts as a nucleation site and reacts to the ligand, with the reaction progresses, if the relative amounts of indole skeleton diacids n(L)/n(M) and c(L) increase, they could be transformed into a hollow structure (Co-CIA and Co-NCIA with different shells), such as (Fig. 1). Since there is no further proof (the single crystal structure), X-ray diffraction (XRD) and XPS tests were performed on it, which initially proved that the catalytic active center is metal Co^{2+} , which was consistent with the literatures.²⁷

To further explore Co-CIA and Co-NCIA, several control experiments and mechanism studies were carried out in water under base-free conditions. Catalytic experiments revealed that Co-CIA could catalyze borrowing hydrogen of ketones with alcohols, alcohols with alcohols, while Co-NCIA was effective for the synthesis of 1-benzyl-2-aryl-1Hbenzo[d]imidazoles from various phenylenediamine and benzyl alcohols. It was noted that cobalt slats, such as CoCl₂, CoBr₂, failed to these two reactions in water under base-free conditions. The intermolecular competitive reaction in the basic steps was involved in kinetics, aiming at explaining the decision-making steps at a competitive rate. Kinetic isotope effect values (KIE: $K_H/K_D = 2.01$) was obtained by the first order reaction plots of ln [3a-d2] and ln [3a] (Scheme 2). The results indicated that dehydrogenation of benzyl alcohol (3a) is the rate-determining step during this borrowing hydrogen transformation.



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Scheme 2. Kinetic plot of acetophenone and benzyl alcohol. A_0 : original concentration of substrate. A_t : concentration of substrate at time t. k: rate constant.

In addition, the kinetic studies were conducted and the possible reaction plots were achieved to better understand these cobalt catalyzed reactions (Scheme 3). The results showed that the formation of benzaldehyde intermediate was the key of this reaction, which also proved the borrowing hydrogen process during this coupling reaction.



Scheme 3. Kinetic investigations for the synthesis of 4a.

Reusability of the catalysts

Furthermore, the reusability of the Co-CIA was examined under water condition. The used catalyst was washed with ethanol and deionized water, centrifuged for four times, and dried. The catalyst was recycled for five times. At each time, the recovery experiment for the alkylation of an alcohol with another alcohol was surveyed in water. It was observed that the yield of the desired product decreased slightly as the increasing of recycle time (Scheme 4). At the same time, the reusability of Co-NCIA catalyst for the reaction of phenylenediamine with

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benzyl alcohol was also examined and similar vresultse were seen DOI: 10.1039/D0GC02341H

Ph 2a	+	Ph ^{OH}		Co-CIA, Aç (F, TBAB, 90	9NTf ₂) °C, <mark>H₂O</mark>	Ph	Ph 4a
Recycled tin	nes	0	1	2	3	4	5
Yields		93%	92%	92%	90%	89%	87%
OH Ph 6a	+	Ph ^{OH}		Co-CIA, A	gNTf ₂ D °C, <mark>H₂O</mark>	(Ph	P Ph 4a
Recycled tin	nes	0	1	2	3	4	5
Yields		86%	84%	84%	83%	82%	81%
NH ₂ NH ₂ 7a	4	Ph 2a	`ОН -	Co-NCIA, KF, TBAB,	, AgNTf₂ 90 ºC, <mark>H₂O</mark>	88	Ph
Recycled tim	nes	0	1	2	3	4	5
Yields		80%	78%	77%	76%	74%	73%

Scheme 4. Recycled experiments.

During this catalytic system, it was noted that the additives were employed, such as, silver reagent, potassium fluoride and TBAB. Therefore, it was necessary to investigate the role of these additives. It was reported many transformations involving silver salts are actually belonged to silver-assisted metal catalysis or bimetallic catalysis.²⁸ Silver nanoparticle (or silver halide) play a key role in some cases. Here, we also conducted several reactions to explore the effects of additives (Table 5). It was observed that silver salt couldn't catalyze this reaction. After removing silver halide through celite, almost the same yield was obtained, which indicated the catalytic activity of cobalt catalyst was enhanced by noncoordinating anions and it was observed that silver slat does not play a role during the synthesis of 1-benzyl-2-aryl-1Hbenzo[d]imidazoles, which was consistent with the relevant literatures.²⁹.

Table 5. The additives experiments.^{*a*, *b*}

7	_NH₂ + Ph^OH - NH₂ 2a a 2a	Co/additives	N N N Ba
Entry	Catalyst	Conditions ^c	Yield (8a) [%]
1	Co-NCIA	-	16
2	-	-	<5
3	AgBr	-	<5
4	AgNTf ₂	-	<5
5	TBAB	-	<5
6	Co-NCIA/AgNTf ₂		47
7	Co-NCIA/ AgNTf ₂ /KF	_	62

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8	Co-NCIA/ AgNTf ₂ /KF	No filtration	80
9	Co-NCIA/ AgNTf ₂ /KF	After filtration	76
10	AgNTf ₂ /KF/TBAB	-	<5
*C 1''		1) (10	> 1.1°.1

^{*a*}Conditions: **7a** (1.0 mmol), **2a** (3.0 mmol), cat.(10 mg), additive (1.0 mmol), H₂O (3 mL), 16 h, 90 °C. ^{*b*}Isolated yields. ^{*c*} The silver sediment was filtrated through celite.

Finally, the summary of the synthesis of 1-benzyl-2-aryl--1H-benzo[d]imidazole was summarized in Scheme 5. The results indicated that Co-NCIA catalytic system shows high efficiency, which enables effective atomic green transformation under water and base-free conditions in terms of recovery.²⁴⁻²⁶ In general, this cobalt catalytic system provided an efficient method for the reactions of ketones with alcohols, alcohols with alcohols and the synthesis of 1benzyl-2-aryl-1H-benzo[d]imidazoles from various phenylenediamine and benzyl alcohols through borrowing hydrogen and dehydrogenation strategy with only water or hydrogen gas as the by-products.

NH ₂ +	2	catalyst conditions	N N	Ba
Catalyst	Solvent	Conditions and yields	Cycles	Reference
TAP-Cu	Toluene	<i>t-</i> BuOK, 120 °C, 70%	-	24 <i>a</i>
[(Cp*)lr(LSe-S)*Cl]/A	Toluene	<i>t-</i> BuOK, N ₂ , 80 °C, 92%	-	25a
Mn(CO) ₅ Br	Toluene	<i>t-</i> BuOK, N ₂ , 130 °C, 67%	-	25e
Pd(OAc) ₂ /Xantphos	CH ₃ CN	80 °C, 48 h, 65%	-	25f
Ni-Cat./L	Toluene	<i>t-</i> BuOK,140 °C, 24 h, 91%	-	25g
Zr-IDA	Toluene	K ₂ CO ₃ , 110 °C, 90%	5	25h
Mn-NNS	alcohol excess	<i>t-</i> BuOK, N ₂ , 140 °C, 79%	-	26 <i>a</i>
Pd-HAP	Toluene	90 °C, 40%	-	26b
Co-NCIA	H ₂ O	base-free, 90 °C, 80%	5	This work

Scheme 5. The comparisons.

Conclusions

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In conclusion, we have successfully developed two cobalt coordination polymers Co-CIA and Co-NCIA using different substituted diacids and auxiliary ligand materials 1,4-bisimidazole. These were fully characterized by SEM, EDS, XRD, XPS and TG. Moreover, it was observed that Co-CIA could promote the borrowing hydrogen reactions of ketones with alcohols, and alcohols with alcohols without extra bases and organic solvents. Meanwhile, the Co-NCIA was found to be effective for the synthesis of 1-benzyl-2-aryl-1H-benzo[d]imidazoles from various phenylenediamine and benzyl alcohols. This provided an efficient method for the development of high active cobalt coordination polymer materials for the dehydrogenation and borrowing hydrogen reactions under water and base-free conditions with excellent recovery performance. In addition, electrocatalytic water splitting reaction was

explored to better display these two cobalt catalysts_{nii}It was found that Co-CIA and Co-NCPA: cotIP be contributed for efficient electrocatalytic oxygen evolution reactions and Co-CIA and Co-NCIA have very similar potentials and Tafel slopes compared to the noble metal IrO₂.

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