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Introduction

 α ,β-Unsaturated carbonyl compounds (*e.g.*, 2-cyclopentenone and 4-hydroxy-2-cyclopentenone) are important building blocks for natural products, drug molecules, and bulk chemicals,¹⁻⁴ as well as versatile synthetic reactants in diverse organic transformations (*e.g.*, Michael addition, Diels–Alder, and Heck reaction) because these compounds simultaneously contain active olefin, carbonyl, and hydroxyl groups in a small

Nanchang 330031, PR China. E-mail: dengqiang@ncu.edu.cn

Double-metal cyanide as an acid and hydrogenation catalyst for the highly selective ring-rearrangement of biomass-derived furfuryl alcohol to cyclopentenone compounds[†]

Xiang Li,^a Qiang Deng, ^b*^a Lian Yu,^a Rui Gao,^a Zhikun Tong,^a Chenxi Lu,^b Jun Wang, ^b^a Zheling Zeng, ^b^a Ji-Jun Zou ^c^c and Shuguang Deng ^b*^b

Herein, novel green synthetic routes to 4-hydroxy-2-cyclopentenone (HCP) and 2-cyclopentenone (CPE) from biomass-derived furfuryl alcohol *via* double-metal cyanide catalysis are proposed. For the synthesis of HCP, in comparison to conventional solid acids (*i.e.*, Amberlyst-15), MOFs with coordinatively unsaturated metal ions as pure Lewis acid sites exhibit advantageous catalytic selectivity in the reaction under an N₂ atmosphere in a bi-phasic water/*n*-hexane solvent system. FeZn and FeZn-P result in an HCP yield of 77.4% and 88.2%, respectively. For the CPE synthesis, the reaction conditions are the same as those for HCP, except a mono-phasic water solvent system and H₂ atmosphere were employed. In addition to the acid-catalyzed rearrangement reaction, FeZn-DMC exhibits catalytic hydrogenation capability *via* heterolytic cleavage of the H–H bond over Zn–N frustrated Lewis pairs, and a CPE yield of 61.5% is obtained. The DFT simulation indicates that the acid sites and catalytic acid sites are ascribed to the tri-coordinatively unsaturated Zn²⁺ site (Zn(N)₃) on the catalyst surface. Moreover, the DMC catalyst shows excellent stability and recycling performance. This work not only provides an efficient and green catalytic system for CPE and HCP preparation but also demonstrates the interesting bifunctional catalysis of both acid and hydrogenation catalysis over DMC.

cyclopentyl molecule.⁵ Therefore, the synthesis of 4-hydroxy-2cyclopentenone (HCP) and 2-cyclopentenone (CPE) is of great interest in organic chemistry. Traditionally, three pathways are available for CPE preparation (Scheme 1). (1) Palladium-catalyzed dehydrosilylation of 1-trisilyloxy-1-cyclopent-1-ene can be achieved with a CPE yield more than 90% using an oxidant



Scheme 1 Synthetic routes for the production of CPE and HCP.

^aKey Laboratory of Poyang Lake Environment and Resource Utilization (Nanchang University) of Ministry of Education, School of Resource, Environmental and Chemical Engineering, Nanchang University, No. 999 Xuefu Avenue,

^bSchool for Engineering of Matter, Transport and Energy, Arizona State University, 51 E. Tyler Mall, Tempe, AZ 85287, USA. E-mail: Shuguang.Deng@asu.edu ^cKey Laboratory for Green Chemical Technology of the Ministry of education,

School of Chemical Engineering and Technology, Tianjin University; Collaborative Innovative Center of Chemical Science and Engineering (Tianjin),

No. 92 Weijin Road, Tianjin 300072, PR China

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(e.g., p-benzoquinone, tert-butyl hydroperoxide, and oxygen) in an organic solvent.⁶⁻⁹ (2) Photo-oxygenation of cyclopentene with 71% CPE yield has been demonstrated using oxygen as the oxidant in dichloromethane solvent in the presence of acetic anhydride, base and an acylation catalyst (i.e., 4-(dimethylamino)pyridine).¹⁰ (3) Palladium-catalyzed dehydrogenative oxidations of cyclopentanone have been reported with a CPE yield of 51% using oxygen as the oxidant with the cocatalytic effect of trifluoroacetic acid under dimethyl sulfoxide.¹¹ The development of these catalytic systems is limited, due to the various issues including the use of expensive noble metal catalysts, difficulty with the separation and reuse of a homogeneous catalyst, corrosivity of acidic agents, large quantities of organic solvent and expensive raw materials. In addition, these synthesis pathways exhibit low atomic economy, and the reactants are derived from fossil resources, which is not conducive to green and sustainable development. Therefore, the development of an innovative green route from biomass-based raw materials to CPE is important.

On the other hand, HCP has been synthesized using biomass-derived furfuryl alcohol (FA) via an acid-catalyzed rearrangement reaction in water. FA, an important biomass platform compound, is primarily derived from hemicelluloses via several chemical transformations.¹²⁻¹⁵ Hronec's group reported that FA can be converted to HCP, which is catalyzed by the hydrogen proton formed by auto-dissociation of water under high temperature (180-200 °C).¹⁶ Unfortunately, the yield of HCP was low (i.e., approximately 50%) under these severe reaction conditions because some intermediates are unstable and easily converted into humins via intermolecular C-C coupling reactions. Zhang's group used a mild solid base to dilute the density of the in situ water-produced hydrogen proton at 240 °C. Although the conversion of FA decreased, the HCP selectivity increased, and a high HCP yield of approximately 80% was obtained.¹⁷ In addition, under the same reaction temperature (i.e., 240 °C), Reiser's group reported an excellent activity of acetic acid catalysis to convert FA to HCP in a high yield of 87% using water-toluene mixed solvent.¹⁸⁻²⁰ However, these catalytic systems employ high reaction temperatures and homogeneous acids that are difficult to separate and reuse, and experience equipment corrosion, restricting their development for real-life applications.

Recently, the hydrogenative ring-rearrangement of furfural to cyclopentanone was widely reported over various Group VIII or IB metals (such as, Au, Ni, Pd) supported acidic supports (such as TiO₂, Al₂O₃, metal-organic frameworks) under H₂ atmosphere and relatively mild reaction temperature $(140-180 \ ^{\circ}C)$.²¹⁻²⁹ In the hydrogenative rearrangement reaction, furfural is first hydrogenated to FA, then acid-catalytically rearranged to HCP, further generated CPE followed by subsequent hydrogenation and dehydration steps. Finally, cyclopentanone is obtained by hydrogenation of CPE. In the bifunctional catalysis, the hydrogenation active sites and acidic sites are attributed to reduced metals and acid supports, respectively. In general, cyclopentanone is synthesized with a yield higher than 80%. In the reaction, it has been widely accepted that the Lewis acidity in the acid support has a crucially positive effect for the rearrangement step of FA to HCP, but the Brønsted acidity more easily promotes the intermolecular C–C coupling reaction of intermediates, leading to the production of humins.^{18–20,30,31} Unfortunately, the hydrogenation of furfural and rearrangement of FA are often ratelimiting steps, and active HCP and CPE are difficult to preserve due to these subsequent rapid steps.^{21–23} Based on the current development of HCP and CPE syntheses, we were inspired to synthesize a pure solid Lewis acid catalyst for the selective synthesis of HCP and CPE from FA under mild reaction conditions.

Metal-organic frameworks (MOFs) with a modular assembly structure, high surface area, tailorable pores and structural versatility have the potential for application for gas storage, separation, catalysis, sensing, drug delivery and proton conductivity.³²⁻³⁶ The coordinately unsaturated metal centers in a MOF can be used as Lewis acid sites to catalyze numerous reactions. However, MOFs often exhibit poor chemical stability and hydrothermal stability, especially for reactions of aqueous solvents.^{37,38} As a classical MOF, double-metal cyanides (DMCs) which are famous for the use of Prussian blue, are constructed by octahedral metal cyanide anion groups bridged with metal ions through a cyanide group (C \equiv N). Typically, on the edge of a DMC, the coordinately unsaturated vacancy metal ions can be used as Lewis acid site. Generally, triblock copolymers that are used as a complexing agent are added to the synthesis process to suppress overgeneration of crystals and adjust the surface area. Currently, these DMCs are primarily used in acid-catalyzed polymerization, esterification, transesterification, polyesterification, polymerization, hydroamination, and Prins condensation reactions.³⁹⁻⁴³ However, in most cases, these DMC catalysts do not exhibit obvious advantages over other catalysts based on activity and selectivity.

In our previous work, Pd supported acidic DMCs show an excellent catalytic activity for the hydrogenative rearrangement of furfural to cyclopentanone. However, the amount of intermediates HCP and CPE is low because of the strong hydrogenation ability of Pd nanoparticles.²⁴ Herein, for the first time, FeZn-DMCs are used as Lewis-acid catalysts for the rearrangement of furfuryl alcohol (FA) in the water at 150 °C. In comparison to the Amberlyst-15, Al-MCM-41 as well as a familiar MOF (i.e. Cr-MIL-101, Fe-MIL-100), DMCs exhibit great catalytic activity and selectivity for HCP preparation under an N₂ atmosphere in a bi-phasic solvent system. FeZn and FeZn-P produce 88.8% and 95.2% conversion of FA with HCP yield of 77.4% and 88.2%, respectively. To our delight, in addition to the acid-catalyzed rearrangement reaction, FeZn-DMC exihibits catalytic hydrogenation abilities, and a CPE yield of 61.5% is obtained in an H2 atmosphere and mono-phasic water solvent system. Moreover, this catalyst exhibits excellent stability and recycling performance under these reaction conditions. This work not only provides a green and efficient route for CPE and HCP synthesis but also demonstrates the interesting hydrogenation performance of DMC.

Experimental

Materials

Furfuryl alcohol, hydrofluoric acid (35% HF), terephthalic acid (H₂BDC), *N*,*N*-dimethyl formamide, ethanol, *n*-hexane, butylenes oxide, isopropanol, dimethyl sulfoxide, potassium hexacyanoferrate (K₄[Fe(CN)₆]·3H₂O), iron powder, chromium(\mathfrak{m}) nitrate nonahydrate (Cr(NO₃)₃·9H₂O), nitric acid (65% HNO₃), trimesic acid (H₃BTC), potassium hexacyanocobaltate K₃Co (CN)₆, zinc chloride (ZnCl₂) and *tert*-butanol were purchased from Sinopharm Chemical Reagent Company. Amberlyst-15, *tert*-butyl alcohol, dichloromethane, *N*-methyl pyrrolidone and acetonitrile were supplied by the Aladdin Reagent Company. Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (P₁₂₃, average molecular weight = 5800) was obtained from Sigma-Aldrich. All chemicals were used without further purification.

Synthesis of catalysts

DMC was synthesized using a simple precipitation method. Typically, for FeZn-DMC, a mixture of 0.1 mol of ZnCl_2 , 20 mL of water and 20 mL of *tert*-butanol was slowly added to 40 mL of a 0.25 mol L⁻¹ K₄[Fe(CN)₆]·3H₂O aqueous solution over 1 h at 50 °C under stirring. Then, 20 g of P₁₂₃ (*i.e.*, complexing agent) in 2 mL of water and 40 mL of *tert*-butanol (*i.e.* co-complexing agent) were added over 10 min and stirred continuously for 1 h. Then, the crystal (FeZn-P) was obtained after filtering and washing with H₂O and drying at 60 °C for 8 h. FeZn was synthesized using the same process without P₁₂₃ and *tert*-butanol. Similarly, ZnCo-P was synthesized by replacing K₄[Fe (CN)₆]·3H₂O with K₃[Co(CN)₆].

For comparison, Cr-MIL-101 and Fe-MIL-100 were synthesized using a hydrothermal method. For the synthesis of Cr-MIL-101, a mixture of $Cr(NO_3)_3 \cdot 9H_2O$ (14 mmol), H_2BDC (14 mmol), HF (14 mmol), and water (70 mL) were stirred, transferred into a Teflon-lined autoclave, sealed and heated at 220 °C for 8 h. The resulting light-green crystal was obtained after filtering and washing with DMF, ethanol, an NH₄F solution and H₂O, followed by drying for 8 h at 150 °C. For the synthesis of Fe-MIL-100, iron powder (4.9 mmol), H₃BTC (3.27 mmol), hydrofluoric acid (4 mmol) and nitric acid (2.78 mmol) were mixed in water (20 mL), and heated for 12 h at 150 °C. The brown Fe-MIL-100 was further purified with water and ethanol, then dried overnight in a 100 °C vacuum drying oven. Al-MCM-41 (SiO₂/Al₂O₃ = 26.8) was synthesized according to previous studies.⁴⁴

Catalyst characterizations

The crystal structures of the catalysts were determined by powder X-ray diffraction (XRD) using a Panalytical Empyrean diffractometer with Cu-K α radiation. The porous structures were characterized by N₂ adsorption–desorption at –196 °C on an ASAP 2460 surface analyzer. Fourier transform infrared (FTIR) spectra were recorded in a range of 400–4000 cm⁻¹ on a Nicolet 5700 FTIR spectrometer using KBr pellets. Elemental analysis of the Fe and Zn elements was carried out using inductively coupled plasma optical emission spectrometry on a PerkinElmer Optima 8000 spectrometer. The N element was characterized using a CHNS elemental analyzer (Vario MICRO). The morphologies were determined using a JEM-2100 transmission electron microscope. The acid properties were evaluated by infrared spectroscopy with adsorbed pyridine using a Bruker VERTEX 70 spectrometer. The self-supported wafers (10 mg cm⁻²) were degassed for 1 h under vacuum at 200 °C. Then, adsorption of pyridine occurred at 60 °C for 30 min followed by desorption at 150 °C for 20 min, and the transmission spectra were recorded. The thermal stabilities were investigated by thermal gravimetric analysis using a NETZSCH-STA 2500 in an N₂ atmosphere.

Catalytic reactions

The synthesis of HCP and CPE from FA was conducted in a 100 mL batch autoclave equipped with a mechanical stirrer (Anhui Kemi Machinery Technology Co., Ltd). For the HCP synthesis, a mixture consisting of 0.1 g of catalyst, 10.2 mmol of furfuryl alcohol, and 40 mL of solvent was heated to 150 °C under an N₂ atmosphere. For the CPE synthesis, the reaction was carried out at 150 °C with 0.1 g of catalyst, 10.2 mmol of furfuryl alcohol and 40 mL of water under an H₂ atmosphere. These reaction mixtures were periodically sampled and analyzed using Agilent 6890N GC/5973 MS detector and quantified using a Trace 1300 gas chromatograph equipped with an FID detector and a TG-WAXMS capillary column (30 m × 0.32 mm).

Computational methodology

All calculations were performed using the DMol³ program in the Materials suite (Accelrys Inc.).45,46 The exchange-correlation energy was calculated using the generalized gradient approximation of Perdew and Wang (PW91) with the Grimme method for DFT-D correction, which yields reliable results for various reactions.^{47,48} The double-numerical basis set with a polarization d-function (DNP) was chosen to expand the valence electron functions. The orbital cutoff range was 4.6 Å, and the smearing value was set to 0.005 Hartrees. The core electrons for the Zn and Fe atoms were represented by densityfunctional semi-core pseudopotentials (DSSPs). The convergence criterion for the optimal geometry was based on the energy, force and displacement convergence (*i.e.* 1×10^{-5} Hartrees, 2×10^{-3} Hartrees Å⁻¹ and 5×10^{-3} Å, respectively). The linear and quadratic synchronous transit (LST/QST) complete search method was used to search for the transition state of the reactions.⁴⁹ The nature of the minima on the potential energy surface was verified by inspection of the harmonic vibrational frequencies.

For the theoretical calculations, a $Zn_{13}Fe_9(CN)_{66}H_{58}$ cluster model was employed to represent the catalytic structure of FeZn-DMC. Due to the high expense of a DFT calculation on a large system, a small cluster with a di-coordinatively or tricoordinatively unsaturated Zn site $(Zn_4Fe_3(CN)_{23}H_{14})$ and $Zn_4Fe_3(CN)_{24}H_{15})$ was employed to study the dissociation of H_2 on the catalyst surface.

Results and discussion

Structural characteristics of DMC

Fig. 1A shows the XRD patterns of FeZn-DMC. In agreement with previous results, the FeZn-DMC has an $R\bar{3}c$ space group structure with tetra-coordinated Zn²⁺ connected to the four N=C groups of octahedral $[Fe(CN)_6]^{4-}$, which is consistent with $K_2 Zn_3 [Fe(CN)_6]_2^{39,40,42}$ The anionic zinc-ferrocyanide framework is characterized by cages of the type depicted in Fig. 1B, where each cage contains two guest K⁺ ions. The TEM image indicates that DMC has a uniform crystal size of 200-300 nm, and the particle size did not change upon addition of the complexing agents (Fig. S1[†]). The N₂ adsorption-desorption isotherm of FeZn is consistent with a type II isotherm, and FeZn-P shows a slight type IV isotherm, indicating the existence of mesopores after using P_{123} (Fig. 1C). The topological pore of FeZn is too small for N₂ to enter. The BET surface area and pore volume of FeZn and FeZn-P are 33.2 and 42.6 m² g⁻¹, 0.051 and 0.068 cm³ g⁻¹, respectively (Table 1). In addition, Fig. 1A and S2[†] show the successful preparation of

FeZn

FeZn-P

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Cr-MIL-101

Fe-MIL-100

60

D

Absorbance

FeZn-P

FeZn Al-MCM-41

2θ (°)

Fig. 1 (A) X-ray diffraction patterns, (B) crystal structure, (C) N₂ adsorption-desorption isotherms and (D) infrared spectra of adsorbed pyridine for FeZn-DMC. ^arepresents the recycled sample.

Table 1	Physicochemical	properties	of catalysts
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Samples	$ \begin{pmatrix} S_{\rm BET} \\ (m^2 g^{-1}) \end{pmatrix} $	$\binom{V_{\mathrm{total}}}{(\mathrm{cm}^3\mathrm{g}^{-1})}$	Lewis acid density (mmol g ⁻¹)	Brønsted acid density (mmol g ⁻¹)	Lewis/ Brønsted
FeZn	33.2	0.051	0.746	0.073	10.2
FeZn-P	42.6	0.068	1.349	0.105	12.8
Cr-MIL-101	3225.7	1.540	2.790	0	_
Fe-MIL-100	841.2	0.542	3.072	0	_
Al-MCM-41	851.2	0.965	0.034	0.012	2.8
Amberlyst-15 ^a	45	0.31	0	4.7	0

 a BET surface area and pore volume value of Amberlyst-15 were obtained from our previous work. 52,53

Samples	N (wt%)	Fe (wt%)	Zn (wt%)	Molar ratio of N : Fe	Molar ratio of Zn : Fe
FeZn-P	18.68	11.76	24.19	6.352	1.771
FeZn	17.89	12.25	24.19	5.842	1.57
FeZn-P ^a	18.15	11.06	22.44	6.562	1.747
^a Represen	ts the recv	cled samp	22,44	0.302	1./4/

Cr-MIL-101 and Fe-MIL-100. In these MIL series MOFs, the Cr^{3+}/Fe^{3+} trimer is coordinated to twelve O atoms from H₂BDC/H₃BTC, one F⁻ and two water molecules. The BET surface area and pore volume of Cr-MIL-101 and Fe-MIL-100 are 3225.7 and 841.2 m² g⁻¹, 1.540 and 0.542 cm³ g⁻¹, respectively.

As shown in Table 2, elemental analysis results indicate that the N: Fe molar ratios of FeZn and FeZn-P (i.e., 5.842 and 6.352, respectively), are close to the stoichiometrically expected value (i.e., 6), demonstrating the stability of the octahedral [Fe $(CN)_6$ ⁴⁻ anion groups. Whereas, the Zn: Fe molar ratio of FeZn is 1.570, which is higher than the theoretical value (i.e., 1.5). Due to the excess Zn^{2+} ions in the synthesis mixture, the Fe^{2+} ions are surrounded by the C=N bonds and Zn^{2+} ions terminate the crystals. The coordinately unsaturated Zn²⁺ ions provide the Lewis acidity.⁴³ Meanwhile, the addition of P₁₂₃ and tert-butanol can suppress overgeneration of the crystal and increases the Zn: Fe molar ratio to 1.771 for FeZn-P. As shown in Fig. 1D, the pyridine-absorbed FTIR spectra were used to determine the acidity of these acid catalysts. The adsorption bands at 1450 and 1540 cm⁻¹ are assigned to the chemisorbed pyridine corresponding to the Lewis and Brønsted acid sites, respectively. The acid density was calculated using the Emeis equation.⁵⁰ FeZn-P shows a larger acid density of both Lewis (1.349 mmol g^{-1}) and Brønsted $(0.105 \text{ mmol g}^{-1})$ acids than FeZn, because more coordinately unsaturated Zn²⁺ ions provide more acid sites that adsorb more pyridine. Both FeZn and FeZn-P exhibit a high acid density ratio (i.e. Lewis/Brønsted) with 10.2 and 12.8, respectively. Al-MCM-41 shows a both Lewis (0.034 mmol g^{-1}) and Brønsted acidity (0.012 mmol g^{-1}) with the ratio of 2.8. For MIL series MOFs, the Lewis acid density of Cr-MIL-101 and Fe-MIL-100 are 2.790 and 3.072 mmol g^{-1} according to its format.⁵¹ This value cannot be obtained from the pyridineabsorbed FTIR spectra because the strong bands of arising from carboxylate and benzene ring vibrations disturb the pyridine adsorption signal in the 1400-1600 cm⁻¹ region. As shown in Fig. S3,† the thermal stability results for FeZn-DMC indicate a weight loss between 60 °C to 200 °C due to the loss of crystal and noncrystal water. The structure remained stable below 300 °C, indicating that their stability under the reaction conditions (150 °C).

Synthesis of HCP

As mentioned above, the rearrangement of FA to HCP involves a hydrolysis reaction to 2-pentene-1,4-dione (PED) intermediate, followed by intramolecular aldol condensation reactions to

А

С

(a) 30

Volume (cm³

FeZn FeZn-F

Fe7n-P



Fig. 2 (A) Proposed reaction pathway for HCP preparation, (B) timedependent product distribution using FeZn-P as a catalyst in 40 mL of water or (C) a bi-phasic solvent with 20 mL of water and 20 mL of *n*-hexane, (D) effect of different solvents, and (E) catalytic performance of several acid catalysts. Reaction conditions: FA (10.2 mmol), catalyst (0.1 g), 150 °C, 4.0 MPa of N₂ pressure. (D) Water (20 mL) and organic solvent (20 mL), FeZn-P catalyst, reaction time 6 h. (E) 20 mL water and 20 mL *n*-hexane, reaction time 6 h.

HCP (Fig. 2A and B).¹⁸⁻²⁰ PED is very reactive, and can only be detected in small amounts with GC (Fig. S4A[†]). The product was identified by GC-MS (Fig. S5A[†]). In addition to the main reaction to HCP, some by-products including levulinic acid (LA) and humins can be generated through ring-opening and intermolecular C-C reactions, respectively. Different from previous reports using a high temperature without an acid catalyst, FA cannot be substantially converted at 150 °C due to a low density of protons formed by H2O auto-dissociation (Fig. 2D).^{16,17} After the addition of FeZn-P, the FA conversion rate largely increased. The amount of HCP, LA, and humins also synchronously increased with the reaction time, indicating the presence of parallel reactions (Fig. 2B). After 6 h of reaction, FA is completely consumed with a HCP yield of only 38.2%, and 56.2% carbon loss due to the generation of humins. A stable increase in the HCP yield implies that the humins are primarily produced by the reactive PED.

Fortunately, as shown in Fig. 2C, when the solvent is changed from 40 mL of water to the bi-phasic solvent consisting of 20 of mL water and 20 mL of *n*-hexane, the reaction exhibits a much higher selectivity in the time-dependent product curve, although the activity is slightly decreased. Subsequently, some other stable organic solvents (*e.g.* ethanol, *n*-hexane, isopropanol, dimethyl sulfoxide, acetonitrile and tetrahydrofuran) were selected to mix with water for use as the reaction medium (Fig. 2D). The polarities of these solvents are as follows:

dimethyl sulfoxide (7.2) > acetonitrile (6.2) > ethanol (6.0) > isopropanol (4.3) > tetrahydrofuran (4.2) > hexane (0.06). Using a strong polar solvent (e.g., dimethyl sulfoxide, acetonitrile, and ethanol), both the FA conversion rate and HCP selectivity are low. Interestingly, the conversion and selectivity increase as the polarity value decreases. The weak polar (e.g., isopropanol, tetrahydrofuran) and non-polar (e.g. n-hexane) solvents exhibit considerable reaction performance. First, the weak polar solvent is more difficult to dissolve in water, which is the reactant for hydrolysis of FA. Therefore, these solvents exert a weak negative influence on the hydrolysis reaction, and the activity in the water/weak-polar solvent is higher than that in the water/strong-polar solvent. Second, because the active PED is generated in the water phase, the weak polar solvent may easily extract it to maintain a low concentration on the acid site. An intramolecular aldol reaction is more likely to occur than some intermolecular C-C bond reactions. Hence, the HCP selectivity is the highest in the water/non-polar solvent biphasic system.

Fig. 2E further compares the catalytic performance of several acid catalysts in the aqueous/n-hexane bi-phasic system. As a common Brønsted acid, Amberlyst-15 exhibits only 16.5% selectivity to HCP, and a large amount of levulinic acid is generated. Al-MCM-41 (42.3%) exhibits a higher HCP selectivity than Amberlyst-15 (16.4%). According to previous work, Brønsted acid (e.g., H2SO4, HCl, p-toluenesulfonic acid, H-ZSM-5, HY and Amberlyst-15) more easily catalyzes the hydrolysis reaction.^{14,15} In contrast, FeZn, FeZn-P, Fe-MIL-100 and Cr-MIL-101 with Lewis acidity possess the high HCP selectivity of more than 70%. However, Cr-MIL-101 and Fe-MIL-100 exhibit relatively low activity below 85% conversion, possibly attributing to the weak acidity of the coordinately unsaturated Cr³⁺/Fe³⁺ ions. In addition, FeZn, which has a low surface area and acid density, exhibits a FA conversion that is lower than that of FeZn-P. Hence, FeZn-P with the highest activity and selectivity is considered as the best catalyst for subsequent optimization of the reaction conditions.

As shown in Fig. S6,† when the reaction temperature decreases to 130 °C, only 52.3% of FA is converted. However, when the reaction temperature is higher than 160 °C, the HCP yield begins to decrease, because some HCP undergoes intermolecular aldol condensation at higher temperatures. If the water/hexane ratio is changed from 40:0 to 0:40, the conversion decreases (Fig. S7†). Under the optimal conditions, 95.2% of FA is converted with a 92.6% HCP selectivity and 88.2% HCP yield *via* FeZn-P catalysis in a 1:1 mixture containing 40 mL of water/hexane at 150 °C for 6 h.

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HCP yield *via* FeZn-P catalysis in a 1:1 mixture containing 40 mL of water/hexane at 150 °C for 6 h.

Synthesis of CPE

In water, when the N₂ atmosphere is changed to 4 MPa of H₂ pressure, FeZn-P exhibits a similar FA conversion, indicating that the hydrolysis of FA is not affected. Surprisingly, the products contained a 52.3% yield of CPE is generated in addition to the HCP yield of 42.0% after 6 h (Fig. 3A, B and Fig. S4B[†]). The experiment was repeated more than five times. In comparison to the N2 atmosphere, the carbon loss decreases from 56.2% to 4.6% under the H₂ atmosphere. Because HCP is unstable under acidic reaction conditions, the transformation of HCP to CPE is presumed to occur via hydrogenation and then dehydration. Whereas, CPE is stable and cannot be further hydrogenated. The fact that HCP is active and CPE is inactive for hydrogenation may be ascribed to the conjugation effect of the hydroxyl group, which increases the electron density in the C=C bond and facilitates the hydrogenation reaction.⁵⁴ When H₂ is replaced with deuterium hydrogen D₂, isotopic labeling investigations with detailed mass fragmenta-

Fig. 3 (A) Proposed reaction pathway for CPE preparation, (B) timedependent product distribution using FeZn-P as catalyst, (C) effect of H_2 pressure, (D) catalytic performance of several acid catalysts, and (E) recycling performance of FeZn-P. Reaction conditions: FA (10.2 mmol), catalyst (0.1 g), water (40 mL), 150 °C (B, D and E) 4.0 MPa H_2 pressure, reaction time 6 h. (C) FeZn-P catalyst, reaction time 6 h.

tion pattern analysis clearly reveal the hydrogenation step (Fig. S5C^{\dagger}). Meanwhile, the yield of CPE is affected by the H₂ pressure (Fig. 3C). The yield of CPE increases from 20.4% to 61.5% with the H_2 pressure from 2.0 to 6.0 MPa. Under a low H₂ pressure (2.0 MPa), it shows a similar time-dependent product curve with that of 4.0 MPa H₂ pressure. The synchronous increase of HCP and CPE indicates their synthesized reactions are parallel (Fig. S8[†]). To explore the reaction mechanism, HCP was used as the reactant but it cannot be transformed without a catalyst under an H₂ pressure of 4.0 MPa (Table S1[†]). After adding FeZn-P, CPE is generated. It clearly proves that FeZn-DMC also can be used as a hydrogenation catalyst in addition to an acid catalyst. However, compared with FA reaction with a CPE yield of 52.3%, the yield is relatively lower (38.3%) with HCP as the reactant under the same reaction conditions. In addition to the HCP pathway, the PED intermediate can also be converted to CPE via hydrogenation, intramolecular aldol condensation, and dehydration. Because PED plays a crucial role in the formation of humins, the PED hydrogenation route can also be used to explain the low humin amount observed under H₂ conditions.

Subsequently, other acidic catalysts were also employed in the reaction under an H₂ atmosphere. Amberlyst-15 and Al-MCM-41 only exhibit acid catalysis abilities and cannot catalyze the synthesis of CPE (Fig. 3D). Meanwhile, Cr-MIL-101, Fe-MIL-100, FeZn, and FeZn-P exhibit considerable CPE yield, indicating the Lewis acidic site is also important for the hydrogenation reaction. Among of them, FeZn and FeZn-P with the highest CPE yield exhibit the strongest both acid and hydrogenation catalytic abilities. In the H₂ atmosphere with a monophasic water solvent, the conversion tendency of various catalysts is the same as that in an N₂ atmosphere with a water/ n-hexane bi-phasic solvent (Fig. 2E and 3D). Therefore, H₂ does not affect the hydrolysis step of FA, but does affect the subsequent hydrogenation steps. Similar to the results obtained for acid catalysis to synthesize HCP, FeZn-P exhibits higher FA conversion of 96.0% than FeZn (90.3%), because of the presence of more acid sites on the surface. Meanwhile, the selectivity of CPE over FeZn-P is also higher than that of FeZn, which indicates that the catalytic hydrogenation active site is on the surface of the crystal. Table S1[†] confirm that FeZn-P has a stronger hydrogenation ability than FeZn when HCP acts as a reactant. In addition, a rapid, hot-catalyst filtration test was performed, and no further generation of CPE in the filtrate was found after the removal of FeZn-P (Fig. S10[†]), which proves the true heterogeneously catalytic nature of this reaction. The recyclability of DMC was evaluated. The catalyst was centrifuged after the reaction, washed with ethanol, and used for the next run. As shown in Fig. 3E, after 5 runs, the conversion and yield remain at 90.5% and 52.6%, respectively, without obvious degradation compared to the first run. The N₂ adsorption-desorption isotherm of reused FeZn-P shows an unclosed loop, which can be ascribed to the structural degradation of pores (Fig. 1C).55 The BET surface area and pore volume are decreased to 28.6 m² g⁻¹ and 0.048 cm³ g⁻¹, respectively (Table S2[†]). Meanwhile, XRD results also show a



slight degradation of the crystalline structure after recycling. The slight decrease of catalytic activity can be attributed to the degradation of specific surface area and crystalline structure (Table 1 and Fig. S11†). The chemical compositions of the used catalysts are well preserved as shown by element analysis (Fig. 1C, Table 2 and Fig. S11†), showing their stability under the current reaction conditions.

Recently, a single-site Zn^{2+} was supported on silica, and the Zn/SiO₂ catalyzed propylene hydrogenation.^{56–59} The coordinatively unsaturated Zn^{2+} activates H_2 via a non-redox (metal) mechanism consisting of heterolytic cleavage of H–H and C–H bonds in contrast to the typical hemolytic mechanism in the metal-catalyzed hydrogenation reaction. In addition, some Zn–N–C compounds with an acid-base pair can hydrogenate imines via heterolytic cleavage of H_2 .^{60,61} Currently, many studies of homogeneous catalysis have been reported for hydrogen heterolysis by frustrated Lewis pairs, such as metal-free, non-noble metal, and noble metal-based catalysts.^{62–65} Due to their convenient processing and separation from the reaction solution, heterogeneous catalysts are favorable for process implementation.

FeZn and FeZn-P exhibit the catalytic hydrogenation ability. To further confirm the importance of the coordinatively unsaturated Zn²⁺ in the Zn-N-C structure of the catalyst surface, CoZn-DMC consistent with K₂Zn₃[Co(CN)₆]₂ was successfully synthesized (Fig. S12[†]). The XRD pattern indicates a Fm3 m space structure, where Zn^{2+} hexa-coordinates with four N=C bonds and two water molecules. It is important to note that ZnCo-DMC cannot catalyze the acid-catalyzed rearrangement reaction for HCP, but it can catalytically convert HCP to CPE with 16.5% yield via hydrogenation reaction (Table S1⁺). This result indicates that the catalytic active site of hydrogenation is attributed to the coordinatively unsaturated Zn²⁺ in the Zn-N-C structure. To best of our knowledge, DMCs catalysts are widely reported acid catalyst, but have not been employed as a hydrogenation catalyst, not mentioned to as the bifunctional catalyst for both acid and hydrogenation catalysis as reported herein.

For hydrogenation catalysis, the catalytic hydrogenation mechanism is proposed in Fig. 4. H₂ heterolytically reacts at the coordinatively unsaturated Zn–N frustrated Lewis pairs, producing Zn–H (hydride ion) and N–H (proton). The heterolytic dissociation of hydrogen can be ascribed to the electron transfer from Zn to N atoms resulting in the charge polariz-



Fig. 4 Proposed catalytic hydrogenation mechanism.

ation. Then, olefin (PED, HCP) insertion occurs at the Zn-H bond followed by proton transfer to the olefin. Ultimately, the hydrogenation compound is desorbed, and the catalytic cycle is complete. The cycle does not change the Zn oxidation state. Based on the structure of FeZn-DMC, the DFT simulation results indicate that the terminal two-coordinative Zn²⁺ site $(Zn(N)_2)$ is unstable but tri-coordinative Zn^{2+} site $(Zn(N)_3)$ is stable (Fig. S13[†]). Compared with the HCP reaction conducted under 4.0 MPa H₂ pressure, a lower CPE yield (38.3% vs. 13.5%) is obtained under 2.0 MPa (Fig. S9[†]). It is shown that the H₂ pressure have a great effect on the product distribution (Table S1[†]). As the pressure increases, the yield of CPE increases gradually. Combined with the result of FA reaction, we can infer that the H₂ pressure does strongly affect the hydrogenation activity and hydrogen heterolysis is rate-limiting. The FTIR spectra of hydrogen-activated catalyst shows a sight new peak at 1734 cm⁻¹, which is assigned to the Zn-H bond (Fig. S14[†]).⁶⁶ The DFT simulation indicates that the energy barrier for H_2 heterolysis on $Zn(N)_3$ is 28.4 kcal mol⁻¹. Therefore, heterolysis hydrogenation is possible over Zn(N)₃. The N-coordinatively unsaturated Zn²⁺ not only coordinates to a lone electron pair for acid-catalyzed reactions but also attacks the H-H covalent bond for hydrogenation reactions.

Conclusions

In summary, we propose a novel synthesis route for 4-hydroxy-2-cyclopentenone and 2-cyclopentenone from biomass-derived furfuryl alcohol via double-metal cyanide catalysis. Under an N₂ atmosphere in a water-organic bi-phasic solvent medium, a DMC with pure Lewis acidity allows for highly selective synthesis of HCP compared with conventional acid catalysts. FeZn-P with stronger acidity and a larger surface area exhibits the highest yield (88.2%). Under an H₂ atmosphere in water, FeZn-P exhibits a CPE yield of more than 61.5% yield via bifunctional catalysis involving both acid and hydrogenation catalysis. The DFT simulation indicates that the tri-coordinatively unsaturated Zn^{2+} site $(Zn(N)_3)$ is used as the acid and hydrogenation active site. Furthermore, this catalyst exhibits great stability and can be reused at least five times. This work not only demonstrates a highly efficient catalytic reaction system to HCP but also provides a green and novel synthesis route to CPE. In addition, it seems opens a new door for DMC hydrogenation catalysis via heterolytic cleavage of H-H bond on frustrated Lewis pairs.

Conflicts of interest

The authors declare no conflict of interests.

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