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1	Cu/Mg/Al/Zr Non-Noble Metal Catalysts for O-Phenylphenol Synthesis
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1 Abstract

2	Cu/Mg/Al/Zr hydrotalcite-like precursors with Zr^{4+} :(Al ³⁺ +Zr ⁴⁺) atomic ratios between
3	0 and 1 were prepared by co-precipitation methods. The precursors were analyzed
4	using X-ray diffraction (XRD), scanning electron microscope (SEM),
5	thermogravimetric (TG) and Fourier Transform infrared spectroscopy (FT-IR). The
6	results confirmed that well-defined layered double hydroxides (LDH) can be
7	synthesized when the content of added Zr content is less than 0.25 in terms of
8	$Zr^{4+}/(Al^{3+}+Zr^{4+})$ atomic ratio. The catalysts of Cu/Zn/Al/Zr mixed oxides can be
9	obtained via thermal decomposition of hydroxides precursors, and can be used in
10	dehydrogenation of 2-(1-cyclohexenyl) cyclohexanone (CHCH) to
11	ortho-phenylphenol (OPP). Copper particles inside the catalyst act as active sites for
12	dehydrogenation. Iransmission electron microscope (IEM), XRD, N_2O
12 13	dehydrogenation. Iransmission electron microscope (TEM), XRD, N_2O chemisorption and N_2 adsorption-desorption were performed to investigate the effect
12 13 14	dehydrogenation. Transmission electron microscope (TEM), XRD, N ₂ O chemisorption and N ₂ adsorption-desorption were performed to investigate the effect of Zr content on determining the copper particle size. Based on the catalytic
12 13 14 15	dehydrogenation. Transmission electron microscope (TEM), XRD, N ₂ O chemisorption and N ₂ adsorption-desorption were performed to investigate the effect of Zr content on determining the copper particle size. Based on the catalytic performance test, it was concluded that the conversion of CHCH depends on the
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1 1. Introduction

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2	Many investigations have been made on the dehydrogenation of alicyclic
3	compounds. For instance, the only important industrial synthesis of o-phenylphenol
4	(OPP) is still the cyclohexanone method, in which 2-(1-cyclohexenyl)cyclohexanone
5	(CHCH) is obtained from cyclohexanone via aldol condensation and dehydration. At
6	present, the catalysts used for OPP dehydrogenation generally use noble metals as the
7	active ingredients such as Pt. ^{1,2} Only a few studies of the non-noble metals catalysts in
8	the OPP synthesis process have been reported in literature. ³ Thus, the synthesis of
9	non-precious metals dehydrogenation catalysts is very important to minimize both
10	capital and operative expenses. Cu-based catalysts are applied in various industrial
11	hydrogenation processes, and most of the catalysts when reduced with care can afford
12	high dispersion of copper, showing good activity. However, the catalysts still suffered
13	from thermal sintering and poisoning due to the poor dispersion. It is shown that the
14	Cu-containing catalysts with high dispersion show good catalytic selectivity and
15	activity in some reactions such as hydrogenation. ⁴⁻⁶ However, Cu-containing catalysts
16	are not widely applied for dehydrogenation reactions of the organic compounds.

Hydrotalcite (HT)-like compounds are a new type of interesting materials which have been applied as ion exchangers, catalyst supports, catalysts, and composites.⁷⁻¹⁴ Their empirical formula is $[M^{II}_{1-x}M^{III}_{x}(OH)_{2}]^{x+}[A^{n-}_{x/n}]^{x-}\cdot mH_{2}O$, where M^{II} is a divalent cation such as Cu^{2+} , Zn^{2+} , or Mg^{2+} , M^{III} is a trivalent cation such as Fe^{3+} , Al^{3+} , or Ga^{3+} . A^{n-} is an anion with a negative charge such as CO_{3}^{2-} and NO_{3}^{-} , and m is the molar amount of water in the interlayers.^{15,16} The as-synthesized metallic oxides

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1	exhibit highly homogeneously dispersed M^{3} and M^{2} at the atomic level, high
2	specific surface area, high sintering stability, and strongly basic properties. ¹⁷⁻¹⁹
3	Thermal treatments leads to dehydroxylation, dehydration, and destruction of
4	interlayer anions, and form the basic metallic oxides with high surface area, high
5	dispersion of the active centers and better resistance to sintering. ²⁰ The homogeneous
6	distributions of metallic oxides in precursors can form the highly dispersed and much
7	stable active metallic centers on catalyst surface after calcination and reduction. ²¹
8	Thus, well dispersed Cu-based catalysts with high stability, large surface area, and
9	moderate or strong basic properties can be synthesized via the thermal decomposition
10	of the hydrotalcite-like precursors.

In addition, the dispersibility and size of copper particles might significantly affect 11 the stability of the catalyst. Some literatures reported the relevant deactivation 12 mechanism for commercial catalysts.²²⁻²⁴ The low catalytic stability is currently a 13 limiting factor in applying Cu-containing catalysts in the hydrogenation process. How 14 to solve this problem is still the key to applying the Cu-containing catalysts in the 15 hydrogenation process. The introduction of Zr has been reported to improve the 16 surface basicity and Cu dispersion, and hence to influence the activity of catalysts.²⁵⁻²⁸ 17 18 Furthermore, the presence of Zr can provide high stability and resistance to redox cycles.²⁹ However, very few studies reported the effect of addition of zirconium on 19 tuning the particle size of Cu inside the catalyst. The detailed structure-activity 20 relationship of the Zr-Cu material is hence lacking and is the subject of this work. 21 22 In this work, a series of Cu/Mg/Al/Zr catalysts obtained from Cu/Mg/Al/Zr layered

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double hydroxides were prepared with $Zr^{4+}/(Al^{3+}+Zr^{4+})$ atomic ratios between 0 and 1. 2 Catalyst were characterized using X-ray diffraction (XRD), scanning electron 3 microscope (SEM), N₂ adsorption-desorption, transmission electron microscope 4 (TEM), high-magnification transmission electron microscope (HRTEM), N₂O 5 chemisorption, thermogravimetric (TG), H_2 temperature programmed reduction 6 (H₂-TPR), Fourier transform infrared spectroscopy (FT-IR) and CO₂ temperature 7 programmed desorption (CO₂-TPD). 8 9 2. Experimental 10 2.1. Preparation of Catalysts 11 The Cu/Mg/Al/Zr hydrotalcite-like samples were prepared by co-precipitation 12 method. The $Cu^{2+}/Mg^{2+}/(Al^{3+}+Zr^{4+})$ atomic ratio was kept at 2.5:3.5:2 in the starting 13 solution, while the atomic ratio of Zr^{4+}/Al^{3+} was changed from 0 to 1. Calculated 14 amount of $Cu(NO_3)_2 \cdot 3H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Zr(NO_3)_4 \cdot 5H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ 15 were added into deionized water to prepare a 200mL mixed salt solution A, where the 16 total concentration of $(Cu^{2+}+Mg^{2+}+Al^{3+}+Zr^{4+})$ is 0.9 mol/L. Another solution (called 17 B) was an aqueous of Na_2CO_3 and NaOH, in which the concentration of Na_2CO_3 and 18 NaOH are both 1 mol/L. The A and B were slowly added to a four-necked flask with 19 vigorous stirring and heated to the reaction temperature of 60 °C with the pH 20 maintained at 9.5. The resulting precipitant were aged for 6 hour and recovered with 21 filtration, then washed with distilled water to remove the trace sodium. Drying was

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performed in the air at 90 °C for 12 hours prior to the calcination conducted in air at

¹ 450 °C for 4 hours. Then the obtained powders were ground and extruded to strip ² catalysts. The catalysts were reduced using H₂ at 300 °C for 2 hours, followed by ³ reacted at 330 °C. Synthesized Cu/Mg/Al/Zr catalysts were denoted as CMAZ-N, ⁴ where N = 0, 1, 2, 3 and 4 denoting the $Zr^{4+}/(Al^{3+}+Zr^{4+})$ ratio of 0, 0.25, 0.5, 0.75 and ⁵ 1, respectively.

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2.2. Characterization of Samples

8 X-ray diffraction (XRD) patterns were measured by the X-ray diffraction 9 instrument (Bruker AXS, D8 Advance) with the wavelength of the Cu K_{α} radiation 10 source being 1.5406Å. The intensity data was collected over the 2θ range of 5-70° 11 with a step size of 0.05° and counting time of 1s each point under the condition of 40 12 kV and 40 mA. SEM images of hydrotalcite-like precursors and catalysts were 13 obtained by a field emission scanning electron microscopy (Hitachi, S-4800II). 14 Thermal decomposition and stability for the catalyst precursors was studied by 15 thermogravimetry analysis (TG-DTG, PerkinElmer Pyris 1) under the N₂ atmosphere 16 (30 mL/min) with the heating rate of 10 °C /min from 50 °C to 750 °C. The infrared 17 spectra of samples were recorded by a Fourier Transform spectroscopy (FT-IR, Bruker, 18 Tensor 27), and measurements were performed in the wavenumber range of 400-4000 19 cm⁻¹. Transmission Electron Microscope (TEM) images of low-magnification were 20 collected using a Tecnai 12 model machine for low-magnification observe samples. 21 High-magnification Transmission Electron Microscope (HRTEM) was performed 22 using Tecnai G2 F30 S-TWIN model machine for high-magnification to observe the

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1	samples. The specific surface areas of the samples were computed from N_2
2	adsorption-desorption isotherms obtained at the temperature of liquid N_2 on a
3	BELSORP-MAX instrument. Firstly, the powders were outgassed at the temperature
4	of 200 °C for 6 h to ensure a clean surface before the measurement of the adsorption
5	isotherms. H ₂ -TPR was performed on the instrument Finesorb-3010. The catalyst was
6	firstly treated in Ar (30 ml/min) with a 10 °C/min heating rate to 200 °C and kept it at
7	200 °C for 30 min. After the samples were cooled down to 100 °C, TPR were
8	conducted in the mixture of H_2/Ar (molar ratio 1:9) flowing at 30 ml/min at a 10
9	°C/min heating rate until 500 °C. Finally, the catalyst was cooled to room temperature
10	in the presence of Ar. The exposed surface area of copper (S_{Cu}) and the dispersion of
11	copper (D_{Cu}) were determined by adsorption of N_2O and performed on Finesorb-3010
12	instrument, using the method similar to that reported by Xia et al. ^{30,31} Catalysts were
13	reduced (the procedure is described in TPR section) in H ₂ /Ar (molar ratio 1:9)
14	mixture with a flow rate of 30 mL/min at a heating rate of 10 °C/min until 450 °C and
15	was kept at 330 $^\circ C$ for 30 min. The consumption amount of H_2 in the TPR was
16	recorded as X. Then the reactor bed was purged in Ar to 50 °C. The mixture of
17	N ₂ O/Ar (the molar ratio 1:4, 30 mL/min) was changed to oxidize copper atoms of
18	surface to Cu_2O at the temperature of 50 °C for 1 hour. The reactor bed was then
19	flushed with pure Ar to get rid of the oxidant. Another TPR procedure was conducted
20	in the mixture of H ₂ /Ar (molar ratio 1:9) with a flow rate of 30 mL/min at a 10 $^{\circ}$ C/min
21	heating rate up to 330 $^\circ C$ and was kept at 330 $^\circ C$ for 30 min. The consumption of H_2
22	in this TPR procedure was recorded as Y. The exposed surface area of copper and the

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dispersion of copper were computed by the following equations:

$$S_{Cu} = (2Y \times N_A) / (1.4 \times 10^{19} \times X \times M_{Cu}) (m^2 \cdot g^{-1})$$
(1)

$$D_{Cu} = \frac{2Y}{X} \times 100\% \tag{2}$$

where S_{Cu} is the exposed surface area of Cu per gram sample, D_{Cu} is the dispersion of 5 Cu, M_{Cu} the Cu atomic mass, N_A is Avogadro constant, and 1.4×10^{19} is the number of 6 Cu atoms per m².³² The basicity of catalysts was measured by CO₂ temperature 7 programmed desorption (CO₂-TPD, Finesorb-3010). The catalysts were firstly treated 8 with Ar (30 ml/min) by raising the temperature at the rate of 10 °C/min to 330 °C and 9 keep it for 30 min. Catalysts were saturated with carbon dioxide (30 ml/min) for 60 10 min after cooling to 100 °C, and then flushed in Ar (30 ml/min) to get rid of all 11 physical adsorbed molecules for 30 min. Finally, the TPD were performed in Ar (30 12 ml/min) flowing at a 10 °C/min heating rate until 600 °C. Finally, the catalyst was 13 cooled to room temperature in the presence of Ar.

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15 2.3 Catalytic Reactions

The dehydrogenation reactions of CHCH were performed in a home-made set-up with a tubular quartz glass flow reactor (Φ 19×560 mm). The reactor temperature was measured by a thermocouple located in the middle of the catalyst bed. The dehydrogenation reactions were carried out at 330 °C and atmospheric pressure. All catalysts were pre-treated by reduction under H₂ (flow rate of 20 mL/min) at 300 °C for 2 hours. Adjusting the H₂ flow rate at 10 mL/min, the reagent was added into the reactor using a syringe pump. The reaction products were dissolved in alcohol and Page 9 of 39

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1 cooled to room temperature and analyzed using a gas chromatograph equipped with a

2 flame ionization detector (FID) detector.

3. Results and Discussions

3.1. Textural and Structural Properties of the Precursors

5 The XRD patterns of the precursors are shown in Figure 1. It is shown that the 6 structure crystallinity of the samples decreases with increase of Zr amount. The 7 reflection peaks for CMAZ-0 and CMAZ-1 show a well-crystallized hydrotalcite 8 structure (JCPDS 48-0601). The introduction of Zr in CMAZ-1 still exist the 9 formation of hydrotalcite structure, which was also observed by Jeong and Gao et 10 al.^{33,34} But, further increasing the amount of Zr, the characteristic peaks of 11 hydrotalcite structure disappeared and the amorphous structure occurred instead. The 12 amorphous structure occurred probably because of the introduction of the distortions 13 in the hydrotalcite sheets as a result of the replacement of Al³⁺ by Zr^{4+, 35} Another 14 reason may be the formation of amorphous precipitates (i.e. Mg and Zr salts of 15 hydroxyl carbonates and hydroxides).³⁶ In these systems, hydrotalcite-like 16 microcrystalline phases consisting of small poorly ordered layers are more likely to be 17 present, leading to the loss of crystallinity for the samples. Therefore, we expect that 18 Zr-containing hydrotalcite-like compounds are the main component in these 19 precursors, especially for the composition of $Zr^{4+}/(Al^{3+}+Zr^{4+})$ less than 0.25.

SEM images of all precursors are shown in Figure 2. It can be observed that a well-developed layered and plate-like structure of hydrotalcite prepared by co-precipitation method without Zr added, could be easily identified in Figure 2a.^{37,38}

1 When the $Zr^{4+}/(Al^{3+}+Zr^{4+})$ ratio is up to 0.25 (i.e. CMAZ-1), the materials still 2 exhibits a plate-like structure of hydrotalcite, though a destructed morphology is 3 observed (Figure 2b). Also, it can be found that the plate-like structures are 4 dense-stacking and homogeneous. However, when the amount of Zr increases as 5 shown in Figures 2c-e, platelet particles tend to break into small pieces for another 6 three samples³⁵ These samples consist of irregular particles that existed in diverse and 7 larger agglomerates with poor crystallinity, which is consistent with the XRD results. 8 We can conclude that the Zr/Al ratio has an obvious influence on the crystal 9 morphology.

10 FT-IR (Supporting Information) was used to identify anion-cation and bond types 11 for the interlayers of the precursors, shown in Figure S1. The intense and broad band 12 at about 3500 cm⁻¹ is ascribed to the bond stretching mode of H₂O molecules of 13 interlayers and the hydroxyl groups on the layers (v_{OHstr}). The broad bands show that 14 the hydroxyl species are hydrogen bonded. A weak absorption band occurs at about 15 1600 cm⁻¹ because of the deformation bending modes of H₂O molecules. The bands 16 between 1300 and 1550 cm⁻¹ are due to bonding stretching modes of the carbonate 17 species. CMAZ-0 and CMAZ-1 exhibit medium vibration at about 420 cm⁻¹ ascribed 18 to O-Metal-O bonds in the sheets. This vibration band gradually disappeared, which 19 can be ascribed to the increase of the Zr content.³⁶ It also shows that introduction of 20 Zr has a significant effect on the crystallinity of hydrotalcite layer structure. 21

To clarify the thermal decomposition process during the calcination, TG and differential thermal gravity (DTG) analysis techniques were performed (Figure S2 in

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	the Supporting Information). The results show that there are three major weight losses
2	for all samples. The first peak of weight loss occurred at 100-200 °C, which can be
3	ascribed to the removal of physically adsorbed H ₂ O molecules in the interlayers. This
4	suggests that the temperature around 150 °C was sufficient for the removal of
5	physisorbed water. The second weight loss occurred at 250-400 °C, which may be
6	ascribed to the decomposition of carbonate ions and laminates hydroxy dehydration.
7	There are some differences for the third weight loss in these materials. The peak of
8	weight loss peak for CMAZ-0 occurred at 600-650 °C. The weight loss peak for
9	CMAZ-1 drops to 500-550 °C compared to CMAZ-0, which is ascribed to the
10	introduction of Zr in the structure. This might reduce the electrostatic interaction
11	between the anions and layers, that can result in lower thermal stability. ^{39,40} For the
12	three samples of CMAZ-2, -3 and -4, the third stage almost disappeared, which
13	implies that hydrotalcite laminate structure disappeared with the increase of Zr
14	content.

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3.2. Textural and Structural Properties of the Calcined Samples

Figure 3 shows the XRD patterns for the samples calcined after H₂ reduction for 2 hours. It can be seen that there are no characteristic peaks of hydrotalcite-like compounds in the XRD patterns. This shows the lamellar framework collapsed and the structure is decomposed. Therefore, crystalline compounds containing Mg and Al were not detected. There are no characteristic peaks of Zr in XRD patterns of CMAZ-0, CMAZ-1 and CMAZ-2, which indicate that Zr was also in the amorphous state.^{26,41} Cu⁰ is the main crystal phase in the CMAZ-0, CMAZ-1 and CMAZ-2. But, with the increase of Zr content (CMAZ-3 and CMAZ-4), the monoclinic zirconia $(m-ZrO_2, 2\theta = 31.5^\circ)$ characteristic peak occurs.

To investigate the effect of Zr content on the size of copper particles, the full width at half maxima (FWHM) in the XRD patterns and the size of the copper particles for different samples are listed in Table 1. The FWHM of the Cu^0 particles was calculated by Gaussian equation and the $d(Cu^0)_{XRD}$ was calculated by Scherrer formula (Equation 3).

$$d(Cu^{0}) = \frac{K\lambda}{FWHM(\pi/180)\cos\theta}$$
(3)

Scherrer formula to calculate $d(Cu^0)$ size of each catalyst (K=0.89; λ =0.154 nm).

The results show that the average size of Cu⁰ crystalline was 3.97-13.23 nm after H₂ reduction. As the Zr content changes, the size of cooper particles reaches the minimum value (3.97 nm) in these samples. Further increase of the Zr content results in the increase of the copper particles size. It is clear that the particle size of Cu is related to the amount of Zr added. Through adding the amount of Zr in the catalyst, the size of copper particles can be controlled. However, excessive introduction of Zr may cause the growth of copper particle.

Figure 4 shows a representative set of TEM images for copper particles synthesized at two different compositions (CMAZ-1 and CMAZ-2) with the statistics of size distributions for copper particles in Figure 4. The mean diameter and min/max diameter were calculated by counting 100 particles (CMAZ-1) and 50 particles (CMAZ-2) with a loupe from the TEM image of 195000 magnifications. From Figure 3 we can observe that CMAZ-1 and CMAZ-2 only present characteristic peaks of

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1	copper. Thus, we can confirm that particles in these two samples are copper
2	nanoparticles, which is confirmed by Zhang et al. ⁴² A copper particle size on surface
3	of CMAZ-1 and CMAZ-2 was obtained from the corresponding size histograms. For
4	CMAZ-1, the average particle size is 3.85 nm, which is smaller than 7.79 nm for
5	CMAZ-2. It can be observed that copper particles are well dispersed in the oxide
6	matrix. Additionally, the dispersion of copper particles in CMAZ-1 is much better
7	than that CMAZ-2. This means that the introduction of Zr can tune the size of the
8	copper particles and have a significant impact on the dispersion of the copper particles
9	in the catalyst. ²⁹ In order to fully understand the inner structure of Cu particles in
10	CMAZ-1, the high-magnification TEM (HRTEM) are obtained shown in Figure 5. Cu
11	particles size in Figure 5(a) is corresponding to the CMAZ-1 sample. Figure 5(b)
12	depicts the fringe spacing of 0.21nm ensures the presence of Cu (111) plane. HRTEM
13	elemental mapping images is shown in Figure S3 (Supporting Information), each
14	element is well dispersed in the catalyst, which illustrated the high dispersion of
15	Cu/Mg/Al/Zr catalyst.
16	The pore volume and surface area of the catalysts after reduction are shown in
17	Table 2. The adsorption and desorption isotherms of samples are shown in Figure S4
18	(Supporting Information). The maximum surface area is 134.07 $m^2 \cdot g^{-1}$ possessed by
19	CMAZ-1. Although CMAZ-0 surface area compare with CMAZ-1 is almost the same
20	(133.11 $\text{m}^2 \cdot \text{g}^{-1}$), but the pore volume is nearly twice lower than CMAZ-1, respectively
21	$0.358 \text{ cm}^3 \cdot \text{g}^{-1}$ and $0.789 \text{ cm}^3 \cdot \text{g}^{-1}$. It is speculated that the introduction of Zr may result
22	in smaller particle size and larger surface area and pore volume. Conversely, surface

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area and pore volume drop significantly in CMAZ-2, -3 and -4. This influence can be ascribed to distortion and destruction of hydrotalcite laminates. The distortion increases with the amount of Zr in the catalysts. The S_{BET} of catalysts decreases because of the destruction and distortion of hydrotalcite. The adsorption and desorption isotherms of samples are shown in Figure S4 (Supporting Information).

The exposed catalyst surface area and dispersion of Cu were measured by N₂O 6 adsorption and are shown in Table 2. When $Zr^{4+}/(Al^{3+}+Zr^{4+})$ ratio is less than 0.25, the 7 exposed surface area of Cu increased with the increase of Zr content. The addition 8 of Zr also enhanced the Cu dispersion, which may be due to the effect of valence 9 compensation and ion doping, i.e. the dissolved Zr in MgO crystal resulted in the 10 formation of cation defects on the surface of Cu-MgO forming more active centers.⁴³ 11 This is consistent with the results observed by Velu et al.,^{44,45} who demonstrated that 12 substitution of Zr could improve the dispersion of Cu. With further increase of the 13 amount of Zr, Zr⁴⁺ may form the m-ZrO₂ crystalline structure and cause the decrease 14 of the proportion of Zr placed in the layered structures.⁴⁶ Therefore, the existence of 15 m-ZrO₂ with little Zr^{4+} in the layered structures caused the lower D_{Cu} for the CMAZ-2, 16 CMAZ-3 and CMAZ-4. 17

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FT-IR spectra of calcined samples are shown in Figure S5 (Supporting Information). Compared with the spectra of the precursors, the stretching vibration and absorption bands positions were retained meaning that the layered structure of hydrotalcite is not completely destroyed at the calcination temperature of 450 °C.

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Figure 6 shows the H₂-TPR profiles for the calcined samples. As shown in Figure 6,

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1	the TPR profiles for all samples with various amount of Zr show a broad band of H ₂
2	consumption at the range of 150-400 °C. To get more insights into TPR results, the
3	band of H_2 consumption were deconvoluted into two Gaussian forms denoted as α and
4	β peaks, respectively. The peak positions and corresponding contributions are listed in
5	the Table 3. The two peaks are attributed to the reduction of two different types of
6	CuO phase. The β peak at high temperature is due to the reduction of dispersed CuO.
7	The α peak is attributed to the reduction of highly dispersed CuO appearing at low
8	temperature. ⁴⁷ As shown in Table 3, α peak proportion in CMAZ-0 only is 14.97 %,
9	the lowest Cu content of all the samples. The proportion suddenly increased to
10	85.32 % in CMAZ-1 and reached the maximum. With the increasing amount of the Zr,
11	this proportion decreases. The addition of Zr caused the broad α peak for the highly
12	dispersed CuO phase. It is because Zr can strengthen the interactions of the Cu^+/Cu^{2+} ,
13	leading to the higher reduction temperature. ³⁵ Excessive Zr amount assists to form the
14	m-ZrO ₂ , as observed in the XRD profile (Figure 3), thus resulting in the decrease of α
15	peak proportion.
16	The surface basicity of the catalysts was detected with CO ₂ -TPD and is shown in
17	Figure 7. The broad band of CO_2 consumption was deconvoluted into three Gaussian
18	forms denoted as weakly (α peak), moderately (β peak) and strongly (γ peak) basic
19	sites. The weakly basic sites are ascribed to hydroxyl groups, moderately basic sites
20	were related to Al-O, Zr-O or Mg-O pairs, and strongly basic sites can be related to
21	oxygen atoms with low coordinations. ^{35,47} The peak positions and corresponding
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contributions are also shown in Table 4. The strength of strongly basic sites is

1 markedly enhanced for CMAZ-1 after the introduction of Zr. While, the strength of 2 strongly basic sites decreased for subsequent CMAZ-2, CMAZ-3 and CMAZ-4. More 3 specifically, in CMAZ-4, strongly basic sites disappeared. CMAZ-1 has the most 4 strongly basic sites among these samples. The number of strongly basic sites increases 5 because of the increase of Zr content in the layered structures. The higher electronic 6 density of the layers in the samples with higher Zr content prohibits some oxygen 7 atoms to coordinate with Zr atoms.⁴⁸ On the other hand, the number of strongly basic 8 sites decreases with further increase of Zr amount in the catalysts due to the 9 transformation of amorphous zirconia $(am-ZrO_2)$ to monoclinic zirconia $(m-ZrO_2)$ 10 (observed in Figure 3). This transformation of structure may lead to less strongly 11 basic sites.49

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3.3. Catalytic Performance

14 Catalytic activity and selectivity of catalysts were tested in dehydrogenation of 15 CHCH to OPP. Figure 8 shows the selectivity and conversions as a function of the 16 $Zr^{4+}/(Zr^{4+}+Al^{3+})$ atomic ratio. Clear differences can be observed between the nature of 17 the catalysts and corresponding catalytic performance. There is a significant change in 18 the activity observed with the increase of the amount of Zr on these samples. The 19 average conversion of CHCH reaches around 98 % for CMAZ-0 to CMAZ-3 and 20 decreased to 67.5 % for CMAZ-4. The selectivity to OPP is also shown in Figure 8. 21 There is a significant difference for these samples. The selectivity of OPP reached a 22 maximum for $Zr^{4+}/(Zr^{4+}+Al^{3+})$ atomic ratio 0.25 (CMAZ-1). Further increase in the

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amount of Zr on the calcined samples leads to drastically toward 4.2 % with

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2	$Zr^{4+}/(Zr^{4+}+Al^{3+})$ atomic ratio of 1. Cu/Mg/Al/Zr catalysts with a better dispersion was
3	prepared with the introduction of an appropriate Zr amount. In addition, the
4	sintering of catalysts can be effectively inhibited because the catalysts can form with a
5	more suitable structural morphology, which was an important factor. The enhanced
6	crystallinity enables more surface are of the catalyst support of the active sites for
7	dehydrogenation. The dehydrogenation performance follows the similar trend as that
8	of dispersion of Cu. For CMAZ-1 where $Zr^{4+}/(Zr^{4+}+Al^{3+})$ atomic ratio is low, the
9	sample has a high pore volume as observed by BET measurement (Table 2). The
10	catalysts exist in the form of the agglomeration of active sites at high $Zr^{4+}/(Zr^{4+}+Al^{3+})$
11	atomic ratio resulting in large-sized particles. From the CO ₂ -TPD profiles in Figure 7,
12	the OPP selectivity is influenced by the distribution of basic sites on the surface of
13	catalysts. The catalytic selectivity is also related to the amount of reducible copper,
14	although the selectivity is not proportional to the atomic ratio of $Zr^{4+}/(Zr^{4+}+Al^{3+})$
15	shown in Figure 8. The appropriate amount of Zr added in the sample is 0.25 for the
16	atomic ratio of $Zr^{4+}/(Zr^{4+}+Al^{3+})$ H ₂ -TPR results and reaction results confirmed this
17	observation CMAZ-1 shows the highest proportion of low temperature peak (around
18	85.3 %) in H ₂ -TPR and the better dispersed CuO in this sample. Guo and Wang et al.
19	reported that catalytic activity of Cu-based dehydrogenation catalysts is related to
20	well dispersed conner species $47, 50$ Therefore, the variation trends of catalytic activity
21	of catalysts would be easy to understand in view of the similar trends of the dispersion
22	of copper species, which was illustrated by XRD and TPR results. In addition it is
	rr r

1 clear that the OPP selectivity is also affected by the Zr amount, which tuned the 2 dispersibility of copper species. The exposed surface area of copper measured by 3 chemisorption of N₂O is an important parameter for Cu-containing catalysts. The 4 catalytic activity depends on the exposed surface area of Cu. The exposed surface area 5 of Cu increased obviously with the increase of Zr content. The maximum dispersion 6 (22.5 %) of Cu is obtained for CMAZ-1 and the selectivity of OPP also reached a 7 maximum. The number of strongly basic sites decreases with further increase of Zr 8 amount in the catalysts because of the transformation of amorphous zirconia 9 $(am-ZrO_2)$ to monoclinic zirconia $(m-ZrO_2)$. This structural transformation may lead 10 to less strongly basic sites. Zhou et al. studied on Cu/ZrO₂ catalysts, which consisted 11 of tetragonal zirconia with Cu content lower than 10 wt%.⁵¹ They referred to as the 12 interaction between Cu species and the ZrO₂ support which hindered the phase 13 transformation to m-ZrO₂ based on the vacancy model of oxygen.⁵²



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Scheme 1 Synthesis route of OPP from CHCH and its byproducts.

The goal of this investigation is to shed light on the effect of different Zr content on the catalytic properties in relation to byproducts. The dehydrogenation process consists of a sequence of hydrogenation or dehydrogenation reactions, in which the CHCH is successively transformed into o-cyclohexylcyclohexanone (OCC),

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1	o-cyclohexylphenol (OCHP) and finally OPP (Scheme 1). ⁵³ Besides, there are small
2	amount of biphenyl (BP) and dibenzofuran (DBF) among byproducts. It is because
3	that OPP can further dehydrogenated to DBF and dehydrated to BP. Catalytic
4	selectivity for primary products of all catalysts is shown in Figure 9. When OPP
5	selectivity increases, the byproducts OCC and OCHP naturally decrease. Moreover,
6	OCC is the main byproducts. According to the route shown in the Scheme, the OPP
7	selectivity is significantly affected by the amount of Zr. Mean Cu ⁰ crystalline sizes is
8	the smallest in CMAZ-1 and OCC content is the lowest. This suggests that smaller
9	copper particles size of catalyst results in the better copper dispersion. Thus, the
10	conversion of CHCH to OPP is more effective. While mean Cu ⁰ crystalline sizes
11	increases, copper distribution becomes worse. The conversion of CHCH mainly
12	occurs in the first step reaction and the main byproduct is OCC. In conclusion, copper
13	particle size has a significant effect on the OPP catalytic activity and selectivity. The
14	introduction of Zr can control the copper particle size. The small mean Cu ⁰ crystalline
15	size is in favor of the conversion of CHCH to OPP.
16	

RSC Advances Accepted Manuscript Figure 10 shows the catalytic selectivity to OPP with the reaction time. The corresponding conversions can be found in Table 1S (Supporting information). During

18 the reactions, CMAZ-1 always shows the highest catalytic performance and the 19 selectivity is still above 65% after 7 hours reaction. With the increase of Zr content, 20 CMAZ-4 almost lost its catalytic activity. The copper particles size and high 21 dispersion of containing active copper centers on surface have a significant impact on 22 the catalytic stability. Chraska et al. studied the effect of the particle size on the

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stability of the catalysts and observed that the stability for small particles can be illustrated by the lower surface energy of ZrO_2 .⁵⁴ Purnama et al. observed a significant stabilizing effect of Cu centers in ZrO_2 .⁵⁵ This may explain the stabilization of the Cu particles with a diameter of about 3 nm. It is clear that the CMAZ-1 catalyst prepared via co-precipitation method shows a stable catalytic performance during this reaction time.

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4. Conclusion

9 Cu-Mg-Al-Zr hydrotalcite-like compounds with different atomic ratio of 10 $Zr^{4+}/(Al^{3+}+Zr^{4+})$ were successfully prepared by co-precipitation methods. The 11 introduction of Zr can improve the catalytic properties of Cu-Mg-Al catalyst prepared 12 via hydrotalcite-like precursors. The catalytic activity and selectivity for OPP 13 synthesis are related to the size of Cu species and the amount of Zr in catalysts. The 14 optimum content of Zr is about $Zr^{4+}/(Al^{3+}+Zr^{4+}) = 0.25$ (CMAZ-1), showing the 15 highest catalytic stability and selectivity above 65% even after 7 hours of reaction. 16 The existence of Cu nanopatricles is confirmed by analysis using XRD, TEM and 17 HRTEM. Introducing Zr affects the size of Cu nanoparticles, smaller Cu nanoparticles 18 always shows the better catalytic performance; and CO₂-TPD results show that Zr 19 can lower the content of Al on the catalyst, and generate the strongly basic sites. This 20 may weaken the interaction between Al₂O₃ and CuO so to avoid the agglomeration of 21 active sites. CMAZ-1 always shows the highest catalytic stability and the selectivity 22 keep above 65% even after 7 hours reaction.

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9	Development of Jiangsu Higher Education Institutions.
10	
11	Supporting Information Available: FT-IR, DG-DTG, N ₂ adsorption-desorption
12	isotherms and elemental mapping images of catalysts. This material is available free
13	of charge via the Internet at http://pubs.rsc.org.
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Fig. 1 XRD patterns of the Cu/Mg/Al/Zr precursors with various Zr content.

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Fig. 2 SEM images of uncalcined samples: (a) CMAZ-0, (b) CMAZ-1, (c) CMAZ-2,

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(d) CMAZ-3, and (e) CMAZ-4.

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Fig. 3 XRD patterns of the calcined Cu/Mg/Al/Zr catalysts after reduction at 300 °C.

(•) Cu^0 ; (•) $\operatorname{Cu}O$; (\bigtriangledown) Cu_2O ; (\blacklozenge) m-ZrO₂





- for 2h.
- 4

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- Fig. 5 (a) HRTEM images of CMAZ-1 catalysts after H2 reduction at 300 °C for 2h.
 - (b) HRTEM image of single particle from (a).

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2 Fig. 6 H₂-TPR profiles of catalysts at 450°C, black solid, red dash and blue dot lines

3 correspond to the TPR, α and β peak, respectively.



2 Fig. 7 CO₂-TPD profiles of the catalysts with various Zr content, black solid, red dash,



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Fig. 8 Effects of the amount of Zr on the conversion of OCC and the selectivity
 toward OPP at 330 °C after 2 h reaction.

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Fig. 9 The catalytic selectivity for three primary products of all catalysts after 2 h

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3 reaction.

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	$Cu^{2+}/Mg^{2+}/Al^{3+}/Zr^{4+}$	FWHM	d(Cu ⁰) _{XRD}
Sample No.	atomic ratio	$(\theta)^{a}$	(nm)
CMAZ-0	2.5:3.5:2:0	1.545	5.47
CMAZ-1	2.5:3.5:1.5:0.5	2.128	3.97
CMAZ-2	2.5:3.5:1:1	1.271	6.65
CMAZ-3	2.5:3.5:0.5:1.5	0.660	12.81
CMAZ-4	2.5:3.5:0:2	0.639	13.23

Table 1 Different samples' FWHM and Cu⁰ particles size through XRD patterns.

2	^a The FWHM of the Cu ⁰	particles

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Table 2 Structural properties of the catalysts with various amount of Zr.

Catalysts	Surface area ^a	Pore volume ^a	Cu surface	Cu dispersion ^b
	$(m^2 \cdot g^{-1})$	$(cm^3 \cdot g^{-1})$	area ^b (m ² ·g ⁻¹)	(%)
CMAZ-0	133.11	0.358	81.85	12.08
CMAZ-1	134.07	0.789	152.45	22.54
CMAZ-2	97.046	0.340	15.75	2.32
CMAZ-3	35.929	0.128	20.12	2.97
CMAZ-4	66.655	0.409	41.40	6.11

^aAfter reduction at 300 °C ^bCalculated from dissociative adsorption

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Table 3 Reduction peak temperatures and the percentage of α peak with different Zr

content.

Sample No.	$T_{\alpha}(^{\circ}C)$	$T_{\beta}(^{\circ}C)$	$A_{\alpha}\!/\!(A_{\alpha}\!\!+\!\!A_{\beta}){}^{\prime\!\!\prime}\!$
CMAZ-0	213	253	14.97
CMAZ-1	249	317	85.32
CMAZ-2	303	330	74.06
CMAZ-3	186	212	38.17
CMAZ-4	186	212	41.38

³

 $^{a}A_{\alpha}$ and A_{β} represent the area of α and β peaks, respectively.

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5 Table 4 The basicity and the distribution of basic sites over catalysts with various Zr

6 content.

	TPD peak position [temperature (°C)] and concentration		
Sample No.		(%) ^a	
	Site α	Site β	Site y
CMAZ-0	232 (6.01)	446 (79.81)	659 (14.18)
CMAZ-1	295 (23.43)	439 (9.22)	473 (67.35)
CMAZ-2	329 (44.44)	447 (41.89)	566 (13.67)
CMAZ-3	371 (72.73)	385 (27.27)	/
CMAZ-4	/	/	/

^a The proportion of different basic sites

⁴



Cu/Mg/Al/Zr Non-Noble Metal Catalysts for O-Phenylphenol Synthesis

Yongping Zeng, 'Tianchi Zhang, Yueyang Xu, Peili Hu', Ting Ye, Zhehua Jia,

Shengui Ju