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Chemistry-Sustainability-Energy-Materials



European Chemical Societies Publishing



Accepted Article

Title: Direct Transformation of Glycerol to Propanal using Zirconium Phosphate-Supported Bimetallic Catalysts

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.202001600

Link to VoR: https://doi.org/10.1002/cssc.202001600

WILEY-VCH

1	Direct Transformation of Glycerol to Propanal using Zirconium	
2	Phosphate-Supported Bimetallic Catalysts	
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10.1002/cssc.202001600

Abstract: Selectively transformation of glycerol to propanal (PA) provides a feasible 1 route towards the sustainable synthesis of high value-added chemicals. In this work, 2 zirconium phosphate (ZrP) was studied as support and Ru and Co as metal sites for 3 glycerol hydrogenolysis in a continuous flow reactor. It was found that ZrP-supported 4 Co-O species had a moderate selectivity to PA (49.5%) in glycerol hydrogenolysis. 5 Notably, once Ru species were doped into CoO/ZrP, the resulting catalyst exhibited not 6 only an outstanding catalytic performance for glycerol hydrogenolysis to PA (a 7 8 selectivity of 80.2% at full conversion), but also a high stability at least a 50 h longterm performance. The spent catalyst could be regenerated by calcining in air to remove 9 carbonaceous deposits. Characterization indicated that the acid sites on ZrP played a 10 very critical role in the dehydration of glycerol into acrolein (AE). Besides, XRD, 11 HAADF-STEM and EDS elemental maps demonstrated that the distribution of Co was 12 uniform, basically consistent with that of Zr, P and Ru, and especially a close contact 13 between Co-O and Ru species was formed on Ru/CoO/ZrP catalyst. The further activity 14 tests and characterizations confirmed that there was a strong interaction between the 15 dispersed Co-O species and Ru⁰ NPs, which endowed Ru sites with high electronic 16 density. This effect could play a role in facilitating the dissociation of H₂, and thus 17 promoting the hydrogenation reaction. Besides, the DFT calculations suggested that the 18 Co-O species can adsorb more strongly the C=C bond of the intermediate AE on a 19 highly coordinatively unsaturated Co (Cocus) site and thus lead to its preferential 20 hydrogenation at the C=C bond of AE to PA. 21

22 Keywords: Glycerol hydrogenolysis; Propanal; Zirconium phosphate; Ruthenium;
23 Cobalt

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1 1. Introduction

Fossil fuel consumption has been sharply increasing for the past decades due to human 2 activity and the development of industry, the non-renewability of fossil energy and the 3 environmental pollution problems force researchers to seek green and renewable energy 4 sources.^[1-4] As a renewable energy, biodiesel is attracting worldwide attention. In the 5 production of biodiesel, glycerol is obtained as a main by-product and the rapid 6 development of biodiesel will inevitably lead to the excess production of glycerol.^[5-8] 7 8 Therefore, the rational conversion of glycerol can not only promote the sustainable development of the economy but also reduce damage to the environment. 9

Accordingly, numerous studies have been performed to the transformation of glycerol by various catalytic processes, such as dehydration, oxidation, hydrogenolysis, reforming, acetalization, and esterification.^[7, 9-12] Among them, one of the most promising approaches is the catalytic hydrogenolysis of glycerol into propanediols, such as 1,3-propanediol (1,3-PDO) and 1,2-propanediol (1,2-PDO).^[13,14] It is worth noting that highly efficient and selective hydrogenolysis of glycerol to 1,2-PDO has been achieved on various catalytic systems.^[7, 15-20]

Although the dehydration of 1,2-PDO to propanal (PA) has also been studied using 17 various types of heterogeneous catalysts, the catalytic activity and selectivity to PA still 18 remains a huge challenge.^[21-26] The PA with a reactive formyl group is an important 19 20 potential intermediate material to produce high value-added chemicals such as rubbers, plastics, paints and pesticides, which are commercially produced from fossil resources 21 now.^[23, 27-29] Obviously, to develop selective and sustainable catalytic system for 22 directly transformation of easily available and inexpensive glycerol into a partially 23 24 hydrogenated product, PA, is extremely attractive and demanded. As far as we have known, the highly selective hydrogenolysis of glycerol into PA has not been disclosed 25 up to now. 26

In the previous studies, our group had found that the zirconium phosphate (ZrP) is a water-tolerant and thermal stability solid acid catalyst, which provided an excellent performance for gas phase selective dehydration of glycerol to acrolein (AE).^[30]

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Thereafter, we have also developed a one-pot hydrogenolysis of glycerol to 1-propanol 1 over sequential two-layer catalysts (ZrP and Ru/SiO₂) or a single Pt/7WO₃-ZrP catalytic 2 system in a continuous flow fixed-bed reactor.^[31,32] As a continuation of our efforts to 3 achieve novel applications of this easily accessible, cheap and stable solid acid catalyst, 4 we report herein a direct PA production from glycerol over ZrP-supported bimetallic 5 catalysts. It was found that the Ru/CoO/ZrP was a highly efficient catalyst for glycerol 6 hydrogenolysis, which can achieve full conversion of glycerol and an excellent 7 8 selectivity to PA (80.2%) by one-step route under continuous-flow conditions. As far as we have known, this is the most effective catalytic approach for the conversion of 9 glycerol to PA. The catalysts used in this paper broadens valuable products range for 10 glycerol upgrading. Inspired by the excellent performance of Ru/CoO/ZrP, detailed 11 structure-activity relationships of the Ru/CoO/ZrP catalyst in the glycerol 12 hydrogenolysis were studied and the mechanism for the enhanced performances was 13 also elucidated. 14

15

16 **2. Experimental**

17 2.1. Materials

Zirconium oxychloride, ammonium dihydrogen phosphate, glycerol, silver nitrate, 18 ruthenium chloride trihydrate, cobalt nitrate hexahydrate were purchased from Sino 19 pharm Chemical Reagent Co. Ltd. (Shanghai, China). The NaZSM-5 with a Si/Al ratio 20 of 23 was bought from ShenTan Catalysts Company (Shanghai, China). Before use, the 21 NaZSM-5 zeolite were exchanged with NH₄Cl (1M) solution three times and washed 22 without Cl⁻ by deionized water. Then the materials were dried at 110°C overnight, 23 followed by calcination in air at 450°C for 4 h to obtain the HZSM-5. ZrO₂ was 24 prepared by a precipitation method according to previous report.^[30] High purity N_2 25 (99.999%) and H₂ (99.999%) was supplied by ShangNong Gas Factory. All other 26 chemicals (analytical grade) were from Sino pharm Chemical Reagent Co. Ltd., and 27 used as received without any further purification. 28

1 2.2 Catalyst preparation

2 2.2.1 Preparation of amorphous ZrP

The amorphous zirconium phosphates were prepared by a precipitation method according to the previous procedure.^[33] Briefly, an aqueous solution of $NH_4H_2PO_4$ (1.0 mol·L⁻¹, 64 mL) was added dropwise to an aqueous solution of $ZrOCl_2 \cdot 8H_2O$, at a molar ratio of P/Zr = 2. The mixture was stirred overnight at room temperature, then filtered, and washed with deionized water until the pH of the filtrate reached 6 and no Cl⁻ was detect by an acidic AgNO₃ solution. The material obtained was dried for 12 h at 100°C, followed by calcination at 400°C for 4 h in a muffle furnace.

10

11 2.2.2 Preparation of the ZrP based catalysts

The catalysts were prepared according to the following methods. The first was 12 sequential impregnation method, as a typical example, 0.52 mmol Co(NO₃)₂·6H₂O 13 was dissolved in 1.2 mL H₂O, and this solution was joined to 1.0 g ZrP. Then the 14 dispersion was stirring vigorously for 2 h, stewing 24 h and dried at 100°C for 12 h, 15 followed by calcination at 400°C for 4 h in a muffle furnace and denoted as CoO_x/ZrP. 16 After that, 0.26 mmol RuCl₃·3H₂O was dissolved in 1.2 mL H₂O, and this solution was 17 joined to 1.0 g CoO_x/ZrP. The resultant dispersion was stirring vigorously for 2 h, 18 stewing 24 h and dried at 100°C for 12 h, followed by calcination at 400°C for 4 h in 19 a muffle furnace and denoted as RuO₂/CoO_x/ZrP. The as-obtained gray 20 RuO₂/CoO_x/ZrP powder was reduced at 270°C for 1 h prior to reaction or various 21 22 characterizations, and was denoted as Ru/CoO/ZrP. The second was co-impregnation 23 method, as a typical example, 0.52 mmol Co(NO₃)₂·6H₂O and 0.26 mmol RuCl₃·3H₂O was dissolved in 1.2 mL H₂O, and this solution was joined to 1.0 g ZrP. Then the 24 suspension was stirring vigorously for 2 h, stewing 24 h and dried at 100°C for 12 h, 25 followed by calcination at 400°C for 4 h in a muffle furnace and denoted as RuO₂-26 CoO_x/ZrP, followed by reducing at 270°C for 1 h prior to reaction or various 27 28 characterizations and denoted as Ru-CoO/ZrP. The other catalysts such as Ru/CoO/ZrO2 and Ru/CoO/HZSM-5 have also been obtained by following the 29

sequential impregnation method. The loading amounts of Ru and/or Co per g of ZrP 1 on all the catalysts was calculated to be 0.26 mmol and/or 0.52 mmol, respectively. 2 For the sake of comparison, the Ru/ZrP was also prepared by incipient wetness method. 3 As a typical example, 0.26 mmol RuCl₃·3H₂O was dissolved in 1.2 mL H₂O, and this 4 solution was joined to 1.0 g ZrP. Then the suspension was stirred vigorously for 2 h, 5 aged 24 h and dried at 100°C for 12 h, followed by calcination at 400°C for 4 h in a 6 muffle furnace and denoted as RuO₂/ZrP. The resulting material was reduced at 270°C 7 8 for 1 h prior to reaction or characterizations and denoted as Ru/ZrP.

9

10 2.3 Catalyst characterization

X-ray diffraction (XRD) analysis of samples was performed in the 2 θ range of 10 $^{\circ}$ -11 80° on an Rigaku D/MAX 2550 VB/PC instrument using a graphite crystal a 12 monochromator. The textural properties from N2 adsorption isotherms were obtained 13 on Quanta chrome NOVA 2200e equipment. The surface area was obtained from the 14 isotherms in the relative pressure range of 0.0-0.35. Pore volume was determined at 15 16 p/p_0 of 0.99. FT-IR spectra were recorded from pressed KBr pellets at room temperature on a Nicolet Fourier transform infrared spectrometer (Magna550). A spectrum of dry 17 KBr was also recorded as background. Temperature-programmed reduction (H₂-TPR) 18 was performed using VDsorb-91i. The catalyst was placed in an Ushaped quartz tube, 19 then purged under pure Ar (10 mL min⁻¹) flow at 400°C for 1 h, and then cooled down 20 to room temperature. After that, it was reduced with $H_2/Ar (1/9, v/v) (10 \text{ mL min}^{-1})$ up 21 to 900°C (ramp rate of 10°C min⁻¹). The amount of acid sites of the different samples 22 was determined by temperature programmed desorption of ammonia (NH₃-TPD). 23 24 About 0.15 g of catalyst was loaded in a quartz tube. Prior to each test, the samples were pre-treated in a flow of He at 400°C for 2 h, cooled to 50°C to remove surface 25 water. Then, the samples were maintain at 50°C for 1 h and saturated with a 10% NH₃-26 in-N₂ mixture, and then flushed by He for 1 h to remove physically adsorbed ammonia. 27 Then, the samples were heated to 800°C at a heating rate of 10°C min⁻¹ in the same 28 flow of He. The profiles of desorption were recorded using a thermal conductivity 29

detector (TCD), which was calibrated by a pulse-gas with known amount of NH₃. A 1 cooling trap was employed to condense the minor water vapor before the carrier gas 2 flowed into the TCD detector in H₂-TPR and NH₃-TPD analyses. The thermal stability 3 of catalysts was determined by Thermogravimetry analysis (TGA) method (heating rate: 4 10°C min⁻¹; air flow, 100 mL min⁻¹) using PerkinElmerPyris Diamond Analyser. The 5 Scanning electron microscopy (SEM) images were performed on JSM electron 6 microscopes (JEOL JSM-6360LV, Japan). High resolution transmission electron 7 8 microscopy (HRTEM) was performed in a JEOL JEM 2010 transmission electron microscope operating at 200 kV with a nominal resolution of 0.25 nm. The samples for 9 HRTEM were prepared by dropping the aqueous solutions containing catalysts onto the 10 carbon-coated Cu grids. Scanning transmission electron microscopy (STEM) 11 characterization was performed using ThermoFisher Talos F200X. High angle annular 12 dark field (HAADF)-STEM images were recorded using a convergence semi angle of 13 11 mrad, and inner- and outer collection angles of 59 and 200 mrad, respectively. 14 Energy dispersive X-ray spectroscopy (EDS) was carried out using 4 in-column Super-15 16 X detectors. EXAFS was performed at the beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy 17 of Sciences (CAS). Raman spectroscopy was performed using a Thermo Scientific 18 DXR Raman microscope, and X-ray photoelectron spectroscopy (XPS) was performed 19 using Thermo ESCALAB 250. The hydrogenation product, PA, was identified by NMR 20 spectra using Bruker AVANCE instrument, the sample was dissolved in CDCl₃ before 21 ¹H NMR and ¹³C NMR measurement. The FT-IR spectra of the pyridine-adsorbed on 22 catalyst were obtained in the transmission mode using a Nicolet Model 710 23 24 spectrometer. First, the catalyst (25 mg) was ground into the powder and pressed into a 25 very thin self-supporting wafer. The disc was mounted in a quartz IR cell equipped with a CaF₂ window. 30 mg of the catalyst was pressed into a self-supporting disk and placed 26 in an IR cell attached to a closed glass-circulation system. The catalyst disk was 27 28 dehydrated by heating at 400°C under vacuum in order to remove physisorbed moisture. 29 The IR spectrum background was recorded at room temperature when the cell cooled

10.1002/cssc.202001600

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down. Pyridine vapor was then introduced into the cell at room temperature until
equilibrium was reached. The quantification of acid sites was performed using the same
expressions (1) and (2) as those in the research article of Angela S. Rocha.^[34]

4
$$C_{B} = k_{B}A_{1540} = \frac{\pi}{IMEC_{B}} \left(\frac{r^{2}}{\omega}\right) A_{1540}....(1)$$

5

$$C_L = k_L A_{1450} = \frac{\pi}{IMEC_L} \left(\frac{r^2}{\omega}\right) A_{1450}....(2)$$

6 C_L and C_B are the concentrations of Lewis acid and Brønsted acid sites in µmol g⁻¹; 7 A₁₄₅₀ and A₁₅₄₀ are the integrated areas of bands at 1450 and 1540 cm⁻¹ in the original 8 data of FTIR spectra, as shown in the section of results and discussion. K_L and K_B are 9 molar extinction constants for Lewis and Brønsted acid sites; IMECL and IMECB are 10 integration molar extinction coefficients, 2.22 and 1.67 cm·µmol⁻¹ for Lewis and 11 Brønsted acids, respectively; r is the wafer radius in cm and ω is the wafer weight in g 12 of the self-supporting catalyst disk.

13

14 **2.4 Catalytic reaction**

15 The hydrogenolysis of aqueous glycerol solution was carried out in a vertical fixedbed stainless-steel reactor (1.1 cm i.d., length 60 cm). The solid catalyst was tableted 16 and then crushed and sieved to 20-40 mesh particles for the catalytic reaction tests. A 17 constant weight (1.0 g) of catalyst layer was sandwiched in the middle of the reactor 18 with guartz wool and guartz sand for supporting the catalyst and evaporation of the 19 reactants. The temperature was controlled by a thermocouple placed in the middle of 20 the catalyst bed. Prior to the reaction, the catalyst was reduced at 270°C for 1 h with 21 10% H₂ in N₂ (0.1 MPa, 30 mL min⁻¹). When the temperature of reactor was constant, 22 23 the feedstock, an aqueous solution containing 10 wt.% glycerol, was then pumped into the reactor (0.04 mL min⁻¹) and driven through the catalyst bed by hydrogen flow (2.0 24 MPa, 30 mL min⁻¹). The reaction products were condensed in a cryogenic cooling 25 system and collected every two hours for offline analysis by using a GC 128 gas 26 chromatograph equipped with an FFAP capillary column (30 m long, 0.32 mm i.d., 0.33 27 µm film thickness). Volatile compounds that were not retained in the cold trap were 28

1	absorbed i	n ethyl acetate ar	nd also an	alyzed	by offli	ine GC.	The gaseo	ous produ	cts were	
2	collected and analyzed by offline GC with thermal conductivity detector (TCD). The									
3	products w	products were identified by an Agilent 6890/5973 GC-MS System equipped with a HP-								
4	5MS colu	mn (30 m long, ().25 mm i	.d., 0.2	25 μm fi	ilm thick	ness) and	flame ic	nization	
5	detector (FID). The gas-p	hase (CC	D ₂ , CO	9, CH4	and pro	pane) pro	oducts an	nd other	
6	unidentifie	ed products are de	efined as '	•others	". The 7	TOS (tim	e of stream	m) value	for each	
7	catalyst w	vas collected at	TOS=24	h unl	ess indi	icated of	therwise.	To exam	nine the	ا ـــــــ
8	reusability	of the catalyst, t	he spent o	catalyst	t was re	generated	d by calci	ning at 5	00°C for	ō
9	4 h in air	and then reduce	ed in situ	at 270	0°C for	1 h prio	or to the r	next run.	For the	
10	quantitativ	ve measurements,	1-butano	l was u	sed as th	ne interna	al standard	d. The co	nversion	$\overline{\mathbf{O}}$
11	of glycero	l, the selectivity a	and yield	of prod	lucts we	ere calcul	ated as fo	ollows:		Š.
12	Conversion (%) = $\frac{\text{amount of gly cerol reacted (mole)}}{\text{total amount of gly cerol used in the reaction (mole)}} \times 100\%$									
13	Selectivity (%) = $\frac{\text{carbon in a product defined (mole)}}{\text{carbon in gly cerol reacted (mole)}} \times 100\%$									
14	Carbon yield in liquid product (%) = $\frac{\text{carbon atoms found in the liquid products(mole)}}{\text{carbon atoms of gly cerol converted (mole)}} \times 100\%$									
15	3. Results	and discussion								0
16	3.1 Cataly	yst activity								Q
	Table 1. (Catalytic perform	nances of	f the l	hydroge	nolysis	of glycer	col over	different	5
	catalysts. ^[a]									
			Con.			S	el. (%)			Ğ
	Entry	Catalysts	(%)	PA	AE	2-PO	1-PO	HA	Other ^[f]	ŏ
	1 ^[b]	ZrP	72.5	-	79.0	-	-	12.0	9.0	
	2	ZrP	74	31	53	-	-	5	11.0	N N

13 Selectivity (%) =
$$\frac{\text{carbon in a product defined (mole)}}{\text{carbon in gly cerol reacted (mole)}} \times 100\%$$

- 15
- 16

		Con.			S	el. (%)		
Entry	Catalysts	(%)	PA	AE	2-PO	1-PO	HA	Other ^[f]
$1^{[b]}$	ZrP	72.5	-	79.0	-	-	12.0	9.0
2	ZrP	74	31	53	-	-	5	11.0
3 ^[c]	Ru/ZrP	95	23.0	8.5	10.5	34.5	7.5	16.0
4	CoO/ZrP	100	49.5	35	-	1.5	8.0	6.0
5	Ru-CoO/ZrP	78	14.5	2.2	26	42.0	2.4	12.9
6	Ru/CoO/ZrP	100	80.2	3.7	-	0.5	9.5	6.1

7 ^[d]	Ru/CoO/ZrP	74.5	74	8.5	-	1	9	7.5
8 ^[e]	Ru/ZrP+CoO/ZrP	93	12	-	24.5	45	8.4	10.1

[a] Reaction conditions: 2 MPa H₂ pressure; gas flow rate 30 mL/min; 270°C; 10 wt.% glycerol solution; feed speed: 0.04 mL/min; 1.0 g Ru/CoO/ZrP catalyst. [b] The reaction was carried out under N₂ atomospere (0.1MPa). [c] The data was adopted at TOS=16 h due to fast catalyst deactivation. [d] The concentration of glycerol aqueous solution was 20 wt.%. [e] Ru/ZrP+CoO/ZrP (physical mixture). PA: Propanal; AE: Acrolein; 2-PO: 2-propanol; 1-PO: 1-propanol; HA: Hydroxyacetone. [f] Others include CO₂, CO, CH₄, propane and other unidentified products. The carbon yield in liquid products is more than 84% for all catalysts in Table 1.

1

The hydrogenolysis of aqueous glycerol solution has been carried out in a 2 continuous-flow fixed-bed reactor. As shown in Table 1, when ZrP was used as catalyst, 3 almost all products resulted from glycerol dehydration (72.5% conversion of glycerol, 4 79% selectivity to AE) under N₂ atmosphere (Table1, entry 1), which were consistent 5 with that reported in our previous work.^[30] The sole ZrP without metals has also been 6 tested in H₂ flow, 74% glycerol conversion with a 53% selectivity of AE was observed, 7 8 along with a decreased selectivity to HA (Table 1, entry 1 and 2). Besides, a small amount of PA (in selectivity 31%) was also formed, likely arising from the effect of the 9 stainless-steel walls of the fixed-bed reactor,^[32] which can be confirmed further by the 10 following control experiment: a low conversion of AE (36.5%) could be achieved even 11 without catalyst in H₂ flow (Table S1, entry 1). Interestingly, in the presence of 12 Ru/CoO/ZrP catalyst, AE was almost converted into PA (in 96% selectivity) (Table S1, 13 entry 2). These results indicated clearly that the hydrogenation of AE was not effective 14 without the catalyst and Ru and Co loading on ZrP can promote the selective 15 16 hydrogenation of AE to PA efficiently.

In this work, we have attempted to explore new approach to selectively achieving a partially hydrogenated product (PA) via hydrogenolysis of glycerol in a one-step process. Since Ru⁰ species were generally considered to own good hydrogenation

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activity, what we started to try was to load Ru on ZrP. Although the resultant Ru/ZrP presented glycerol conversion of 95% (at TOS = 16 h), a wide range of products were formed, including PA (in 23% selectivity), 1-propanol (1-PO, in 34.5% selectivity) and 2-propanol (2-PO, in 10.5% selectivity) (Table 1, entry 3). It can be seen that the products on Ru/ZrP catalyst were mainly monoalcohols because Ru sites were high active for catalytic hydrogenation and also C-O bond cleavage.^[35-41]

Next, if the Co-O species (designated as CoO) was loaded on ZrP, the resulting 7 CoO/ZrP catalyst was evaluated for the hydrogenolysis of glycerol. Although glycerol 8 was completely consumed, the PA was formed with only 49.5% selectivity, along with 9 AE as a side-product (in 35% selectivity), showing the insufficient reactivity for the 10 hydrogenation of C=C bond in AE over Co-O sites (Table 1, entry 4). With regard to 11 the evaluation of Ru/ZrP and CoO/ZrP, we speculated whether the doping of Ru species 12 can further promote the catalytic performance of CoO/ZrP in glycerol hydrogenolysis. 13 Sequentially, the two metal species (Ru and Co) were introduced into ZrP in order to 14 examine if Ru distribution has an effect on the hydrogenolysis of glycerol to PA. In the 15 16 first route, the Ru-CoO/ZrP catalyst was prepared by the co-impregnation of Ru and Co precursors on the ZrP. It was found that the product distribution was actually similar to 17 that of Ru/ZrP catalyst, although the selectivity of AE became slightly lower (Table 1, 18 entries 3 vs 5). This revealed that the introduction of Ru and Co species by co-19 impregnation route did not obviously improve the catalytic performance as compared 20 with that of Ru/ZrP. In the second route, when we introduced the two metals to ZrP by 21 a sequential impregnation to obtain Ru/CoO/ZrP catalyst. Surprisingly, the catalyst 22 showed a full glycerol conversion and the excellent selectivity to PA (80.2%), while AE, 23 hydroxyacetone (HA) and 1-PO were detected only as minor by-products in liquid 24 phase (Table 1, entry 6). To the best of our knowledge, the present Ru/CoO/ZrP catalyst 25 can afford two or three times higher PA yield than that of the previous report (PA 26 yield<35%) via a direct hydrogenolysis of glycerol.^[42,43] Moreover, since high glycerol 27 concentration is preferable in industrial applications, the high concentration of glycerol 28 aqueous solution (20 wt.%) was used as feed. The activity and selectivity to PA showed 29

1 a slight decrease due to a short contact time (Table 1, entries 6 vs 7).

After reaction under the optimum condition, the effluent was distilled under the 2 vacuum to separate PA from the aqueous solution and then analyzed with ¹H NMR and 3 ¹³C NMR (Figure S1), which indicated that the purity of as-obtained PA was more than 4 95% only through such a simple isolation. The dramatic enhancement of the selectivity 5 on the catalyst prepared by the second method may be related to stronger interactions 6 between Co-O species and Ru⁰ nanoparticles (NPs). Inspired by the above results, 7 comprehensive and in-depth characterization, and DFT calculations were performed to 8 9 reveal that why such a simple change in the impregnation sequence of Ru can cause such an obvious improvement. 10

- 11
- 12 **3.2 Catalyst characterization**

At first, XRD patterns of the calcined catalysts were shown in Figure S2. The 13 diffraction peaks corresponding to Ru species were not observed in RuO₂/ZrP and 14 RuO₂-CoO_x/ZrP, indicating the presence of highly dispersed Ru species (Figures S2a 15 16 and S2b). However, the XRD patterns of the RuO₂/CoO_x/ZrP showed two main strong diffraction peaks at 28° and 34.9°, corresponded to the characteristic diffraction peaks 17 of RuO₂ (JCPDS 43-1027), which meant the particle size of RuO₂ NPs was likely larger 18 on the RuO₂/CoO_x/ZrP (Figure S2c), as compared with that of RuO₂/ZrP and RuO₂-19 CoO_x/ZrP. After the catalysts were reduced, the XRD patterns were shown in Figure 1a. 20 The presence of two broad peaks in the ranges of 10°-40° and 40°-70° indicated that the 21 amorphous nature remained intact on all ZrP-based catalysts, as compared with that of 22 bare ZrP.^[44-46] In case of the Ru/ZrP and Ru-CoO/ZrP catalysts, there were no any 23 diffraction peaks corresponding to crystalline Ru⁰ phases, implying that the reduced Ru 24 species were highly dispersed. Comparatively, the XRD patterns of the Ru/CoO/ZrP 25 showed three weak diffraction peaks at 38.2°, 42.4°, 44.0° (JCPDS 65-1863), 26 corresponding to the characteristic diffraction peaks of crystalline Ru⁰. This revealed 27 that the properties of Ru⁰ NPs on the Ru/CoO/ZrP were different from that on the Ru-28 29 CoO/ZrP and the reduction process did not redistribute Ru species. Notably, no any

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observable diffraction peaks related to Co-O species have been observed, attributing to
the highly dispersed Co species or low Co contents beyond the detection limit of the
diffractometer (Figure 1a).

Next, Figure 1b showed the FT-IR spectra of the catalysts. It was obvious that ZrP 4 showed the transmission band at 1432 cm⁻¹ corresponded to the bending mode of OH 5 groups. The transmission bands at 1000-1100 cm⁻¹ corresponded to the P-O stretching 6 vibration, and the bands at 1628 cm⁻¹ and 3460 cm⁻¹ were attributed to the OH 7 asymmetric stretching vibration.^[47,48] Besides, the transmission band at 755 cm⁻¹ 8 corresponded to the P-O-P deforming vibration (poly phosphate), indicating the 9 existence of the P-O-P bond in all catalysts. There were two peaks at 525 cm⁻¹ and 2400 10 cm⁻¹, corresponded to (P)-O-H stretching vibration and deformation vibration.^[30] All 11 above peaks were all consistent with characteristic of ZrP. Notably, when the metal 12 species were loaded on the ZrP, the intensity of transmission band at 525 cm⁻¹ was 13 weakened, this phenomenon was caused from a consequent replacement of (P)-O-H 14 protons of ZrP by Co or Ru cations in the course of impregnation.^[49,50] 15

16 H₂-TPR profiles have been carried out to investigate the redox properties of the catalysts. As shown in Figure 1c, the RuO₂/ZrP catalyst presented a main hydrogen 17 consumption peak with a maximum at around 200°C, corresponding to the reduction of 18 RuO_2 to Ru^0 . The CoO_x/ZrP catalyst presented a broad hydrogen consumption peak 19 with a maximum at around 811°C, corresponded to the reduction of CoO_x to Co^{0.[51-53]} 20 The RuO₂-CoO_x/ZrP catalyst presented two hydrogen consumption peaks, and the first 21 (200°C) was related to the reduction of RuO₂, which was the same as that of RuO₂/ZrP. 22 The second peak (811°C) also showed no obvious difference from that of CoO_x/ZrP , 23 arising from the reduction of CoO_x. In the case of RuO₂/CoO_x/ZrP catalyst, two 24 hydrogen consumption peaks, with maximums at 200°C and 729°C can be observed, 25 respectively, the first (200°C) was related to the reduction of RuO₂ and the second 26 (729°C) was attributed to the reduction of CoO_x. It was worth noting that the presence 27 of Ru species caused a dramatic decrease in its reduction temperature on 28 RuO₂/CoO/ZrP catalysts compared to that of CoO_x/ZrP (shifted from 811°C to 729°C), 29

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10.1002/cssc.202001600

1 implying that H_2 can be dissociated on Ru sites, which could facilitate the reduction of 2 CoO_x species on the RuO₂/CoO_x/ZrP catalyst. In addition, H₂-TPR studies indicated 3 that Co species existed in the form of positive valence state under pre-reduction 4 condition (270°C) and the Ru promoting effect on CoO_x reduction might derive from a 5 strong interaction between Ru and Co-O species.

Subsequently, acidic properties of the catalysts were investigated by NH₃-TPD 6 analysis as shown in Figure 1d. The bare ZrP showed three temperature regions around 7 100-200°C, 200-350°C and 350-750°C, respectively. Three regions corresponded to 8 weak acid sites, middle strong acid sites and strong acid sites, respectively.^[54] 9 Ru/CoO/ZrP also exhibited three broad temperature regions, but its acid sites were 10 mainly concentrated in medium strong and strong acid sites. Moreover, the total 11 amounts of acid sites slightly decreased compared with that of bare ZrP due to a 12 consequent replacement of protons of ZrP by metal species during preparation or 13 partially covering of acid sites by metal NPs in line with FT-IR characterization (Figure 14 1b). The similar phenomenon has also been observed in the ZSM-5-supporting metal 15 16 catalysts, where the partial covering of acid sites by metal clusters can result in a decrease of acidity.^[50] Comparatively, Ru-CoO/ZrP showed even a more obvious loss 17 in acidity, which probably was ascribing to much more covering of strong acid sites by 18 two individual metal species introduced by a co-impregnation method in comparison 19 with that of Ru/CoO/ZrP. 20



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Figure 1. (a) XRD patterns of the catalysts; (b) FT-IR spectra of the catalysts; (c) H₂TPR profiles of the calcinated catalysts; (d) NH₃-TPD profiles of the catalysts.

4

The types of acidic sites on the ZrP-based catalysts were then determined by FT-IR 5 spectra of adsorbed pyridine (Figure S3) and the acid densities of all catalysts were also 6 summarized in Table 2. It should be noted that the amount of Brønsted acid sites and 7 Lewis acid sites (PyL) decreased on all catalysts, respectively, when compared to the 8 bare ZrP support (Table 2, entries 1-4), which was in well agreement with the results of 9 FT-IR and NH₃-TPD (Figures 1b and 1d). Pyridine adsorbed FT-IR spectra of the 10 catalysts showed strong bands at 1545 cm⁻¹, which was the characteristic bands of the 11 12 typical pyridinium ion (PyH⁺), confirming the presence of Brønsted acid sites. Notably, the band of the typical pyridinium ion (PyH⁺) of Ru/CoO/ZrP catalyst was much 13 stronger than that of Ru-CoO/ZrP catalyst (Figures S3c and S3d), reflecting that the 14 density of Brønsted acid (PvH⁺) sites of Ru/CoO/ZrP catalyst (198.6 µmol·g⁻¹) was 15 much more than that of Ru-CoO/ZrP catalyst (108.3 µmol·g⁻¹) (Table 2, entries 3 and 16 4). This reveals that Brønsted acid sites were lost more seriously due to the effect of Co 17

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or Ru species in the Ru-CoO/ZrP catalyst, being consistent with the results of its FT-IR 1 and NH₃-TPD (Figures 1b and 1d). Further, the band at 1490 cm⁻¹ could be attributed 2 to the adsorption of pyridine in both Brønsted acid and Lewis acid sites (Figure S3), 3 while the band at 1447 cm⁻¹ was attributed to the adsorbed pyridine only at the Lewis 4 acid sites (PyL). It can be seen that the two catalysts actually showed no great difference 5 in Lewis acidity (Table 2, entries 3 and 4). As such, the results reveal that the stronger 6 7 Brønsted acidity on Ru/CoO/ZrP catalyst can give the better selectivity toward PA in 8 glycerol hydrogenolysis. This is because that Brønsted acid sites are more active and selective than Lewis acid sites for the protonation of the secondary hydroxyl group of 9 the glycerol molecule,^[30] and thus play an more important role in high selective 10 dehydration of glycerol to AE, which is a key intermediate in the production of PA 11 (Table 1, entry 6). 12

The physicochemical properties of the ZrP-based catalysts were listed Table 2. The 13 results illustrated that the incorporation of metal species into ZrP decreased its BET 14 surface areas (Table 2, entries 1-4). Interesting, the BET surface area of the Ru-CoO/ZrP 15 (109 m²·g⁻¹) catalyst is lower than that Ru/CoO/ZrP (142 m²·g⁻¹) even if the same 16 loading amount of metal components (Ru and Co) has been used (Table 2, entries 3 and 17 4). This result indicates that more metal species may block the pores of the ZrP on Ru-18 CoO/ZrP catalyst, attributing to the different distribution or location of Ru species on 19 the surface of the two catalysts. 20

Table 2. Physicochemical properties of the catalysts.						
		SSA	B acid	L acid	B acid/	Total acidity
Entry	Catalysts	$(m^2 \cdot g^{-1})$	$(\mu mol \cdot g^{-1})$	$(\mu mol \cdot g^{-1})$	L acid	(µmol·pyridine·g ⁻¹⁾
1	ZrP	199	259.9	776	0.33	1139.9
2	CoO/ZrP	158	211.2	743.3	0.28	1067.5
3	Ru/CoO/ZrP	142	198.6	722.5	0.27	1020.7
4	Ru-CoO/ZrP	109	108.3	715.6	0.15	923.9
5	Ru/CoO/HZSM-5	268	697	269.7	2.6	966.7

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8	Ru/CoO/ZrP ^[b]	91	164.7	567.9	0.29	732.6	
7	Ru/CoO/ZrP ^[a]	62	46.6	320.6	0.15	367.2	
6	Ru/CoO/ZrO ₂	32	0	1286.5	0	1286.5	

SSA=Specific Surface Area. B acid=Brønsted acid. L acid=Lewis acid. [a] The spent catalyst;[b] The regenerated catalyst.

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2 Characterization of XPS was performed to clarify the chemical state of Ru and Co after reduction. The Co 2p XPS spectra of the CoO/ZrP, Ru/CoO/ZrP and Ru-CoO/ZrP 3 catalysts were characterized and shown in Figure 2. From binding energy of Co 2p XPS 4 on the catalysts, it can be seen that Co species existed all in the form of Co(II).^[55] 5 Especially, the binding energy of the Co $2p_{3/2}$ signal for CoO/ZrP was 782.0 eV (Figure 6 2a), while the binding energy of Co $2p_{3/2}$ for Ru/CoO/ZrP (Figure 2c) shifted by 0.1 eV 7 to 782.1 eV compared with that of CoO/ZrP, which might reflect an electronic transfer 8 from Co-O species to Ru species in the Ru/CoO/ZrP. Conversely, the binding energies 9 of the Co 2p_{3/2} signal for the Ru-CoO/ZrP did not show any change, as compared with 10 that of CoO/ZrP (Figure 2b). This revealed that there was almost no electronic 11 interaction between Ru and Co-O species in the Ru-CoO/ZrP catalyst, where mostly 12 13 possibly Ru and Co-O species existed individually, which were also consistent with that of H₂-TPR characterization. 14





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18 CoO/ZrP; (b) Ru-CoO/ZrP; (c) Ru/CoO/ZrP.



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Figure 3. Ru 3d X-ray photoelectron spectroscopy (XPS) spectrum of the catalysts. (a)
Ru/ZrP; (b) Ru-CoO/ZrP; (c) Ru/CoO/ZrP.

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Ru 3d XPS spectra results were shown in Figure 3. The binding energy of the Ru 5 3d_{5/2} signal for Ru/ZrP was 280.2 eV, which can be assigned to Ru⁰ (Figure 3a).^[56] The 6 binding energy of Ru 3d_{5/2} on Ru/CoO/ZrP (Figure 3c) moved from 280.2 eV to 280.0 7 eV, as compared with that of Ru/ZrP, which indicated a significant electronic transfer 8 from Co-O species to Ru^0 . In contrast, the binding energies of the Ru $3d_{5/2}$ signal on the 9 Ru-CoO/ZrP remained almost the same as that of Ru/ZrP (Figure 3b and 3a). These 10 results suggested that there was no significant electronic transfer between Ru and Co-11 O species, which was in well agreement with that of the Co 2p XPS on the Ru-CoO/ZrP 12 catalyst (Figures 2a and 2b). 13



Figure 4. SEM images of the different catalysts. (a) ZrP; (b) CoO/ZrP; (c) Ru/CoO/ZrP
(Scale bar: 10.0 μm); (d) Ru/CoO/ZrP. (e) Ru-CoO/ZrP; (f) Ru/CoO/ZrP (Spent
catalyst).

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The SEM images of the catalysts were presented in Figure 4. It was observed that 6 7 the surface morphology of ZrP kept untouched after loading metal species (Figures 4ae). The HRTEM images of the Ru/CoO/ZrP and Ru-CoO/ZrP catalysts were shown in 8 Figure 5a and Figure S4a, respectively. It is worth noting that the (100) facet, which is 9 10 experimentally observed to be dominantly exposed, and the lattice spacing of 0.235 nm and 0.214 nm are consistent with the (100) and (002) planes of Ru⁰, respectively.^[35,36] 11 On the basis of the HAADF-STEM image (Figure 5b and Figure S4b), it can be seen 12 that Ru⁰ NPs show the highest Z contrast, and this is further demonstrated by EDS 13 14 elemental maps (Figures 5c-5f and Figures S4c-4f). As for the Ru/CoO/ZrP (Figure 5), HAADF-STEM image and EDS elemental maps demonstrate that Co shows a 15 preferential distribution of Ru in addition to Zr and P. Figures S4b-4f show HAADF-16 STEM image and EDS elemental maps of Ru-CoO/ZrP. In contrast, it is found that the 17 distribution of Co is uniform and basically consistent with that of Zr and P rather than 18 Ru, which indicated that Co (II) is most likely to be strongly bonded with the phosphate 19

group of ZrP through Co-O bonds. Especially, for Ru/CoO/ZrP catalyst, Ru species 1 tend to slightly grow up on the surface of CoO/ZrP in comparison with that of Ru-2 3 CoO/ZrP catalyst, being consistent with results of XRD (Figure 1a). Obviously, the differences in the distribution or location of Ru species on the two catalysts are 4 attributed to the different preparation methods. Based on the results of HAADF-STEM 5 and EDS elemental maps (Figure 5 and Figure S4), it can be seen that Co-O species 6 7 tend to be fine-dispersed on the surface of ZrP on two catalysts but Ru species tended 8 to distributed with Co-O species and formed a close contact between Co-O and Ru species on the Ru/CoO/ZrP catalyst (Figures 5c and 5d). In particular, the close contact 9 might induce mutual interaction, as reflected by the above characterizations of H₂-TPR 10 (Figure 1c) and XPS (Figure 2 and Figure 3). 11

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14 Figure 5. HRTEM image (a) and HAADF-STEM image (b) of Ru/CoO/ZrP; (c-f) are

15 corresponding to the elemental maps of Ru, Co, Zr and P of Ru/CoO/ZrP, respectively.

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To gain a deeper understanding of the involvement of the Ru species during 1 different stages, transmission-mode X-ray absorption spectroscopy was also performed 2 Ru K-edge (22.12 keV). The radial distribution function obtained by Fourier 3 transformation of the k3-weighted EXAFS data of the calcined catalysts were shown in 4 Figure 6a, together with that of Mo foil for comparison (the signal of Mo foil is similar 5 with that of Ru foil). Two major peaks centered at approximately 1.6 Å and 3.2 Å related 6 to the Ru–O and Ru–Ru coordination shells are characteristic for RuO₂, being 7 consistent with the results of XRD (Figure S2c). Apparently, RuO₂ was generated from 8 calcination of the RuCl₃·3H₂O precursor under air. At this step, the different preparation 9 methods did not significantly influence the chemical state of Ru. After being reduced 10 by H₂, however, Ru species of Ru/CoO/ZrP and Ru-CoO/ZrP have shown clear 11 distinctions. As shown in Figure 6b, both Ru samples have one major peak at the same 12 position, respectively. A comparison with Mo foil suggested that the peak can be 13 ascribed to Ru-Ru shell, indicating Ru species in both samples are in metallic state. 14 This was further supported by the X-ray absorption near edge structure (XANES, 15 Figure 6c). The intensity of the absorption edge, often referred to "white line" can 16 reflect the oxidation state of Ru. In contrast to the RuO₂/CoO_x/ZrP and RuO₂-CoO_x/ZrP, 17 Ru/CoO/ZrP and Ru-CoO/ZrP have much weaker "whitle lines", indicating they are 18 indeed reduced by H₂. Nonetheless, the EXAFS peak height of Ru in Ru-CoO/ZrP was 19 much smaller than that of Ru in Ru/CoO/ZrP (Figure 6b). In general, the EXAFS peak 20 intensity is in proportion with the coordination number. The smaller peak indicated 21 lower coordination number of Ru-Ru. In other words, the size of the Ru⁰ NPs in Ru-22 CoO/ZrP have smaller size, which is in line with the results of XRD (Figure 1a), 23 HAADF-STEM and EDS (Figure S4). The surprise is that Co seems to be immune to 24 the oxidative or reductive treatment. At either conditions, Co has similar coordination 25 environment (Figure 6d). All Co samples have a similar EXAFS peak centered at ca. 26 1.5 Å, indicating Co is bonded with O atoms. Considering the stability and highly 27 dispersed of such Co species (Figure 1, Figure 5 and Figure S4), it is likely that Co (II) 28 was bonded with the phosphate group of ZrP through Co-O bonds, being consistent 29

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- 1 with the characterizations of FT-IR, XRD and EDS.
- 2





Figure 6. (a, b) k3-weighted Fourier-transformed EXAFS of different catalysts; (c) Ru
K-edge XANES spectra of different catalysts; (d) k3-weighted Fourier-transformed
EXAFS of Co.

7

On the basis of both the activity evaluation (Table 1, entries 2-6) and catalyst 8 characterizations above, it can be concluded that Ru⁰ NPs and Co (II) species showed 9 almost no interaction with each other over Ru-CoO/ZrP catalyst prepared by the co-10 impregnation method. Conversely, Ru/CoO/ZrP catalyst where the Co species were first 11 12 impregnated, and subsequently Ru particles tended to be distributed with the dispersed Co-O species to form a close contact (Figure 5). As such, there existed strong interaction 13 between Co-O species and Ru⁰ NPs as confirmed by H₂-TPR and XPS spectra. 14 Obviously, it can be seen that the product distribution for the hydrogenolysis of glycerol 15 is strongly dependent on the compositions and metal location on the surface of catalysts 16 (Table 1). The highly selective hydrogenolysis of glycerol into PA on Ru/CoO/ZrP 17 catalyst can be unambiguously attributed to the strong Brønsted acidity and a close 18 contact between Co-O species and Ru⁰ NPs. 19

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2 **3.3 Structure-activity correlation.**

In order to get a deep insight into the crucial role of Co-O species and Ru⁰ NPs in 3 catalyzing the selective hydrogenolysis on Ru/CoO/ZrP catalyst, a physically mixed 4 catalyst (Ru/ZrP+CoO/ZrP) was employed for the hydrogenolysis of glycerol under the 5 same reaction conditions (Table 1, entry 8). Nevertheless, the product selectivities on 6 the mixed catalysts were actually similar to that of Ru-CoO/ZrP (Table 1, entry 5), 7 8 although the conversion slightly increased up to 93%. These results demonstrated that no positive cooperative interaction between Co-O species and Ru⁰ NPs on Ru-CoO/ZrP 9 catalyst (Table 1, entries 3, 5 and 8). The lower conversion of glycerol on Ru-CoO/ZrP 10 catalyst can be attributed to weaker Brønsted acidity, which did not favor the 11 dehydration of glycerol to AE (Table 2, entry 3). The positive cooperative interaction 12 was the primary reason that the Ru/CoO/ZrP catalyst offered both the excellent activity 13 and selectivity to PA in glycerol hydrogenolysis. It should be noting that only a small 14 amount of gaseous products such as CO₂, CO, CH₄ and propane was detected by GC 15 with TCD over the present catalyst, CO₂ and CH₄ are the major by-products, which 16 could be formed via the C-C cleavage of the intermediates and products. This was 17 attributed to the unique acidity of the present ZrP-based catalyst only capable of 18 selective dehydration of glycerol to AE according to our previous report,^[30] and then 19 20 selective hydrogenation of C=C bonds of AE molecules afforded PA on Ru/CoO/ZrP catalyst. 21

To clarify further the role of the ZrP in the catalytic hydrogenolysis of glycerol, 22 different supports have also been employed and their catalytic performances have been 23 24 given in Table S2. It can be seen that both Ru/CoO/HZSM-5 and Ru/CoO/ZrO2 catalysts displayed full conversion of glycerol (Table S2, entries 1 and 2), but the 25 distribution of main product was quite different. The Ru/CoO/HZSM-5 catalyst gave 26 only 62.5% selectivity to PA while Ru/CoO/ZrO₂ catalyst did not afford PA but 1,2-PDO 27 (48.5% selectivity) (Table S2, entries 1 vs 2). The reason for the difference on two 28 catalysts was attributed to different acid sites (Figures S5a-5c). The Ru/CoO/HZSM-5 29

catalyst showed too high density of Brønsted acid (Table 2, entry 5), and thus it caused 1 side-reactions such as coking and cracking and fast deactivation of the catalyst. 2 Conversely, Ru/CoO/ZrO₂ catalyst had large amount of Lewis acid sites (1286.5 3 μ mol·g⁻¹) but contained almost no Brønsted acid sites (Table 2, entry 6). Thus the 4 dominant Lewis acid sites were responsible for the protonation of the primary -OH of 5 glycerol, followed by the subsequent dehydration of glycerol to produce HA, and 6 thereafter HA was hydrogenated into 1,2-PDO (Table S2, entry 2).[46,51,57,58] 7 8 Comparatively, ZrP has appropriate acid sites and it has been proved to be highly efficient for the dehydration of glycerol into AE (in 79% selectivity). Subsequently, the 9 C=C bond of AE was hydrogenated on the active sites modulating by a close contact 10 between Ru⁰ NPs and Co-O species on the catalyst. 11

The reaction conditions were also screened in detailed including the effects of 12 temperature, hydrogen pressure, feed flow rate and gas flow rate on glycerol 13 hydrogenolysis. As shown in Figure S6a, it can be seen that the conversion of glycerol 14 increased from 45.2% to 100% as temperature increased from 210°C to 270°C. While, 15 16 the selectivity to PA increased to a maximum at 270°C and then slowly decreased under higher temperature. Meantime, the selectivity to the by-product (1-PO) increased 17 slightly, indicating that PA would be hydrogenated fully into 1-PO under higher reaction 18 temperature. This can be further evidenced by the fact that when PA was used as a feed 19 and hydrogenated by Ru/CoO/ZrP catalyst, although the reactivity of PA is quite low 20 on the present catalyst, 1-PO was formed as a sole product (Table S1, entry 3). Besides, 21 the low reactivity of PA was the important reason that the present Ru/CoO/ZrP catalyst 22 afforded the excellent selectivity to PA. 23

Figure S6b showed the effect of hydrogen pressure on the catalytic performance of glycerol hydrogenolysis over Ru/CoO/ZrP catalyst. The selectivity of PA enhanced from 25.3% to 80.2% while the selectivity of AE decreased sharply from 64.5% to 3.7% as the hydrogen pressure increased from 5 bar to 20 bar, indicating that PA mainly resulted from the AE hydrogenation and increasing hydrogen pressure facilitated the formation of PA. This implied that Ru/CoO/ZrP was highly selective for the hydrogenation of AE into PA at an appropriate high hydrogen pressure. Moreover, when
AE was used as a feed and hydrogenated by Ru/CoO/ZrP catalyst, the conversion of
AE was 91% and the selectivity to PA reached up to 96% (Table S1, entry 2), which
was a very strong evidence that PA mainly resulted from the highly selective
hydrogenation of AE over the catalyst.

Sequentially, the effects of feed flow rate on the catalytic performance for glycerol 6 hydrogenolysis over the catalyst were shown in Figure S6c. It can be seen that the 7 conversion of glycerol decreased with feed flow rate increased (1.2 mL/h-6.0 mL/h). 8 Meantime, the selectivity of PA reached a maximum at the feed flow rate of 2.4 mL/h 9 but decreased sharply when the feed flow rate increased from 2.4 mL/h to 6.0 mL/h, 10 accompanying with the AE selectivity significantly increased from 3.7% to 45.5%, 11 which also suggested strongly that PA was produced via the selective hydrogenation of 12 AE. Figure S6d showed that the glycerol conversion decreased obviously as the gas 13 flow rate increased. The selectivity of PA achieved a maximum at the gas flow rate of 14 30 ml/min and slowly decreased as the gas flow rate increased. The lower glycerol 15 16 conversion and selectivity of PA resulted from short contact time of substrate and catalyst as the feed flow rate or gas flow rate further increased. 17

18

3.4 Identification of active sites for AE hydrogenation via DFT calculations

20 Model and computational details were given in the Supplementary Note 1. The experimental characterization from XRD, EXAFS, STEM and EDS elemental maps 21 22 indicated that only the highly dispersed Co-O species was observed on Ru/CoO/ZrP catalysts due to very strong interaction between Co-O species with ZrP. To mimic the 23 local configuration exposed by Co-O species, the most stable surface of crystalline CoO 24 oxide, (100), was used as a model, which was constructed with a large $p(3\times3)$ periodic 25 slab containing four atomic layers of CoO-units. For Ru catalyst, the (100) facet, which 26 was experimentally observed to be dominantly exposed, was calculated with a $p(4 \times 2)$ 27 28 supercell with four Ru atomic layers. To shed light on the origin of selective hydrogenation of the intermediate AE over Ru/CoO/ZrP catalyst and identifying the 29

active site, we performed the first-principles DFT calculations to investigate the 1 adsorption behaviors of AE on CoO(100) and Ru(100), considering that the adsorption 2 3 is generally the preliminary step triggering the subsequent hydrogenation reaction. Firstly, various possible adsorption configurations with the C=C or C=O bond serving 4 as the anchoring site were examined on CoO(100), and the located stable ones were 5 6 shown in Figures 7a-7d. One can see that AE preferentially to adsorb on a coordinatively unsaturated Co site (Co_{cus}) via its C=C bond in a π -bond adsorption 7 configuration (Figure 7b), corresponding to an adsorption energy of -0.97 eV. In 8 9 contrast, the adsorption of AE on Co_{cus} site involving its O-end (see Figures 7c and 7d) 10 are weak with an adsorption energy of -0.82 and -0.67 eV, respectively. Therefore, such 11 a selective adsorption of AE on CoO(100) could lead to its preferential hydrogenation at the C=C bond (Table 1, entries 3 and 6). Actually, it was expected that the highly 12 13 dispersed Co-O species might adsorb more strongly the C=C bond of AE on a highly 14 coordinatively unsaturated Co (Cocus) site.



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Figure 7. (a-d) Four possible configurations of adsorption of AE on CoO(100). (e-h)
Four possible configurations of adsorption of AE on Ru(100). The white, red, grey, blue
and green balls represent H, O, C, Co and Ru, respectively. The value at the top right
of each configuration is the corresponding adsorption energy, all energies are in eV.

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6 Secondly, we also explored the adsorption configurations and energies of AE on Ru(100) surface, and Figures 7e-7h show the relatively stable and representative 7 adsorption configurations. It was found that the C=C and C=O bonds of AE tends to 8 9 collectively adsorb at the Ru(100) step, giving an adsorption energy as large as -2.63 eV; such an unselective adsorption mode would inherently give rise to the low 10 selectivity of AE hydrogenation on Ru catalyst (Table 1, entries 3, 5 and 8). It is worth 11 noting that, Ru(100) surface shows a very strong adsorption ability toward AE in 12 comparison with that on CoO(100), and such a strong AE adsorption could lead to a 13 limited activity for its subsequent hydrogenation. Specifically, we identified further the 14 transition states of AE hydrogenation on Ru(100), as shown in Figure S7, and one can 15 16 see that the activation energies are as high as ~1.2 eV through either the C-terminal pathway or the O-terminal pathway, indicating a kinetic obstacle in AE hydrogenation 17 on Ru(100). Overall, these computational results support that the selective 18 hydrogenation of AE could be accomplished on the CoO(100) active site rather than 19 Ru(100). 20

Based on the characterizations and DFT calculations, the possible reaction 21 pathway involved in glycerol hydrogenolysis has been proposed in Scheme 1. The 22 preferential Brønsted acid-catalyzed dehydration of glycerol over the ZrP initially 23 24 formed AE as a main intermediate product and HA as a minor by-product. On one hand, the high catalytic activity for the C=C bond hydrogenation of AE can be tentatively 25 attributed to an exclusive binding of C=C bonds to fine Co-O species, which also 26 endowed Ru⁰ sites with high electronic density through charge transfer (Figures 2 and 27 3). It has been known that as the homolytic dissociation of H_2 normally requires the 28 denotation of d-electrons of metal to H₂, and therefore a high electron density of the 29

Ru⁰ sites is beneficial for the H₂ dissociation.^[59] The dissociated hydrogen atoms could 1 diffuse into the adjacent unsaturated Co sites and facilitate hydrogenation reaction. It 2 has been reported that the selective hydrogenation of C=C bonds could be improved by 3 the metal-support/promoter interaction to modulate the electronic properties of metal 4 active site.^[60-63] On the other hand, the hydrogenation of the C=C double bond is more 5 thermodynamically favorable and also generally a C=C bond hydrogenates more easily 6 and quickly than a C=O one, which in turn leads to an increase in the hydrogenation 7 8 selectivity for the C=C bond.

It is worth noting that the selectivity of HA is very low for dehydration of glycerol 9 (Table 1, entry 1), and also the catalytic activities for PA and HA hydrogenation are also 10 poor over Ru/CoO/ZrP catalyst (Table S1, entries 3 and 4), indicating that the pathway 11 (gray drawing) forming PA via 1,2-PDO dehydration is highly improbable, and the poor 12 reactivity of PA endows the excellent selectivity to PA over the present catalyst. 13 Interestingly, 1-PO could undergo dehydrogenation reaction to give PA even in high 14 pressure H₂ (Table S1, entry 5), revealing that the pathway forming PA arisen from 1-15 16 PO dehydrogenation cannot be excluded in glycerol hydrogenolysis. Meantime, the processes such as dehydration of glycerol and subsequent hydrogenation would 17 generate minor gas by-products including CO₂, CO, CH₄ and propane. 18

19



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21 Scheme 1. Reaction pathway of glycerol hydrogenolysis over Ru/CoO/ZrP catalyst.

22

3.5 Long-term performance and Recyclability of the Catalyst.

In the next step, Ru/CoO/ZrP has been evaluated for long-term performance of the glycerol hydrogenolysis, conducted at 270°C, 20 bar H₂ and the results were shown in Figure 8. The activity of the catalyst did not decline within 50 h under the present

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reaction conditions. Meanwhile, the distribution of the products did not show any 1 appreciable changes during the whole test. It can be seen that the surface morphology 2 of the spent Ru/CoO/ZrP catalyst did not show obviously change in comparison with 3 the fresh one (Figures 4d vs 4f), indicating that the ZrP-based catalyst is a water-tolerant 4 and thermally stable. As a result, this catalyst demonstrated attractive applications for 5 the hydrogenolysis of glycerol even under hydrothermal conditions. Particularly, after 6 7 the spent catalyst was regenerated by calcining at 500°C for 4 h in air, followed by 8 reducing in situ at 270°C for 1 h, it was then reused for another 40 h in continuous-flow process. After regeneration, the conversion of glycerol decreased from 100% to 95%, 9 and the selectivity to PA decreased slightly (around 78%). 10

11



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Figure 8. The long-term performance of glycerol hydrogenolysis over Ru/CoO/ZrP
catalyst. (■) glycerol conversion; (●) PA selectivity; (▼) HA selectivity; (▲) AE
selectivity. Reaction conditions: 2 MPa H₂ pressure; gas flow rate 30 mL/min; 270°C;
10 wt.% glycerol solution; feed speed: 0.04 mL/min; 1.0 g Ru/CoO/ZrP catalyst.

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Next, the spent Ru/CoO/ZrP catalyst after the first run (TOS=70 h) was further characterized in order to figure out the deactivation reason of the present catalyst. As shown in Table 2, the BET surface area of the spent Ru/CoO/ZrP catalyst sharply decreased from 142 m²·g⁻¹ to 62 m²·g⁻¹, as compared with the fresh one (Table 2, entries 3 vs 7), which revealed the catalyst deactivated probably due to the carbonaceous deposits on surface of the spent catalyst. Thus TGA was performed from 50°C to 800°C

and the results of TGA were shown in Figure S8. The fresh Ru/CoO/ZrP catalyst 1 showed a fast weight loss from 50°C to 200°C due to the continuous dehydration, and 2 a wide platform from 200°C to 800°C indicated that the catalyst has a good thermal 3 stability. Comparatively, the spent Ru/CoO/ZrP catalyst showed an obvious weight loss 4 around 350-520°C due to coking removal, besides a weight loss resulting from the 5 dehydration. Additionally, the BET surface area of the regenerated Ru/CoO/ZrP catalyst 6 increased from 62 m²·g⁻¹ to 91 m²·g⁻¹, as compared with the spent one (Table 2, entries 7 7 and 8). These results indicated that the carbon deposition indeed occurred in the 8 continuous reaction and can be removed by calcinations in air, which promised 9 generating for a long-lasting catalytic activity. Sequentially, the various carbon deposits 10 of the spent catalyst were proved by Raman spectroscopy and the result was shown in 11 Figure S9. The spent catalyst spectra showed two major peaks around 1346 cm⁻¹ and 12 1573 cm⁻¹. The peak at 1573 cm⁻¹ represented graphitic, designated as G-band and the 13 peak at 1346 cm⁻¹ was attributed to defects present in the structural units of graphite 14 named as D-band. 15

16 To identify further the reason for the deactivation of catalyst, the acid sites of the spent Ru/CoO/ZrP catalyst were determined, which indicated that the acid sites have 17 been blocked by the carbonaceous deposits (Table 2, entries 3 and 7). This might be one 18 of critical reasons why the catalyst deactivated gradually after TOS was longer than 50h 19 (Figure 8, left). Nevertheless, it can be seen that the acid amounts of the regenerated 20 Ru/CoO/ZrP catalyst increased obviously by calcination at 500°C for 4 h, as compared 21 with that of the spent Ru/CoO/ZrP (Table 2, entries 7 vs 8). This was also confirmed by 22 the pyridine adsorbed FT-IR spectra of the spent Ru/CoO/ZrP. As shown in Figures S3e 23 24 and S3f, after regeneration, most of Brønsted acid (82.9%) and Lewis acid (78.6%) sites can be recovered (Table 2, entries 3 vs 8) by the removal of carbonaceous deposits 25 blocking the active sites in long-term performance of glycerol hydrogenolysis (Figure 26 8, right). On the other hand, the carbonaceous deposits might also have a detrimental 27 effect on metal sites, which was reflected by lower selectivity to PA but an increasing 28 selectivity to AE as TOS was longer than 50 h (Figure 8). 29

1 4. Conclusion

This work demonstrated that Ru/CoO/ZrP catalyst can be employed for glycerol 2 hydrogenolysis and exhibited a superior selectivity to PA (80.2%) at full of glycerol 3 conversion. The studies indicated that Brønsted acid sites on ZrP can catalyze the 4 selective dehydration of glycerol into AE and Ru⁰ sites and the fine-dispersed Co-O 5 species on Ru/CoO/ZrP catalyst played a cooperative role in promoting the selective 6 hydrogenation of the conjugated C=C bond of AE into PA. The characterization and 7 8 DFT calculations demonstrated that Co-O species not only can adsorb more strongly the C=C bond of the intermediate AE on a highly coordinatively unsaturated Co (Co_{cus}) 9 site, causing the preferential hydrogenation at the C=C bond of AE, but also endowed 10 Ru⁰ sites with high electronic density through charge transfer. The electron-rich Ru⁰ 11 sites enabled to dissociate active hydrogen which moved to the adjacent Co-O sites, 12 enhancing catalytic activity and selectivity in glycerol hydrogenolysis. Notably, the 13 present catalyst showed at least a 50 h long-term performance and then could be 14 regenerated for reuse only by calcining in air to remove carbonaceous deposits. The 15 16 present strategy to develop an effective and green process for hydrogenolysis of glycerol to PA might provide guidance for the catalyst structural design in sustainable 17 production of valuable chemicals from glycerol. 18

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20 Acknowledgements

The authors are grateful for support from the National Natural Science Foundation of China (21773061, 21978095), the innovation Program of Shanghai Municipal Education Commission (15ZZ031). S. D. acknowledges the support by Shanghai Rising-star Program (20QA1402400). Additional support was provided by Feringa Nobel Prize Scientist Joint Research Center.

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The zirconium phosphate-supported Ru and Co bimetallic catalyst was developed for
glycerol hydrogenolysis and exhibited a superior selectivity to propanal (80.2%) at full
of glycerol conversion. The present catalyst also showed high stability in long-term
performance and could be regenerated by removal of carbonaceous deposits.