Supporting Information

Catalytic cascade conversion of furfural to 1,4-pentanediol in a single reactor

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Experimental Section

Chemical. Furfural, furfuryl alcohol and 3-Acetyl-1-propanol were purchased from Aladdin. γ-valerolactone and 1,4-pentanediol were purchased from Sigma-Aldrich. Levulinic acid was purchased from Acros Organic. Deionized water was homemade by a Millipore Autopure system. All reagents were used without further purification. Helium (99.99%), hydrogen (99.99%) and carbon dioxide (99.99%) were purchased from Dalian Special Gases Company.

Catalyst preparation.

1) CMK-3: CMK-3 support was synthesized by a nanocasting method. In detail, 12.0 g of furfuryl alcohol (90 wt%) and 1.2 g of oxalic acid were dissolved in 30.0 g of ethanol.

The solution was then infiltrated into 12.0 g of SBA-15 by incipient wetness impregnation at room temperature, followed by heating in water bath at 40 ^oC for 8 hours to evaporate the ethanol. The resultant solid was then dried at 80 ^oC for 8 h in air and heated at 350 ^oC in N_2 for 4 h. The above infiltration, drying and calcination procedure was repeated twice. Afterwards, the solid was submitted to N_2 atmosphere at 900 ^oC for 4 h for carbonization, followed with treatment with HF acid (4 wt%) for 24 h to remove the silica framework. The resultant mesoporous carbon was washed completely with water and dried at 80 ^oC overnight.

The procedure to synthesize the microporous carbon is the same as in method CMK-3 support except that SBA-15 was not added. In detail, 12.0 g of furfuryl alcohol (90 wt%) and 1.2 g of oxalic acid were dissolved in 30.0 g of ethanol. The solution was followed by heating in water bath at 40 ^oC for 8 hours to evaporate the ethanol. The resultant solid was then dried at 80 ^oC for 8 h in air and heated at 900 ^oC in N_2 for 4 h.

2) Ru/CMK-3 was prepared by an impregnation method. Typically, 1 g of CMK-3 was placed in a round-bottom flask. 15 ml of $RuCl_3$ solution with appropriate Ru containing was added quickly to the flask and the mixture was then subjected to a rotary evaporator to evaporate the solution at 50 ^oC under vacuum for 2 h. The recovered sample was heated at 300 ^oC for 3 h under N_2 flow with a flowrate of 20 $ml \cdot min^{-1}$, and denoted as Ru/CMK-3. Before reaction the Ru/CMK-3 was further subjected to a temperature programmed reduction (TPR) treatment under 10% H_2/He gas from ambient temperature to 200 and 400 °C with a heating rate of 10 ^oC min^{-1}, and denoted as

Ru/CMK-3-R200 and Ru/CMK-3-R400, respectively. The procedure to prepare Ru/C is the same as in method Ru/CMK-3.

Catalytic performance evaluation. All the reactions were conducted in a 50 mL Parr batch reactor. In a typical experiment, 30 mg Ru/CMK-3 was added to a mixture of H_2O (5 mL) and furfural (100 mg, 1.04 mmol) to make a metal/substrate ratio of 0.57 mol%. This solution was placed inside the autoclave and was flushed with H_2 for several times. Next, the autoclave was pressurized with H_2 to 10 bar and then CO_2 was added up to a total pressure of 40 bar. The reaction mixture was stirred and heated to 80 ^{o}C for 20 h (including the time to heat the reactor). After reaction, the autoclave was cooled down to room temperature, vented, and opened. A syringe filter was used to remove the catalyst from the reaction mixture, and the recovered solution was then analyzed by gas chromatography (GC), with *n*-butanol as the internal standard, on Agilent 7890B equipped with an FID detector (270 ^{o}C) and an HP-INNOWAX column (30 m x 0.32 mm, 0.5 μm).

Note: In the present work, we did not attempt to isolate 1,4-PD, mostly because experiments were conducted on a milligram scale. Because we are using water as a solvent, one may envisage (after up-scaling to the gram scale) first the removal of the catalyst by filtration followed by distillation of water which has a lower boiling point than 1,4-PD. According to this strategy, a technical grade 1,4-PD should be obtained using the conditions reported in the entry 4 of table 1.

Characterization techniques. The actual Ru loadings of various catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

X-ray diffraction (XRD) patterns were collected at a PW3040/60 X' Pert PRO (PANalytical) diffractometer equipped with a copper target (Cu Kα, $\lambda = 0.15432$ nm), operating at 40 kV and 40 mA. A continuous mode was used for data collecting in the 2θ range from 5° to 80° at a scanning speed of 10° min^{-1}.

The acidities of Ru/CMK-3 catalysts used in this work were characterized by the NH_3-TPD which was carried out with a Micromeritics AutoChem II2920. Before each test, 0.1 g sample was placed in a quartz reactor, pretreated in He flow at 473 K or in 10%H_2/He flow at 473 K and 673 K and cooled down in He flow to 373 K. After the saturated adsorption NH_3, the sample was heated at 373 K in He for 45 min to remove the physically adsorbed NH_3. Desorption of NH_3 was conducted in He flow from 373 K to 1073 K at a heating rate of 10 K min^{-1}. The desorbed NH_3 molecules were detected by a mass spectrometry (MS) OminiStar equipped with the software quadstar 32-bit. In the measurement, m/e =16 was monitored to analyze the desorbed NH_3 to avoid the interference of water.

High-angel annual dark-field scan transmission electron microscopy (HAADF-STEM) analyses were performed with a JEOL JEM-2100F microscope operated at 200 kV. And the abreaction-corrected HAADF-STEM images were obtained on a JEM ARM microscope. For all microscopy analysis the samples were ultrasonically dispersed in ethanol and then a drop of the solution was put onto microgrid carbon polymer supported on copper grid.

The synchrotron radiation experiment was performed at the BL14B1 of Japan Atomic Energy Agency/Super Photon ring-8 (JAEA/SPring-8). The pretreatment conditions of in situ X-ray adsorption near edge structure (XANES) measurement was 10%H_2/He reduction at 200 ^{o}C and 400 ^{o}C, respectively, for 20 min.

Table S1. Catalytic performance of different catalysts for the conversion furfural to pentanediol

Entry	**catalyst**	**Temp (°C)**	**$P(H_2)$ (MPa)**	**Solvent**	**Conv. (%)**	**1.4-PD Yield(%)**	**1.2-PD Yield(%)**	**1.5-PD Yield(%)**	**Ref**
1	Ru/CMK-3	80	1	H_2O	>99	90	--	--	This work
2	Pt/HT	150	3	2-PrOH	>99	--	73	8	Ref 1
3	Cu/LDO	140	6	EtOH	>99	--	51.2	28.8	Ref 2
4	Pt/CeO_2	170	1	H_2O	>99	--	65	8	Ref 3
5	Pt/Co_2AlO_4	140	1.5	2-PrOH	>99	--	16.2	34.9	Ref 4
6	$Pd\text{-}Ir\text{-}ReO_x/SiO_2$	100	6	H_2O	>99	5.8	1.4	71.4	Ref 5
7	$Rh\text{-}Ir\text{-}ReO_x/SiO_2$	100	8	H_2O	>99	3.4	0.5	71.1	Ref 6

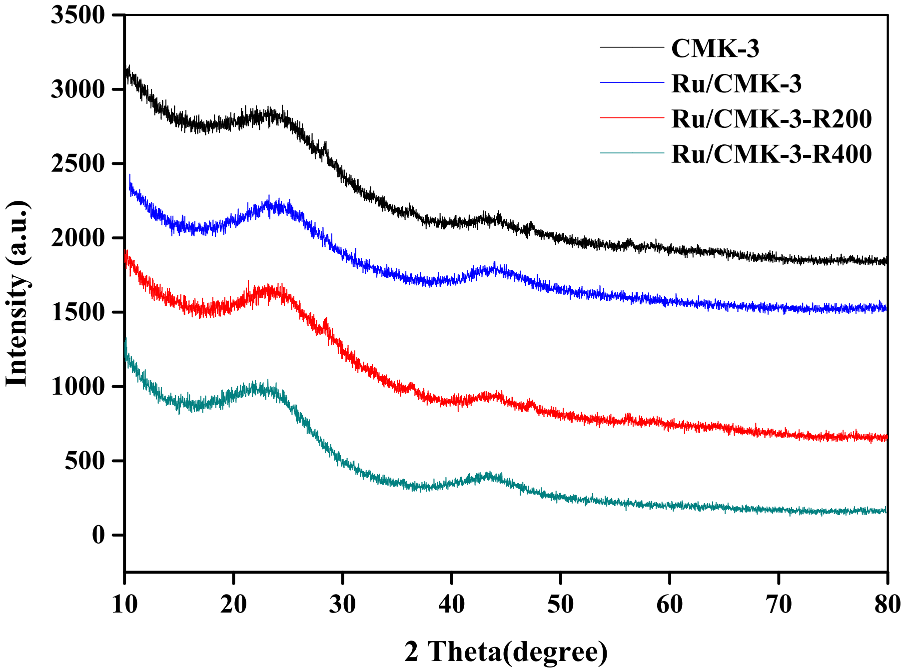


Figure S1: XRD patterns of CMK-3, Ru/CMK-3, Ru/CMK-3-R200 and Ru/CMK-3-R400.

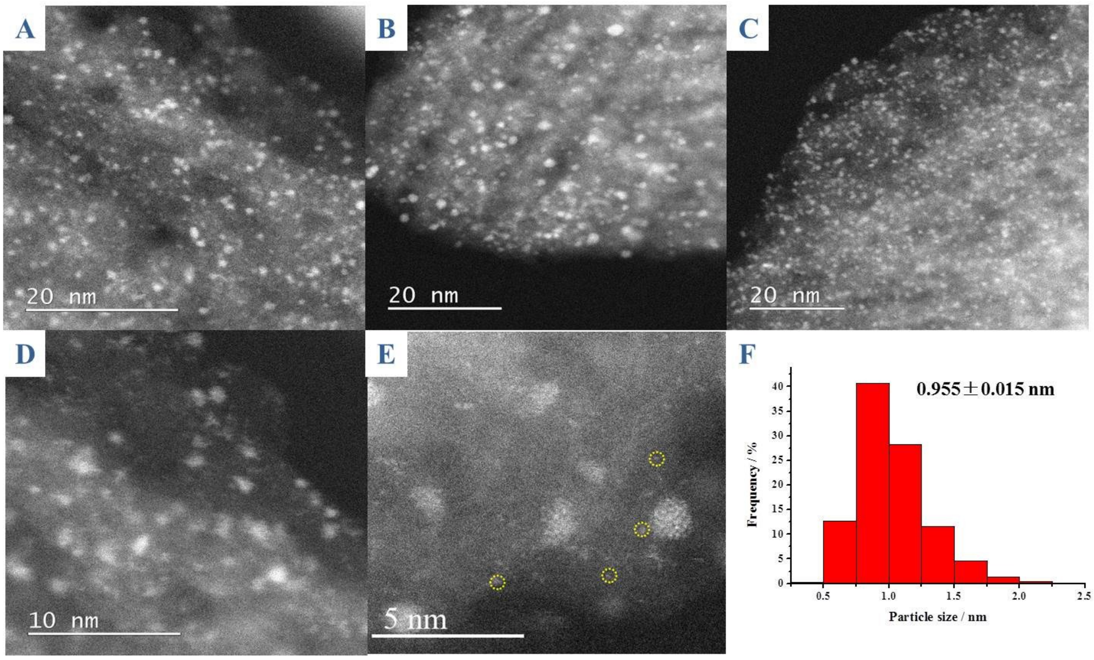


Figure S2: HAADF-STEM images of Ru/CMK-3-R200 (A-E) and the corresponding size distribution (F).

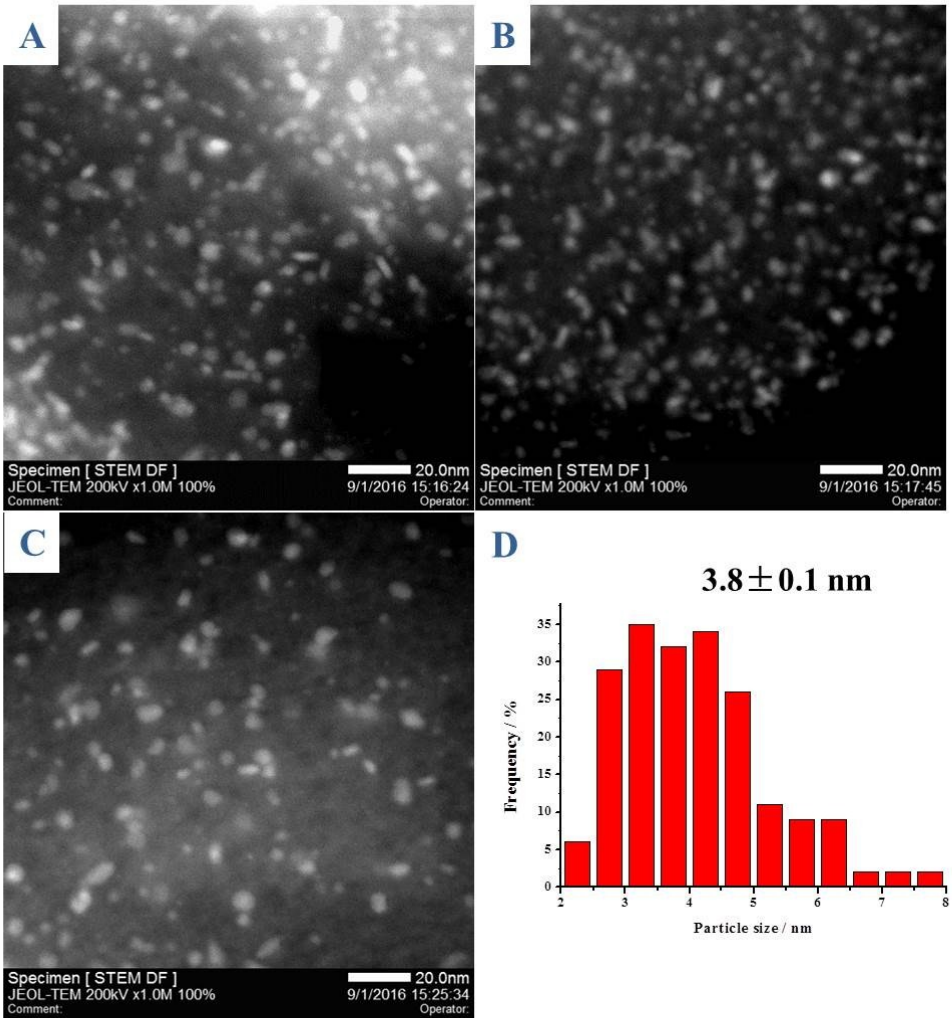


Figure S3: Typical HAADF-STEM images of Ru/CMK-3-R400 (A-C) and the corresponding size distribution (D).

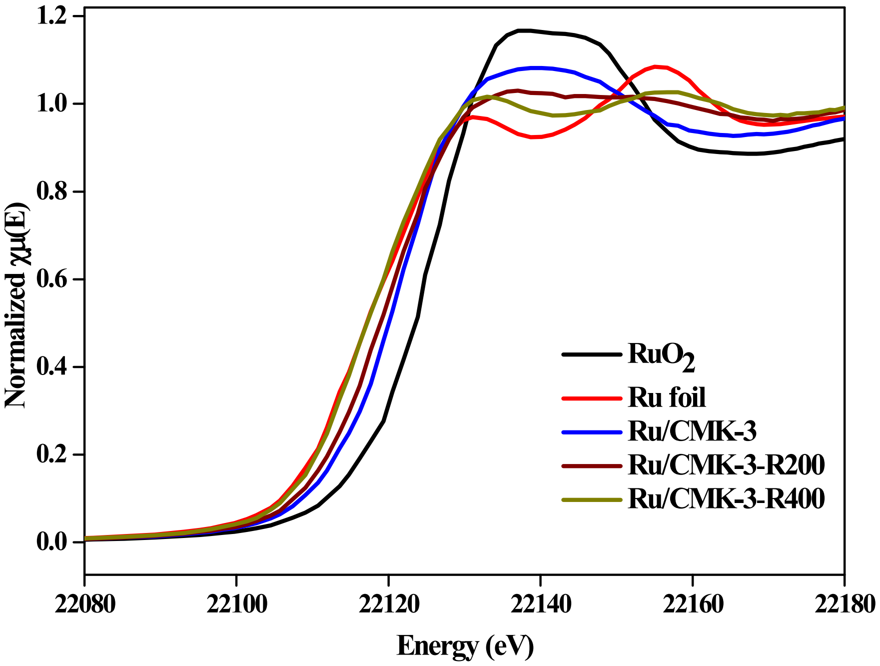


Figure S4: In situ XANES spectra of Ru/CMK-3-unred, Ru/CMK-3-R200 and Ru/CMK-3-R400 compared with RuO_2 and Ru foil.

Table S2. EXAFS data fitting results of Ru/CMK-3 samples

Sample	Shell	N	R(Å)	ΔE_0 (eV)	$\Delta\delta^2$(Å^2)
Ru foil	Ru-Ru	12	2.67		
RuO_2	Ru-O	6	1.97		
$RuCl_3$	Ru-Cl	6	2.38		
Ru/CMK-3-unred	Ru-Ru	1.5	2.73	5.5	0.011
	Ru-Cl	2	2.34	-8	0.007
	Ru-O	3.1	2	6.2	0.007
Ru/CMK-3-R200	Ru-Ru	6.6	2.67	3.2	0.012
	Ru-Cl	2.3	2.38	3.2	0.018
Ru/CMK-3-R400	Ru-Ru	10.2	2.63	-6.5	0.014

Table S3. Acid concentrations of Ru/CMK-3 catalysts

Catalyst	**Amount of acid sites(μmol/g)**[a]
Ru/CMK3-R400	205
Ru/CMK3-R200	425
Ru/CMK3-unred	271
CMK3	61
Ru/C	91

[a] Total acid concentrations were determined by the microcalorimetric measurements of ammonia adsorption.

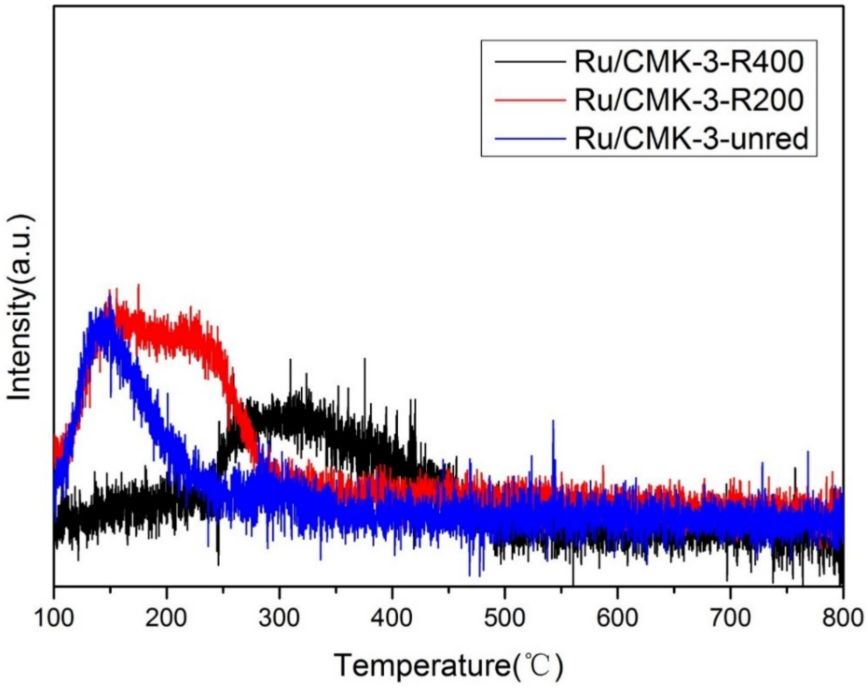


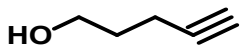
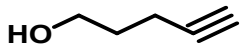
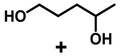
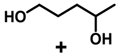
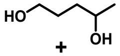
Figure S5: NH_3-TPD profiles of Ru/CMK-3 catalyst

Table S4. Comparison of the present work with literature reports for the synthesis of 1,4-PD

Entry	**Reactant**	**Catalyst**	**Temp (^{o}C)**	**$P_{(H_2)}$ (MPa)**	**Solvent**	**Conv. (%)**	**1.4-PD Yield(%)**	**Ref**
1	Furfural	Ru/CMK-3	80	1	H_2O	>99	90	This work
2	LA	Ru-Re/C	140	15	H_2O	>99	82	Ref 7
3	LA	Pt-Mo/HAP	130	5	H_2O	>99	93	Ref 8
4[a]	LA	$Rh-MoO_x/SiO_2$	80	6	H_2O	>99	70	Ref 9
5	GVL	Cu/ZrO_2	200	6	EtOH	97	96	Ref 10

a: fixed-bed reaction.

Table S5. Synthesis of 3-AP via several processes

Entry	**Reactant**	**Catalyst**	**Additive**	**Temp (^{o}C)**	**$P_{(H_2)}$ (MPa)**	**Solvent**	**3-AP Yield(%)**	**Ref**
1	Furfural	Ru/CMK-3	--	60	1	H_2O	84	This work
3	LA	*Pyrococcus furiosus*	sodium phosphate buffer	40	0.5	H_2O	51	Ref 11
2		NHC-Au-OTf	NBu_4OTf	50	--	H_2O	>99	Ref 12
3		$Na[PtCl_2(dmso)(NHC)]$	--	80	--	H_2O	>99	Ref 13
4	 + H_2O_2	tris(cety1-pyridinium) 12-tungstophosphate	--	reflux	--	tBuOH	60	Ref 14
5	 + H_2O_2	$(\eta^5\text{-}Ph_4C_4COH)(CO)_2RuCl$	$NaCO_3$	90	--	$CHCl_3$	50	Ref 15
6	 + H_2O_2	$Na_4H_3[SiW_9Al_3(H_2O)_3O_{37}]12H_2O$	--	90	--	H_2O	62	Ref 16

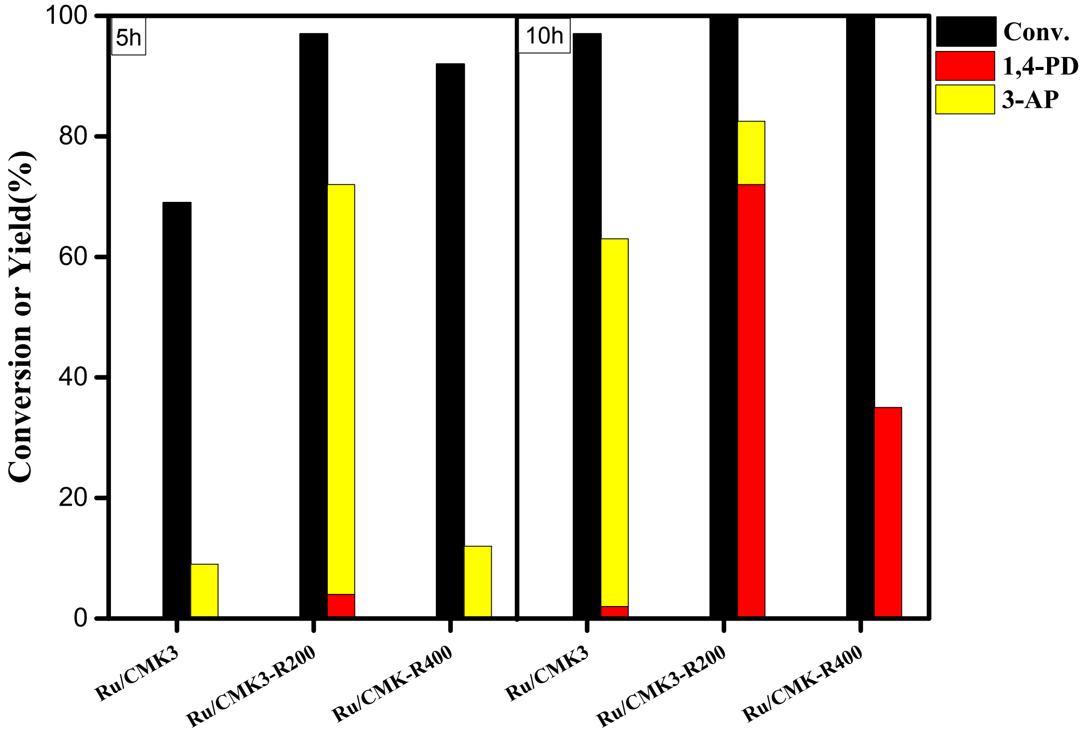


Figure S6: The time-course plot for the conversion of Furfural on various Ru/CMK-3 catalysts. Reaction conditions: T: 353 K, 3MPa CO_2 and 1MPa H_2 (at room temperature), 2 wt% furfural in H_2O, and a metal/substrate ratio of 0.57 mol%.

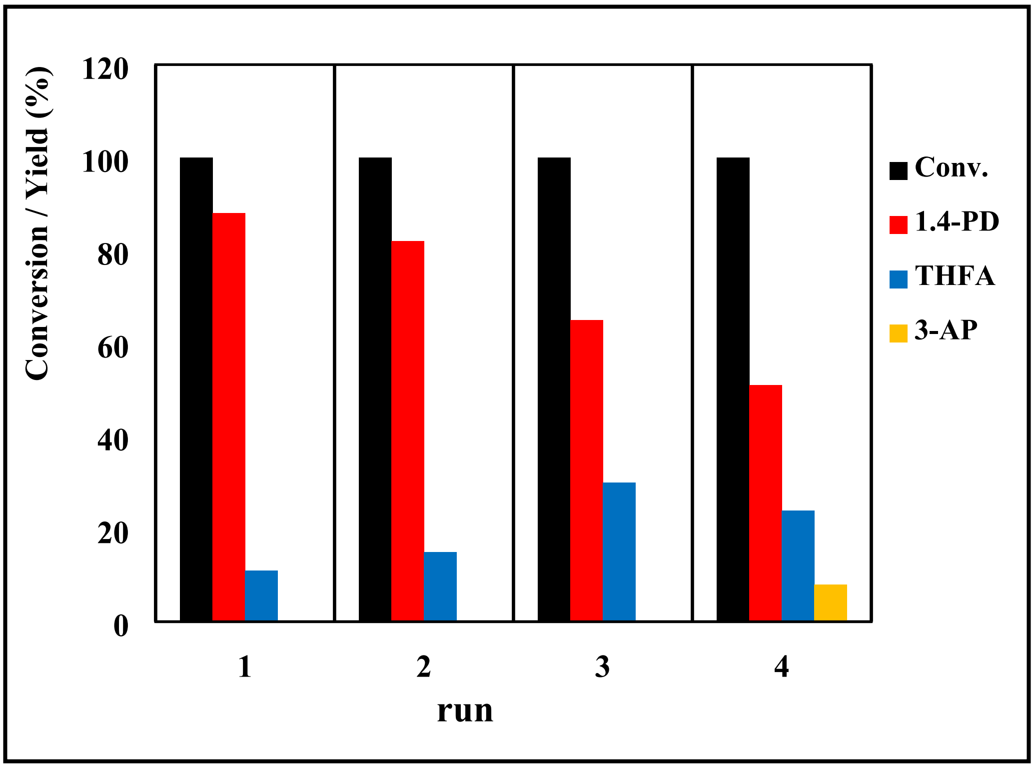


Figure S7: Recycling test of Ru/CMK3-R200 catalyst. Reaction conditions: 2 wt% furfural in H_2O, 5 mL H_2O, 20h and a metal/substrate ratio of 0.57 mol%.

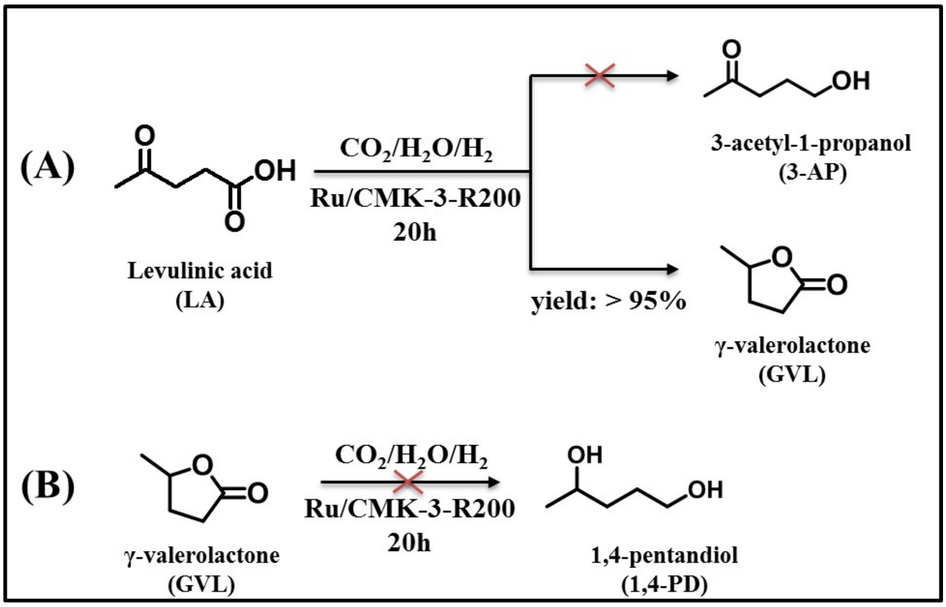


Figure S8: Catalytic conversion of LA and γ-valerolactone.

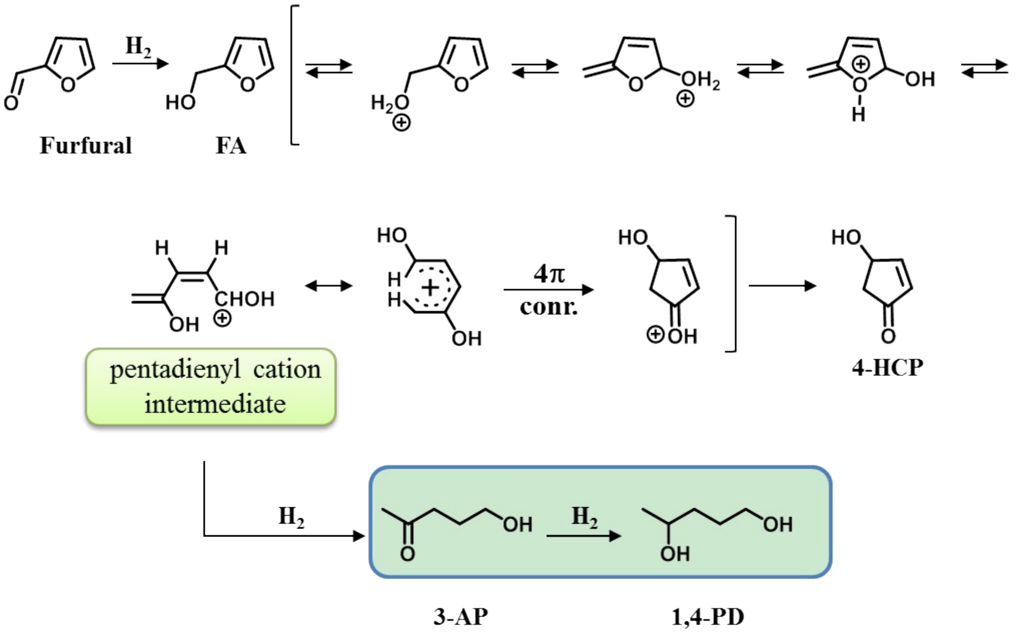


Figure S9: Proposed mechanism for 3-AP and 1,4-PD synthesis through a cascade sequence that terminates with the hydrogenation of a pentadienyl cation intermediate.

References

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