

Electronic Supplementary Information (ESI)

Novel Ru nanoparticles catalysts for Catalytic Transfer Hydrogenation of biomass-derived furanic compounds

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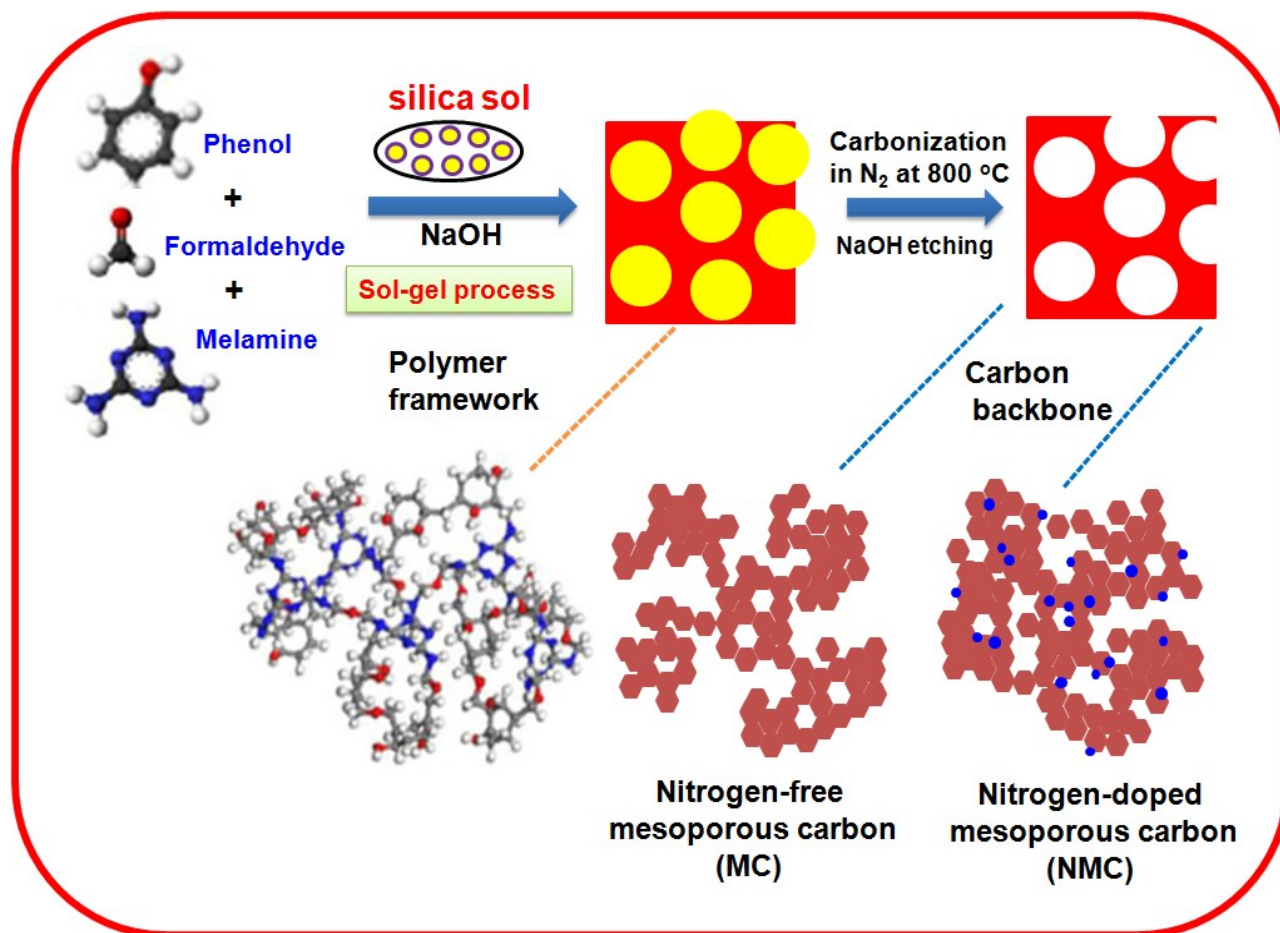
1. Experimental section:

1.1. Preparation of catalysts

1.1.1. Preparation of nitrogen-doped mesoporous carbons (NMC's)

The NMC's with tunable N-content were prepared by sol-gel process, employing melamine as a nitrogen precursor (Scheme S1).^[1,2] In a typical synthesis method, 78 mmol of formaldehyde (37 wt%, 6.33 g) along with 39 mmol of phenol (3.67 g) was added dropwise into 50 mL of aqueous sodium hydroxide solution (10 mmol, 0.2 M) at constant stirring. The resulting mixture was continuously stirred for 20 min at room temperature and subsequently heated to 70 °C in an oil bath, which was continued for 40 minutes. To this, 39 mmol of melamine (4.92 g) as nitrogen source plus additional amount of formaldehyde (107 mmol, 9.5 g) was added and the mixture was stirred again for 30 minutes. After that, Ludox SM-30 sol (50 g, 30 wt% SiO₂) was added with vigorous stirring for 1 h. The final mixture was subsequently added into a sealed bottle and continuously heated again for 3 more days at 80 °C temperature. The acquired gel was dried out at 80 °C and made into fine powder. The material was carbonized in presence of nitrogen gas flow at 800 °C temperature for 3 h by growing the temperature at a heating rate of 5 °C per minute. The obtained material contained SiO₂, which was completely removed through treatment with aqueous NaOH (2 M) under constant stirring for 12 h at 80 °C. The final material was properly washed by deionized water until the pH reached neutral. Afterward, the sample was dry for 10 h at 100 °C temperature. The NMC's with different N-contents were prepared via

altering the melamine to phenol molar ratio. The nitrogen-free mesoporous carbon (MC) was also prepared by using above process without addition of melamine.



Scheme S1 Schematic illustration of NMC's and MC synthesis.^[2]

1.1.2. Preparation of 2wt% M-NMC (M = Ru, Pd, Au, Pt, Ni, Rh and Cu) catalysts

The metal nanoparticles catalysts supported on NMC's were prepared by a modified ultrasonic-assisted method.^[2] For the preparation of 2wt% Ru-NMC catalyst, NMC material (100 mg) was initially dispersed in deionized water (50 mL) by ultrasonication for 20 minutes. To this, an aqueous solution of RuCl₃ (0.5 mL, Ru amount 4 mg per mL) was added under agitation in an ultrasonicator. The resulting suspension was constantly stirred for 6 h at 80 °C and this mixture was cooled under room temperature. To this, NaBH₄ aqueous solution (Ru/NaBH₄ = 1:4 mol mol⁻¹) was added slowly under ultrasonication for 30 minutes to get Ru into metallic state. This mixture was filtered, also washed by deionized water until Cl⁻ ions were absent (silver nitrate test). The resulting 2wt% Ru-NMC catalyst was dry for 10 h at 80 °C temperature. Activated carbon (AC) and MC supported Ru catalysts were also prepared by following the

above procedure. Furthermore, a analogous method was applied for the synthesis of 2wt% Pt-NMC, 2wt% Rh-NMC, 2wt% Pd-NMC, 2wt% Au-NMC, 5wt% Ni-NMC and 5wt% Cu-NMC catalysts.

1.1.3. Preparation of 2wt% Ru-metal oxide catalysts (metal oxide = CeO₂, MgO, Mg(Al)O, γ -Al₂O₃ and TiO₂)

Metal oxide supported Ru catalysts were synthesized by deposition-precipitation process.^[3] In a typical preparation of 2wt% Ru-CeO₂ catalyst, required amount of aqueous solution of RuCl₃ (7.5×10^{-4} M) was heated at 70 °C under steady stirring. To this, 1 g of CeO₂ was added. Subsequently, the solution pH was maintained to 9 by dropwise addition of 0.2 M aqueous sodium hydroxide. Afterward, the mixture was stirred for 2 h at 70 °C and allowed to cool at room temperature. Following this, aqueous solution of NaBH₄ (Ru/NaBH₄ = 1:4 mol mol⁻¹) was added dropwise to above suspension under constant stirring at room temperature for 30 minutes to get Ru into metallic state. The solution was filtered as well as washed with deionized water to remove Cl⁻ ions (silver nitrate test). The 2wt% Ru-CeO₂ catalyst was dried out for 10 h at 80 °C. Similar procedure was used for the preparation of 2wt% Ru-MgO, 2wt% Ru-Mg(Al)O, 2wt% Ru- γ -Al₂O₃ and 2wt% Ru-TiO₂ catalysts.

1.2. Characterization techniques

The XRD of all the materials were collected by means of a PANalytical X'pert Pro dual goniometer. Copper K α light having wavelength of 1.5406 Å operating at 40 kV and 30 mA with Nickel filter was employed to obtain the spectra. The XRD spectra was recorded from 5–90° of 2 θ range (through 0.02° step size).

N₂ sorption isotherm was used to estimate BET surface area of all the materials over Quantachrome Autosorb IQ instrument at -196 °C. Prior to N₂ sorption, the materials were evacuated to a residual pressure of 2×10^{-3} Torr for 3 h at 250 °C. BJH method were utilized to calculate average pore diameter of the materials by the use of desorption branch of N₂ sorption isotherm.

LabRAM HR800 instrument was employed to gather Raman spectra of the materials using He-Ne Laser ($\lambda = 632.84$ nm) working at 20 mW of power.

FEI Technai TF-30 equipment functioning at 300 kV were exploited to collect the TEM images of the samples. For taking TEM images of the materials, the samples were prepared via introducing a drop of diluted sample (made in 2-propanol solvent in ultrasonicator) on top of a carbon-covered copper grid. After that, grid was allowed to dry at room temperature.

VG Microtech Multilab ESCA 3000 instrument were utilized to collect XPS spectra of the samples with Mg K α light having energy of 1253.6 eV. In analyzing chamber the base pressure of $3\text{--}6 \times 10^{-10}$ mbar was maintained. Peak associated to carbon 1s (appearing at binding energy of 284.5 eV) was consider as standard in measuring the binding energy of other elements in the sample.

TENSOR-27 (Bruker Optic) instrument were employed to collect FT-IR spectra of the samples. The material was thoroughly mixed with KBr and analyzed in the frequency range of 500-4000 cm⁻¹.

ICP-OES (Spectro Arcos, FHS-12) instrument was exploited to calculate the amount of metal present in the catalysts. Standard solutions containing different elements were used for the calibration purpose. The catalysts were digested with aqua-regia before ICP-OES analysis.

Micromeritics Autochem-2920 instrument was used to estimate the basicity of the samples by CO₂-TPD study. Previous to the analysis, the sample was heated at 300 °C temperature for 1 h under steady Helium gas flow (40 mL/min). Subsequently, the sample temperature was decreased to 50 °C. Afterward, sample was exposed to 10% CO₂ in Helium gas flow for 0.5 h (30 mL per min). Next, the sample temperature was elevated to 100 °C in order to take out physisorbed CO₂ through flushing with Helium gas (1 h). Further, temperature was raised from 100 to 800 °C for CO₂ gas desorption in Helium gas flow at a steady heating speed (10 °C per min) and the extent of CO₂ desorbed was estimated quantitatively by TCD detector. Before CO₂-TPD study TCD detector was calibrated.

Micromeritics Autochem-2920 device having calibrated TCD detector was exploited for H₂-TPR study of metal catalysts. Earlier to TPR run, the sample was heated under 300 °C temperature using 5% O₂ in Helium gas mixture at a steady heating speed (10 °C per min) for 1 h. Consequently, sample was cooled to 40 °C and gas flow has altered to 5% H₂ in Argon gas (at speed of 30 mL per min), also the sample was heated to 700 °C temperature at a steady heating speed (5 °C per min). The difference in H₂ gas amount at the outlet was measured quantitatively by TCD.

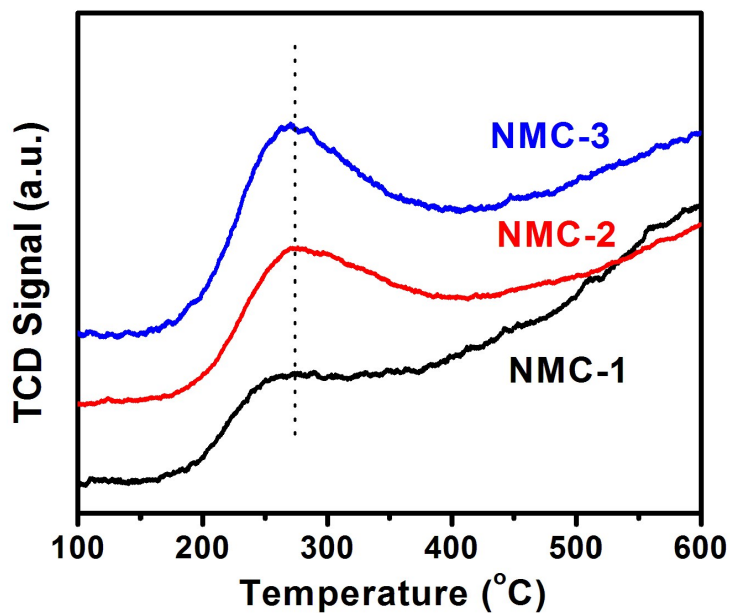
Table S1 Physico-chemical properties of supported metal catalysts.			
Catalyst	BET surface area (m ² /g)	Metal content ^[a] (wt%)	Average Metal particle size ^[b] (nm)
2 wt% Pt-NMC-3	780	1.86	2.7
2 wt% Pd-NMC-3	791	2.05	2.4
2 wt% Rh-NMC-3	765	1.93	2.3
2 wt% Au-NMC-3	760	1.82	5.6
5 wt% Ni-NMC-3	730	4.76	4.2
5 wt% Cu-NMC-3	725	4.84	4.5
2 wt% Ru-AC	991	1.81	3.5
2 wt% Ru-CeO ₂	105	1.76	2.9
2 wt% Ru-MgO	91	1.82	3.2
2 wt% Ru-Mg(Al)O	130	1.79	3.7
2 wt% Ru-TiO ₂	36	1.86	3.4
2 wt% Ru-γ-Al ₂ O ₃	240	1.82	2.9

[a] Estimated by ICP-OES. [b] Calculated from TEM analysis.

Table S2 Physico-chemical properties of fresh and used Ru catalysts.

Catalyst	Fresh Catalysts					Used Catalysts				
	Ru content ^[a] (wt%)	Average Ru particle size ^[c] (nm)	BET surface area (m ² /g)	Total pore volume ^[b] (cc/g)	Nitrogen-content ^[d] (wt%)	Ru content ^[a] (wt%)	Average Ru particle size ^[c] (nm)	BET surface area (m ² /g)	Total pore volume ^[b] (cc/g)	Nitrogen-content ^[d] (wt%)
2 wt% Ru-MC	1.92	6.1	722	0.71	--	1.71	6.9	701	0.60	--
2 wt% Ru-NMC-1	1.89	3.1	792	1.04	5.0	1.86	3.4	763	0.88	4.8
2 wt% Ru-NMC-2	1.91	2.5	849	1.10	8.0	1.89	2.8	827	1.06	7.7
2 wt% Ru-NMC-3	1.95	1.9	805	1.05	11.4	1.93	2.0	780	1.02	11.2

[a] Estimated by ICP-OES. [b] Total pore volume at $P/P_0 = 0.9$. [c] Calculated from TEM analysis. [d] Calculated using elemental analysis.

**Fig. S1** CO₂-TPD profiles of NMC-1, NMC-2 and NMC-3 sample.

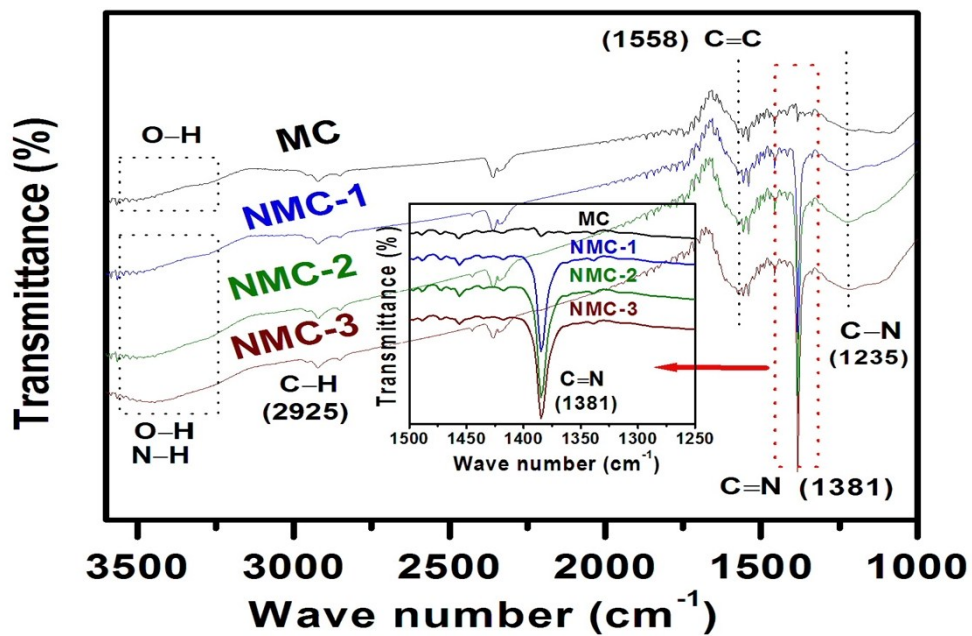


Fig. S2 FT-IR spectra of MC, NMC-1, NMC-2 and NMC-3.

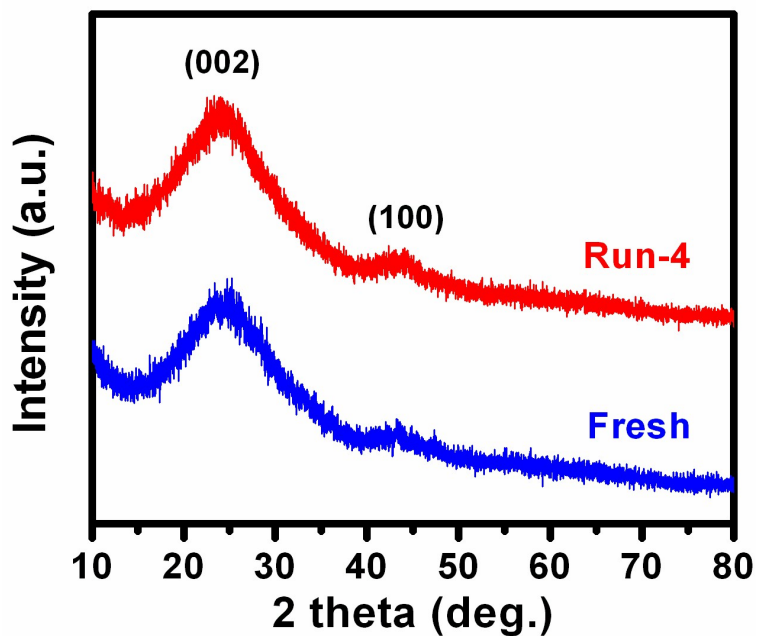


Fig. S3 XRD patterns of the fresh and used (after 4 cycles) 2wt% Ru-NMC-3 catalyst.

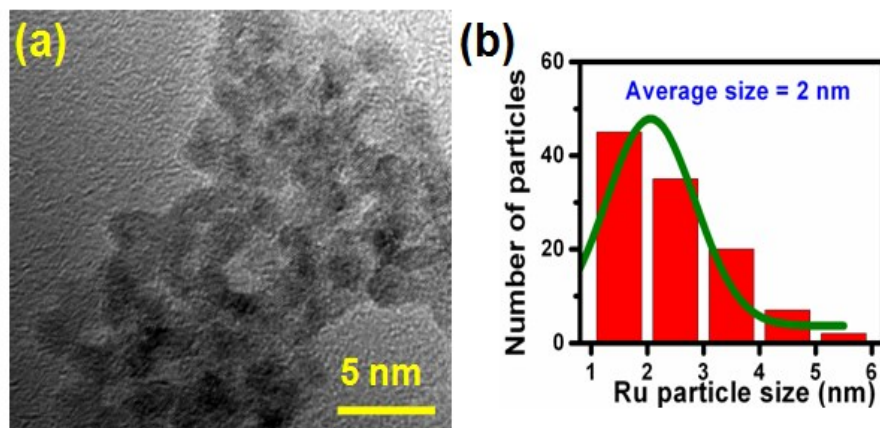


Fig. S4 (a) TEM image and (b) Ru nanoparticles size distribution of reused (after 4 recycles) 2wt% Ru-NMC-3 catalyst.

2. Estimation of Ru metal dispersion using average Ru metal nanoparticles size:

The average particle size of Ru metal nanoparticles in various Ru-NMC catalysts was exploited to estimate Ru metal dispersion by taking into consideration spherical shape of nanoparticles as well as using the equation given by Scholten et al.^[4]

$$D = 10^{21} \times \frac{6 \times M \times \rho_{\text{site}}}{d \times \rho_{\text{metal}} \times N}$$

Ru metal dispersion (%) = Ru metal dispersion (D) x 100

D = Ru metal dispersion

M = atomic weight of Ru (101 g/mol)

ρ_{site} = metal surface site density for Ru (16.3 atoms/nm²)

d = average metal particle size estimated from TEM in nanometers

ρ_{metal} = metal density for Ru (12.3 g/cm³)

N = Avogadro constant, giving **D** = 1.33/**d** (nm) for Ru.

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Table S3 Literature review for selective conversion of 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) and furfural to 2-methylfuran (MF) over metal catalysts.

Part A: Hydrogenolysis of HMF to DMF over various metal catalysts.

Entry	Catalyst	Hydrogen source	Solvent	Temp. (°C)	Time (h)	HMF conv. (%)	DMF yield (%)	Ref.
1.	2wt% Ru-NMC-3	2-propanol	2-propanol	160	8	100	84	This work
2.	CuCrO ₄	H ₂ (6.8 bar)	1-butanol	220	10	100	61	1
3.	Cu-Ru/C	H ₂ (6.8 bar)	1-butanol	220	10	100	71	1
4. [a]	Cu-Ru/C	H ₂ (6.8 bar)	1-butanol	220	10	100	49	2
5.	10 wt% Pd/C	H ₂ (62 bar)	[EMIM]Cl & acetonitrile	120	1	47	15	3
6.	5wt% Ru/C	H ₂	1-butanol	260	1.5	99.8	60.3	4
7.	5wt% Ru/Co ₃ O ₄	H ₂ (7 bar)	THF	130	24	100	93.4	5
8.	Ru-Sn/C	H ₂	lactones	200	4	--	46	6
9.	5wt% Pd/C	H ₂ (10 bar)	CO ₂ and H ₂ O	80	2	100	100	7
10.	Pt-Co @ Hollow Carbon Sphere (Pt = 11.99 wt% & Co = 12.23 wt%)	H ₂ (10 bar)	1-butanol	180	2	100	98	8
11.	Ni-W ₂ C/AC (Ni = 10.28 wt% & W = 47.78 wt%)	H ₂ (40 bar)	THF	180	3	100	96	9
12.	Pd-Au/C + HCl	H ₂ (1 bar)	THF	60	6	100	96	10
13.	Ru/hydrotalcite (Ru = 0.56 wt%)	H ₂ (10 bar)	2-propanol	220	4	100	58	11
14.	2wt% Ru/NaY	H ₂ (15 bar)	THF	220	1	100	78	12
15.	Cu-Porous Metal Oxides	methanol	methanol	260	3	100	48	13

[a] Corn stover derived crude HMF.

Part B: Hydrogenolysis of Furfural to MF over various metal catalysts.

Entry	Catalyst	Hydrogen source	Solvent	Temp. (°C)	Time (h)	Furfural conv. (%)	MF yield (%)	Ref.
16.	2wt% Ru-NMC-3	2-propanol	2-propanol	140	10	100	87	This work
17.	Ni-Fe/SiO ₂	H ₂	--	250	W/F = 0.1 h	96.3	39	14

18.	5wt% Ru/C	2-propanol	2-propanol	180	10	95	61	15
19.	5wt% Ru/C	2-butanol	2-butanol	180	10	100	76	16
20.	Cu–Fe Catalyst	H ₂ (90 bar)	Octane	220	14	99	51	17
21.	5wt% Pt/C	H ₂ (80 bar)	1-butanol	175	0.5	99.3	40.4	18
22. [b]	5wt% Pt/C	H ₂ (30 bar)	1-butanol + H ₂ O	175	0.5	100	36.6	19
23.	2wt% Pd/Fe ₂ O ₃	2-propanol	2-propanol	180	7.5	100	13	20
24. [c]	Cu–Fe/SiO ₂	H ₂	toluene	252	--	99	98	21
25.	5wt% Ru/C	H ₂	1-butanol	260	1.5	99.8	61.9	4

[b] Furfuryl alcohol as reactant with H₃PO₄ as an additive. [c] Vapour phase hydrogenation of furfural.

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