

# Hydrogenolysis of Furfuryl Alcohol to 1,2-Pentanediol Over Supported Ruthenium Catalysts

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Hydrogenolysis of the furan rings of furfural and furfuryl alcohol, which can be obtained from biomass, has attracted attention as a method for obtaining valuable chemicals such as 1,2-pentanediol. In this study, we examined the hydrogenolysis of furfuryl alcohol to 1,2-pentanediol over Pd/C, Pt/C, Rh/C, and various supported Ru catalysts in several solvents. In particular, we investigated the effects of combinations of solvents and

supports on the reaction outcome. Of all the tested combinations, Ru/MgO in water gave the best selectivity for 1,2-pentanediol: with this catalyst, 42% selectivity for 1,2-pentanediol was achieved upon hydrogenolysis of furfuryl alcohol for 1 h at 463 K. In contrast, reaction in water in the presence of Ru/Al<sub>2</sub>O<sub>3</sub> afforded cyclopentanone and cyclopentanol by means of hydrogenation and rearrangement reactions.

## 1. Introduction

Lignocellulosic biomass, which is composed mainly of the polysaccharides cellulose and hemicellulose, has attracted much attention as a sustainable source of raw materials for the production of value-added chemicals.<sup>[1–3]</sup> For example, cellulose (a polymer of the hexose D-glucose) can be converted to 5-hydroxymethylfurfural,<sup>[4,5]</sup> which can in turn be transformed into chemicals such as 2,5-furandicarboxylic acid, 2,5-dimethylfuran, and 2,5-dihydroxymethylfuran.<sup>[6]</sup> Hemicellulose is composed mainly of pentoses such as xylose, which can be converted into furfural and furfuryl alcohol.<sup>[7,8]</sup> Hydrogenolysis of the furan rings of furfural and furfuryl alcohol has attracted attention because these reactions generate valuable chemicals such as 1,2-pentanediol (1,2-PeD) and 1,5-pentanediol (1,5-PeD).<sup>[9]</sup> 1,2-PeD is used as a monomer for the production of polyester, as an antimicrobial agent, and as a moisturizing ingredient in cosmetics. Because this compound is currently produced from petroleum-based resources, the development of methods for producing pentanediols from biomass would be desirable.

The selective production of 1,2-PeD from furfural and furfuryl alcohol with supported Pt catalysts has been

achieved.<sup>[10–16]</sup> For example, Mizugaki et al. reported that hydrocalcite-supported Pt nanoparticles catalyze the production of 1,2-PeD in high yield (up to 80%) from furfuryl alcohol in 2-propanol (2-PrOH) solvent and that basic sites on the support play an important role in the transformation.<sup>[10]</sup> Ma et al. reported that a CeO<sub>2</sub>-supported Pt catalyst gives 1,2-PeD with 65% selectivity by hydrogenolysis of furfuryl alcohol in water and that water molecules participate in the reaction.<sup>[11]</sup> Other precious metals such as Rh,<sup>[17]</sup> Pd,<sup>[18]</sup> and Ru<sup>[19–21]</sup> have also been used for hydrogenolysis of furfural and furfuryl alcohol to afford pentanediols. For example, Date et al. reported that montmorillonite-supported Pd catalyzes the conversion of furfural to 1,2-PeD with a selectivity of 66% and that the acidic nature of the support plays an important role in the conversion.<sup>[18]</sup> Zhang et al. studied the effects of the support on the ability of Ru-based catalysts to selectively afford 1,2-PeD from furfuryl alcohol in water; these investigators found that Ru/MnO<sub>x</sub> affords 1,2-PeD with a selectivity of 42.1%.

However, none of these previous studies thoroughly explored combinations of reaction solvents and catalyst supports. Therefore, in this study, we investigated the effects of various solvent/support combinations on the hydrogenolysis of furfuryl alcohol to 1,2-PeD with the goal of developing an efficient and selective catalytic system. We used not only water and 2-PrOH as solvents but also supercritical carbon dioxide, which has been shown to accelerate the hydrogenation of organic chemicals in some cases.<sup>[22–25]</sup> We found that in water, hydrogenolysis of furfuryl alcohol over Ru/MgO at 463 K afforded 1,2-PeD with 42% selectivity.

## Experimental Section

### Materials

Furfuryl alcohol, 1,2-PeD, cyclopentanone, and cyclopentanol were purchased from Tokyo Chemical Industry Co. Tetrahydrofurfuryl alcohol (THFA), 1,4-pentanediol (1,4-PeD), and 2-methyltetrahydrofuran were purchased from Sigma-Aldrich Co. 1,5-PeD was purchased from Wako Pure Chemical Industries.

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Charcoal-supported Pd, Pt, Rh, and Ru (5 wt% metal loading; designated Pd/C, Pt/C, Rh/C, and Ru/C, respectively) and alumina-supported Ru (5 wt% metal loading; designated Ru/Al<sub>2</sub>O<sub>3</sub>) were purchased from Wako Pure Chemical Industries.

Ruthenium (III) nitrosyl nitrate (Ru(NO)(NO<sub>3</sub>)<sub>3</sub>) solution in dilute nitric acid was purchased from Sigma–Aldrich Co. Zirconium oxide (ZrO<sub>2</sub>) was obtained from Daiichi Kigenso Kagaku Kogyo Co. via the Catalysis Society of Japan (JRC-ZRO-7). Magnesium oxide (MgO) was obtained from Ube Industries via the Catalysis Society of Japan (JRC-MGO-3 1000 A). Cerium oxide (CeO<sub>2</sub>) was obtained from Kanto Chemical Co. Titanium dioxide (TiO<sub>2</sub>) was obtained from Degussa (P-25). Graphite powder was obtained from Timrex (HSAG300). H-ZSM-5 powder (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=60) was purchased from JGC Catalysts and Chemicals.

### Catalyst Preparation

ZrO<sub>2</sub>, MgO, CeO<sub>2</sub>, TiO<sub>2</sub>, graphite, and H-ZSM-5 were impregnated with Ru(NO)(NO<sub>3</sub>)<sub>3</sub> as follows. Aqueous Ru(NO)(NO<sub>3</sub>)<sub>3</sub> and the catalyst support were stirred for 12 h at ambient temperature, and then the mixture was evaporated to dryness at 323 K under reduced pressure on a rotary evaporator. The residue was oven-dried for 10 h at 373 K and then heated at 673 K for 2 h under flowing hydrogen. The amount of Ru in the resulting supported catalysts was 5 wt%. The following catalysts were prepared by using the corresponding supports: Ru/ZrO<sub>2</sub>, Ru/MgO, Ru/CeO<sub>2</sub>, Ru/TiO<sub>2</sub>, Ru/graphite, and Ru/H-ZSM-5.

### Hydrogenolysis Procedure

Hydrogenolysis of furfuryl alcohol was carried out in a stainless steel high-pressure reactor with an inner volume of 50 cm<sup>3</sup>. In a typical procedure, the reactor was loaded with a catalyst (0.02 g), furfuryl alcohol (0.34 g), a magnetic stir bar, and solvent (10 cm<sup>3</sup>) or no solvent. Then the inside of the reactor was purged with argon (0.1 MPa) to remove air, and the reactor was heated to the desired reaction temperature with an oil circulation heater. Hydrogen gas (3.0 MPa) was introduced into the reactor, followed quickly by carbon dioxide (15.0 MPa, via a pump) if carbon dioxide was used for the reaction. The reactor was kept at the desired reaction temperature for the desired reaction time and then quickly cooled by submersion in an ice-water bath. After reactor depressurization, the slurry inside was filtered and the solid was rinsed with acetone.

Hydrogenolysis of furfuryl alcohol was also carried out in a larger batch reactor (inner volume, 100 cm<sup>3</sup>; OM Lab-Tech, MMJ-100) as follows. The reactor was charged with catalyst (0.06 g), furfuryl alcohol (1.0 g), and solvent (30 cm<sup>3</sup>); purged with hydrogen gas; and then charged with hydrogen gas (3.0 MPa) at ambient temperature. The reactor was heated to the desired reaction temperature with a heating band and then maintained at that temperature for the desired reaction time with screw stirring at 600 rpm. After the reaction, the slurry was filtered to separate the solid materials from the liquid fraction.

Products and unreacted furfuryl alcohol were quantitatively analyzed by means of gas chromatography (GC) on an instrument equipped with a flame ionization detector (Agilent HP-6890) and a DB-WAX capillary column; ethylbenzene was used as an internal standard. The conversion of furfuryl alcohol and the selectivity for each product were calculated as follows:

$$\text{Conversion (\%)} = \frac{\{1 - [(\text{moles of unreacted furfuryl alcohol}) / (\text{moles of initial furfuryl alcohol})]\} \times 100}{1} \quad (1)$$

$$\text{Selectivity (\%)} = \frac{\{(\text{moles of product}) / [(\text{moles of initial furfuryl alcohol}) - (\text{moles of unreacted furfuryl alcohol})]\} \times 100}{1} \quad (2)$$

### Characterization of Catalysts

X-ray diffraction (XRD) patterns of the catalysts were recorded by using a Rigaku SmartLab with CuK $\alpha$  radiation ( $\lambda = 0.15406$  nm) at a current of 30 mA, a voltage of 40 kV, and a  $2\theta$  range of 20–70° with a step size of 0.02.

The dispersion of metal particles was defined as the ratio of metal atoms exposed at the surface to all the metal atoms of metal particles, as determined by measuring the amount of hydrogen adsorbed at 313 K in a volumetric gas-adsorption analyzer (Micromeritics 3FLEX 3500). Saturation monolayer uptake was estimated by extrapolating isotherms to zero pressure.

Nitrogen adsorption and desorption were measured at 77 K on the 3FLEX 3500 gas-adsorption analyzer (Micromeritics) with samples that had been degassed at 473 K for 2 h. The relative surface areas of the catalysts were determined by the Brunauer-Emmett-Teller method.

## 2. Results and Discussion

### 2.1. Characterization of Catalysts and Evaluation of Catalyst/Solvent Combinations for Furfuryl Alcohol Hydrogenolysis

The Pd/C, Rh/C, Pt/C, and Ru/C catalysts were characterized by XRD analysis (Figure S1 in the Supporting Information). The XRD pattern of the Pd/C catalyst showed a sharp diffraction peak at 40.1° due to Pd(111), and the mean Pd crystallite size was calculated to be 24.2 nm by means of the Scherrer equation. The XRD patterns of the Rh/C, Pt/C, and Ru/C catalysts showed that the metals were dispersed on the support surfaces.

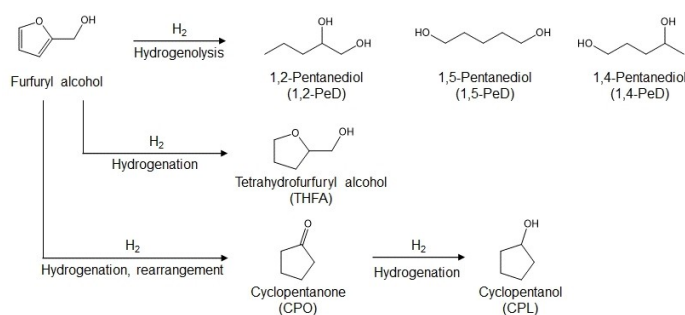
Using these four catalysts, we carried out hydrogenolysis reactions of furfuryl alcohol at 403 K in various solvents (Table 1). When Pd/C was the catalyst, the reaction selectively generated THFA by hydrogenation of the furan ring (Figure 1), regardless of the solvent. Notably, in 2-PrOH, the conversion of furfuryl alcohol was 98%, and the THFA selectivity was 90%. Essentially no 1,2-PeD was obtained from the Pd/C-catalyzed reactions. The products not listed in Table 1 were 2-pentanol, 2-methyltetrahydrofuran, furfural, 2-cyclopenten-1-one, which were quantified using the GC analysis. Some peaks in the GC chart could not be identified; thus, the total value of selectivity did not reach 100%.

When Rh/C was used as the catalyst, cyclopentanone (11% in 2-PrOH) and products such as 2-methyltetrahydrofuran and 2-cyclopenten-1-one were obtained (data not shown). The

**Table 1.** Screening of carbon-supported metal catalysts and solvents for hydrogenolysis of furfuryl alcohol.<sup>[a]</sup>

Catalyst	Solvent	Conv./%	Selectivity/%					
			THFA	1,2-PeD	1,5-PeD	1,4-PeD	CPO	CPL
Pd/C	none	46	73	0.1	0.0	0.0	0.0	0.0
	CO <sub>2</sub> <sup>[b]</sup>	64	85	0.0	0.0	0.0	0.0	0.0
	water <sup>[c]</sup>	84	77	0.1	0.0	0.0	0.4	0.0
	2-PrOH <sup>[d]</sup>	98	90	0.0	0.0	0.0	0.0	0.0
Rh/C	none	69	2.9	0.1	0.0	0.0	0.0	0.0
	CO <sub>2</sub> <sup>[b]</sup>	33	5.3	0.1	0.0	0.0	0.0	0.0
	water <sup>[c]</sup>	94	2.5	0.2	0.0	0.0	11	0.0
	2-PrOH <sup>[d]</sup>	100	41	1.7	0.1	0.0	0.0	0.2
Pt/C	none	12	21	1.9	0.9	0.0	0.0	0.0
	CO <sub>2</sub> <sup>[b]</sup>	4.5	23	1.9	0.5	0.0	0.0	0.1
	water <sup>[c]</sup>	5.7	48	9.0	3.6	0.0	9.9	0.6
	2-PrOH <sup>[d]</sup>	19	15	2.0	1.4	0.0	0.0	0.3
Ru/C	none	33	2.1	0.2	0.0	0.0	0.0	0.0
	CO <sub>2</sub> <sup>[b]</sup>	31	6.7	0.7	0.0	0.0	0.0	0.1
	water <sup>[c]</sup>	98	5.6	2.0	0.3	0.7	4.6	0.8
	2-PrOH <sup>[d]</sup>	100	55	8.6	0.6	0.7	0.0	0.0

[a] Reaction conditions, unless otherwise stated: furfuryl alcohol (0.34 g), catalyst (0.02 g), 3.0 MPa H<sub>2</sub>, 403 K, 1 h. Abbreviations: conv., conversion; THFA, tetrahydrofurfuryl alcohol; PeD, pentanediol; CPO, cyclopentanone; CPL, cyclopentanol. [b] CO<sub>2</sub> pressure, 15 MPa. [c] Water volume, 10 cm<sup>3</sup>. [d] 2-PrOH volume, 10 cm<sup>3</sup>.

**Figure 1.** Products generated by hydrogenolysis and hydrogenation of furfuryl alcohol.

THFA and 1,2-PeD selectivities were highest in 2-PrOH (41% and 1.7%, respectively), but these selectivities were lower than those achieved with the other catalysts.

The Pt/C catalyst showed the lowest furfuryl alcohol conversion of all the tested catalysts. In water, Pt/C showed a 1,2-PeD selectivity of 9.0%, but the furfuryl alcohol conversion was only 5.7%. When the reaction time was increased to 3 h, the conversion increased to 29%, but the 1,2-PeD selectivity decreased to 7.3% (data not shown); that is, the 1,2-PeD selectivity decreased with increasing furfuryl alcohol conversion.

When the catalyst was Ru/C, the conversion was about 30% in supercritical carbon dioxide and in the absence of a solvent, whereas the conversion was 98% in 2-PrOH and 100% in water; the selectivity for 1,2-PeD was 8.6% in the latter solvent. Taken together, the results shown in Table 1 indicate that both the metal and the solvent strongly affected the furfuryl alcohol conversion and the 1,2-PeD selectivity.

## 2.2. Effect of Solvent and Reaction Temperature on the Reaction over Ru/C

Because Ru/C gave better 1,2-PeD selectivity and higher furfuryl alcohol conversion in 2-PrOH than in carbon dioxide or water or in the absence of solvent (Table 1), we examined the Ru/C-catalyzed hydrogenolysis of furfuryl alcohol at 403 K in some additional solvents (Table 2). Of all the solvents tested in this study, 1-PrOH showed the highest 1,2-PeD selectivity (12%). In protic solvents (water and alcohols), the conversion of furfuryl alcohol was 98–100%, whereas considerable amounts of unchanged furfuryl alcohol remained when the aprotic solvents *n*-heptane and supercritical carbon dioxide were used.

Next we explored the effect of temperature on the 1,2-PeD selectivity of the reaction in 1-PrOH (Table 3). (Note that the reactor was heated with a heating band at temperatures of 423 K and above because of the limitations on the maximum temperature achievable with the oil circulation heater that was used at the lower temperatures.) We found that the 1,2-PeD selectivity increased to 19% at 423 K but then decreased as the temperature was increased further.

**Table 2.** Effect of solvent on furfuryl alcohol conversion and product selectivity of hydrogenolysis catalyzed by Ru/C<sup>[a]</sup>

Solvent	Conv./%	Selectivity/%					
		THFA	1,2-PeD	1,5-PeD	1,4-PeD	CPO	CPL
none <sup>[b]</sup>	33	2.1	0.2	0.0	0.0	0.0	0.0
CO <sub>2</sub> <sup>[b,c]</sup>	31	6.7	0.7	0.0	0.0	0.0	0.1
water <sup>[b,d]</sup>	98	5.6	2.0	0.3	0.7	4.6	0.8
2-PrOH <sup>[b,e]</sup>	100	55	8.6	0.6	0.7	0.0	0.0
1-PrOH <sup>[f]</sup>	100	65	12	0.5	0.7	0.1	0.0
EtOH <sup>[g]</sup>	100	57	12	0.5	0.8	0.0	0.4
MeOH <sup>[h]</sup>	100	52	9.2	0.6	0.7	0.0	0.0
<i>n</i> -heptane <sup>[i]</sup>	62	25	3.4	0.1	0.1	0.0	0.0
water + CO <sub>2</sub> <sup>[j]</sup>	99	7.6	1.7	0.2	0.8	3.0	0.3

[a] Reaction conditions, unless otherwise stated: furfuryl alcohol (0.34 g), Ru/C (0.02 g), 3.0 MPa H<sub>2</sub>, 403 K, 1 h. Abbreviations: conv., conversion; THFA, tetrahydrofurfuryl alcohol; PeD, pentanediol; CPO, cyclopentanone; CPL, cyclopentanol. [b] Data are shown in Table 1. [c] CO<sub>2</sub> pressure, 15 MPa. [d] Water volume, 10 cm<sup>3</sup>. [e] 2-PrOH volume, 10 cm<sup>3</sup>. [f] 1-PrOH volume, 10 cm<sup>3</sup>. [g] Ethanol volume, 10 cm<sup>3</sup>. [h] Methanol volume, 10 cm<sup>3</sup>. [i] *n*-Heptane volume, 10 cm<sup>3</sup>. [j] Water volume, 10 cm<sup>3</sup>; CO<sub>2</sub> pressure, 15 MPa.

**Table 3.** Effect of reaction temperature on furfuryl alcohol conversion and product selectivity for hydrogenolysis reactions over Ru/C<sup>[a]</sup>

Reaction temperature	Conv./%	Selectivity/%					
		THFA	1,2-PeD	1,5-PeD	1,4-PeD	CPO	CPL
403 <sup>[b]</sup>	100	65	12	0.5	0.7	0.8	0.0
423 K	100	59	19	1.7	2.1	0.6	0.0
443 K	100	72	18	1.6	1.1	0.8	0.0
463 K	100	65	17	1.3	1.1	0.8	0.0

[a] Reaction conditions, unless otherwise stated: furfuryl alcohol (1.0 g), Ru/C (0.06 g), 1-PrOH (30 cm<sup>3</sup>), 3.0 MPa H<sub>2</sub>, 1 h. Abbreviations: conv., conversion; THFA, tetrahydrofurfuryl alcohol; PeD, pentanediol; CPO, cyclopentanone; CPL, cyclopentanol. [b] Data are shown in Table 2. Reaction conditions: furfuryl alcohol (0.34 g), Ru/C (0.02 g), 1-PrOH (10 cm<sup>3</sup>), 3.0 MPa H<sub>2</sub>, 1 h.

### 2.3. Characterization of Supported Ru Catalysts and Effects of the Support on Hydrogenolysis

Finally, we prepared several supported Ru catalysts: Ru/Al<sub>2</sub>O<sub>3</sub>, Ru/ZrO<sub>2</sub>, Ru/MgO, Ru/CeO<sub>2</sub>, Ru/TiO<sub>2</sub>, Ru/graphite, and Ru/H-ZSM-5. In the XRD patterns of these catalysts (Figure S2 in the Supporting Information), there were no clear peaks at 38.8, 42.4, or 44.4° attributable to Ru metal, indicating that the metal particles were dispersed on the support surfaces. The Ru dispersions for these catalysts ranged from 17.9% to 76.9%, as determined by means of hydrogen adsorption analysis (Table 4), indicating that the Ru metal particle sizes ranged from 1.7 nm to 7.5 nm. The Ru particle sizes of the catalysts

**Table 4.** Characterization of supported Ru catalysts.

Catalyst	Metal dispersion/ % <sup>[a]</sup>	Metal particle size/ nm <sup>[a]</sup>	Surface area/ m <sup>2</sup> g <sup>-1b)</sup>
Ru/C	42.8	3.1	1041
Ru/Al <sub>2</sub> O <sub>3</sub>	58.9	2.3	112
Ru/ZrO <sub>2</sub>	76.9	1.7	104
Ru/MgO	50.8	2.6	47.7
Ru/CeO <sub>2</sub>	45.9	2.9	19.8
Ru/TiO <sub>2</sub>	23.7	5.6	51.9
Ru/graphite	17.9	7.5	207
Ru/H-ZSM-5	23.3	5.7	349

[a] Metal dispersions and particle sizes were determined by hydrogen adsorption analysis. [b] Surface areas were determined by nitrogen adsorption analysis.

decreased in the order Ru/graphite > Ru/H-ZSM-5 > Ru/TiO<sub>2</sub> > Ru/C > Ru/CeO<sub>2</sub> > Ru/MgO > Ru/Al<sub>2</sub>O<sub>3</sub> > Ru/ZrO<sub>2</sub>. The surface areas of the catalysts ranged from 19.8 to 1041 m<sup>2</sup> g<sup>-1</sup> and decreased in the order Ru/C > Ru/H-ZSM-5 > Ru/graphite > Ru/Al<sub>2</sub>O<sub>3</sub> > Ru/ZrO<sub>2</sub> > Ru/TiO<sub>2</sub> > Ru/MgO > Ru/CeO<sub>2</sub>; that is, there was no correlation between surface area and Ru particle size.

We evaluated the activities of these supported Ru catalysts for hydrogenolysis of furfuryl alcohol at 403 K in supercritical carbon dioxide, water, and 2-PrOH and in the absence of solvent (Table 5). The solvent that gave the best conversion of furfuryl alcohol to 1,2-PeD depended on the catalyst support. With Ru/ZrO<sub>2</sub>, Ru/TiO<sub>2</sub>, Ru/graphite, Ru/H-ZSM-5, and Ru/C (Table 1), the 1,2-PeD selectivity was very low in water but better in 2-PrOH. Conversely, with Ru/Al<sub>2</sub>O<sub>3</sub>, Ru/MgO, and Ru/CeO<sub>2</sub>, water gave higher 1,2-PeD selectivity than carbon dioxide or 2-PrOH. The reason for the low 1,2-PeD selectivity of the reactions catalyzed by Ru/ZrO<sub>2</sub>, Ru/TiO<sub>2</sub>, Ru/graphite, Ru/H-ZSM-5, and Ru/C in water was unclear. Of the catalysts used in this study, Ru/graphite and Ru/ZrO<sub>2</sub> showed the largest (7.5 nm) and smallest (1.7 nm) Ru particles sizes, respectively, indicating that the 1,2-PeD selectivity was not determined by particle size. There was also no relationship between catalyst surface area and 1,2-PeD selectivity. Therefore, we reasoned that the 1,2-PeD selectivity was determined by some property of the support. H-ZSM-5, charcoal, and graphite are known to be acidic, whereas MgO is basic. The other supports have both acidic and basic sites on the surfaces. We speculate that the basic sites on MgO, Al<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub> may have enhanced the hydrogenolysis of

**Table 5.** Effect of catalyst support and solvent on Ru-catalyzed hydrogenolysis of furfuryl alcohol<sup>[a]</sup>

Catalyst	Solvent	Conv./%	Selectivity/% THFA	1,2-PeD	1,5-PeD	1,4-PeD	CPO	CPL
Ru/Al <sub>2</sub> O <sub>3</sub>	none	30	75	12	0.4	0.2	0.0	0.0
	CO <sub>2</sub> <sup>[b]</sup>	19	54	6.2	0.1	0.1	0.0	0.0
	water <sup>[c]</sup>	76	72	17	0.6	0.6	5.6	0.5
	2-PrOH <sup>[d]</sup>	43	49	9.5	0.2	0.0	0.0	0.1
Ru/ZrO <sub>2</sub>	none	83	76	16	0.3	0.4	0.0	0.0
	CO <sub>2</sub> <sup>[b]</sup>	68	77	14	0.2	0.3	0.0	0.0
	Water <sup>[c]</sup>	100	12	4.7	0.2	3.7	6.9	14
	2-PrOH <sup>[d]</sup>	100	73	16	0.4	0.2	0.0	0.0
Ru/MgO	none	31	74	11	0.3	0.1	0.0	0.0
	CO <sub>2</sub> <sup>[b]</sup>	16	64	8.0	0.2	0.1	0.1	0.0
	water <sup>[c]</sup>	86	86	27	0.4	0.5	0.1	0.0
	2-PrOH <sup>[d]</sup>	34	48	8.0	0.2	0.0	0.0	0.0
Ru/CeO <sub>2</sub>	none	23	71	12	0.2	0.1	0.0	0.0
	CO <sub>2</sub> <sup>[b]</sup>	12	46	6.0	0.0	0.1	0.0	0.0
	water <sup>[c]</sup>	49	65	15	0.7	0.2	13	1.9
	2-PrOH <sup>[d]</sup>	43	62	14	0.2	0.1	0.0	0.0
Ru/TiO <sub>2</sub>	none	90	70	12	0.3	0.3	0.0	0.0
	CO <sub>2</sub> <sup>[b]</sup>	83	77	11	0.3	0.2	0.0	0.0
	water <sup>[c]</sup>	100	4.3	1.7	0.1	3.2	7.4	14
	2-PrOH <sup>[d]</sup>	100	63	11	0.5	0.1	0.0	0.0
Ru/graphite	none	87	57	8.5	0.0	0.4	0.0	0.0
	CO <sub>2</sub> <sup>[b]</sup>	84	69	8.3	0.3	0.3	0.0	0.0
	water <sup>[c]</sup>	99	5.5	1.9	0.3	1.4	2.9	1.4
	2-PrOH <sup>[d]</sup>	100	69	9.7	0.7	0.3	0.0	0.0
Ru/H-ZSM-5	none	39	1.6	0.1	0.0	0.0	0.0	0.0
	CO <sub>2</sub> <sup>[b]</sup>	20	6.8	0.7	0.0	0.0	0.1	0.1
	water <sup>[c]</sup>	98	2.0	0.7	0.4	0.3	0.7	0.0
	2-PrOH <sup>[d]</sup>	100	58	8.6	0.3	0.8	0.0	0.0

[a] Reaction conditions, unless otherwise stated: furfuryl alcohol (0.34 g), catalyst (0.02 g), 3.0 MPa H<sub>2</sub>, 403 K, 1 h. Abbreviations: conv., conversion; THFA, tetrahydrofurfuryl alcohol; PeD, pentanediol; CPO, cyclopentanone; CPL, cyclopentanol. [b] CO<sub>2</sub> pressure, 15 MPa. [c] Water volume, 10 cm<sup>3</sup>. [d] 2-PrOH volume, 10 cm<sup>3</sup>.

furfuryl alcohol to 1,2-PeD, which is consistent with previously reported results.<sup>[10,18,21]</sup>

Finally, we investigated the effect of reaction temperature on the 1,2-PeD selectivity of hydrogenolysis of furfuryl alcohol over Ru/Al<sub>2</sub>O<sub>3</sub> or Ru/MgO in water (Table 6), which were the catalyst/solvent combinations that gave the highest 1,2-PeD selectivity at 403 K. When Ru/Al<sub>2</sub>O<sub>3</sub> was used as the catalyst, the 1,2-PeD selectivity decreased with increasing temperature, whereas the selectivities for cyclopentanol and cyclopentanone

increased with increasing temperature. The Ru/Al<sub>2</sub>O<sub>3</sub> catalyst was active for the conversion of furfuryl alcohol to cyclopentanol and cyclopentanone with high selectivity. The conversion of furfural to cyclopentanol and cyclopentanone was reported using copper-based catalysts<sup>[26]</sup> or noble metals such as Pt, Pd, and Ru on carbon.<sup>[27]</sup> We found the selectivity can be changed drastically by catalyst supports. When Ru/MgO was the catalyst, the 1,2-PeD selectivity increased with increasing temperature, reaching a maximum of 42% at 463 K and then decreasing slightly (to 40%) at 483 K. These final experiments revealed that of all the catalyst/solvent combinations used in this study, Ru/MgO in water gave the best 1,2-PeD selectivity.

**Table 6.** Effect of reaction temperature on furfuryl alcohol conversion and product selectivity of hydrogenolysis over Ru/Al<sub>2</sub>O<sub>3</sub> and Ru/MgO<sup>[a]</sup>

Catalyst	Reaction temperature	Conv./%	Selectivity/%					
			THFA	1,2-PeD	1,5-PeD	1,4-PeD	CPO	CPL
Ru/Al <sub>2</sub> O <sub>3</sub>	403 K <sup>[b]</sup>	76	72	17	0.6	0.6	5.6	0.5
	423 K	100	13	6.2	0.3	3.9	9.1	41
	443 K	100	5.7	2.8	0.1	2.2	16	41
Ru/MgO	403 K <sup>[b]</sup>	86	86	27	0.4	0.5	0.1	0.0
	423 K	58	64	32	0.8	1.4	0.2	0.0
	443 K	83	58	38	1.3	2.1	0.6	0.0
	463 K	100	51	42	2.9	2.8	0.8	1.1
	483 K	100	46	40	3.1	3.4	0.5	6.2

[a] Reaction conditions, unless otherwise stated: furfuryl alcohol (1.0 g), catalyst (0.06 g), water (30 cm<sup>3</sup>), 3.0 MPa H<sub>2</sub>, 1 h. Abbreviations: conv., conversion; THFA, tetrahydrofurfuryl alcohol; PeD, pentanediol; CPO, cyclopentanone; CPL, cyclopentanol. [b] Data are shown in Table 5. Reaction conditions: furfuryl alcohol (0.34 g), catalyst (0.02 g), water (10 cm<sup>3</sup>), 3.0 MPa H<sub>2</sub>, 1 h.

### 3. Conclusions

We investigated the hydrogenolysis of furfuryl alcohol to 1,2-PeD over Pd/C, Pt/C, Rh/C, Ru/C, Ru/Al<sub>2</sub>O<sub>3</sub>, Ru/ZrO<sub>2</sub>, Ru/MgO, Ru/CeO<sub>2</sub>, Ru/TiO<sub>2</sub>, Ru/graphite, and Ru/H-ZSM-5 in various solvents, including water, 2-PrOH, and supercritical carbon dioxide and without a solvent. When Pd/C was the catalyst in 2-PrOH, the reaction selectively generated THFA, which was produced by hydrogenation of the furan aromatic ring. In contrast, a Ru/Al<sub>2</sub>O<sub>3</sub>-catalyzed reaction in water gave cyclopentanone and cyclopentanol by means of hydrogenation and rearrangement reactions. The highest 1,2-PeD selectivity (42%)



was obtained when the reaction was carried out with Ru/MgO catalyst in water for 1 h at 463 K.

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## Conflict of Interest

The authors declare no conflict of interest.

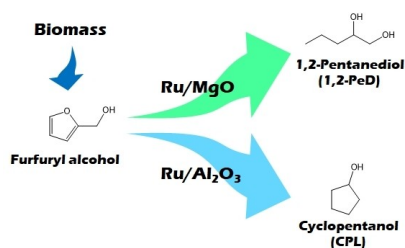
**Keywords:** 1,2-pentanediol · furfuryl alcohol · hydrogenolysis · solvent effects · supported ruthenium catalysts

- [1] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411–2502.
- [2] H. Kobayashi, A. Fukuoka, *Green Chem.* **2013**, *15*, 1740–1763.
- [3] A. Yamaguchi, N. Mimura, M. Shirai, O. Sato, *ACS Sustainable Chem. Eng.* **2019**, *7*, 10445–10451.
- [4] I. K. M. Yu, D. C. W. Tsang, *Bioresour. Technol.* **2017**, *238*, 716–732.
- [5] L. T. Mika, E. Csefalvay, A. Nemeth, *Chem. Rev.* **2018**, *118*, 505–613.
- [6] L. Hu, L. Lin, Z. Wu, S. Zhou, S. Liu, *Renewable Sustainable Energy Rev.* **2017**, *74*, 230–257.
- [7] C. M. Cai, T. Zhang, R. Kumar, C. E. Wyman, *J. Chem. Technol. Biotechnol.* **2014**, *89*, 2–10.
- [8] R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba, M. L. Granados, *Energy Environ. Sci.* **2016**, *9*, 1144–1189.
- [9] S. Chen, R. Wojcieszak, F. Dumeignil, E. Marceau, S. Royer, *Chem. Rev.* **2018**, *22*, 11023–11117.
- [10] T. Mizugaki, T. Yamakawa, Y. Nagatsu, Z. Maeno, T. Mitsudome, K. Jitsukawa, K. Kaneda, *ACS Sustainable Chem. Eng.* **2014**, *2*, 2243–2247.
- [11] R. Ma, X.-P. Wu, T. Tong, Z.-J. Shao, Y. Wang, X. Liu, Q. Xia, X.-Q. Gong, *ACS Catal.* **2016**, *7*, 333–337.
- [12] Y. Zhu, W. Zhao, J. Zhang, Z. An, X. Ma, Z. Zhang, Y. Jiang, L. Zheng, X. Shu, H. Song, X. Xiang, J. He, *ACS Catal.* **2020**, *10*, 8032–8041.
- [13] T. Tong, X. Liu, Y. Guo, M. N. Banis, Y. Hu, Y. Wang, *J. Catal.* **2018**, *365*, 420–428.
- [14] T. Tong, Q. Xia, X. Liu, Y. Wang, *Catal. Commun.* **2017**, *101*, 129–133.
- [15] S. Bhogeswararao, D. Srinivas, *J. Catal.* **2015**, *327*, 65–77.
- [16] W. Xu, H. Wang, X. Liu, J. Ren, Y. Wang, G. Lu, *Chem. Commun.* **2011**, *47*, 3924–3926.
- [17] D. S. Pisal, G. D. Yadav, *ACS Omega* **2019**, *4*, 1201–1214.
- [18] N. S. Date, R. C. Chikate, H.-S. Roh, C. V. Rode, *Catal. Today* **2018**, *309*, 195–201.
- [19] B. Zhang, Y. Zhu, G. Ding, H. Zheng, Y. Li, *Green Chem.* **2012**, *14*, 3402–3409.
- [20] D. Götz, M. Lucas, P. Claus, *Reaction Chem. Engineer.* **2016**, *1*, 161–164.
- [21] X. Wang, Y. Weng, X. Zhao, X. Xue, S. Meng, Z. Wang, W. Zhang, P. Duan, Q. Sun, Y. Zhang, *Ind. Eng. Chem. Res.* **2020**, *59*, 17210–17217.
- [22] A. Baiker, *Chem. Rev.* **1999**, *99*, 453–474.
- [23] N. Hiyoshi, C. V. Rode, O. Sato, M. Shirai, *Appl. Catal. A* **2005**, *288*, 43–47.
- [24] N. Hiyoshi, O. Sato, A. Yamaguchi, C. V. Rode, M. Shirai, *Green Chem.* **2012**, *14*, 633–638.
- [25] H. Nanao, Y. Murakami, O. Sato, A. Yamaguchi, N. Hiyoshi, M. Shirai, *ChemistrySelect* **2017**, *2*, 2471–2475.
- [26] X. Zhou, Z. Feng, W. Guo, J. Liu, R. Li, R. Chen, J. Huang, *Ind. Eng. Chem. Res.* **2019**, *58*, 3988–3993.
- [27] M. Hronec, K. Fulajtarova, *Catal. Commun.* **2012**, *24*, 100–104.

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## FULL PAPERS

The hydrogenolysis of furfuryl alcohol to 1,2-pentanediol over Pd/C, Pt/C, Rh/C, and various supported Ru catalysts in several solvents has been investigated. In particular, we investigated the effects of combinations of solvents and supports on the reaction outcome. The highest selectivity was obtained when the reaction was carried out with Ru/MgO catalyst in water.



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Hydrogenolysis of Furfuryl Alcohol to 1,2-Pentanediol Over Supported Ruthenium Catalysts

