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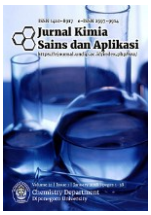

Modified-ZrO_2 Supported Bimetallic Ruthenium-Tin Catalysts for Selective Hydrogenolysis of Furfuryl Alcohol to 1,5-Pentanediol

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Abstract

Biomass-derived platform C5-furanic compounds such as furfural (FFald) and furfuryl alcohol (FFalc) can be converted into 1,5-pentanediol (1,5-PeD), an important intermediate for textiles and plastics, via catalytic hydrogenolysis reaction. However, catalyst selectivity for the hydrogenolysis reaction of FFalc to 1,5-PeD remains a challenge. In this study, modification of ZrO_2 with metal oxides such as TiO_2(R), TiO_2(A), g-Al_2O_3, and active carbon (C) as the supports of bimetallic ruthenium-tin (Ru-Sn) catalysts for the selective hydrogenolysis of furfuryl alcohol (FFalc) to 1,5-pentanediol (1,5-PeD) has been investigated systematically. The modified-ZrO_2 supports were prepared by physical mixing using oxalic acid as a binder at room temperature, followed by calcination under N_2 at 300°C (ramping 2.5°C min^{-1}) for 2 h. The supported Ru-Sn catalysts were synthesised by using the coprecipitation-hydrothermal method at 150°C for 24 h and reduced with H_2 at 400°C (ramping 3.3°C min^{-1}) for 2 h. The synthesised catalysts were characterised by means of XRD, H_2-TPR, and NH_3-TPD. The pristine structures of ZrO_2, TiO_2, and g-Al_2O_3 were maintained during the preparation of catalysts. Ru-Sn/ZrO_2-TiO_2(A) catalyst (Ru = 4 wt%, Sn = 1.30 wt%, ZrO_2 = 67 wt%, and TiO_2 (A) = 33 wt%) with calcination temperature of 300°C gave the highest yield of 1,5-PeD (72%) at 140°C, H_2 10 bar for 3 h.

1. Introduction

The catalytic conversion of biomass feedstocks into fuels and chemicals via green chemistry and green economy approaches has been identified as the sustainable biomass-biorefinery [1, 2]. Lignocellulosic biomass consisted of lignin, cellulose, and hemicellulose, which can be converted into a variety of derived compounds such as substituted aromatics, phenol, reduced C5-C6 sugars, aldehydes, ketones, and organic acids. Furfural (FFald) is one of the important platform chemicals that can be produced by multiple acidic dehydration of C5-C6 sugars in cellulose or hemicellulose [3, 4]. Downstream upgrading of FFald via selective hydrogenation of FFald in the presence of heterogeneous transition metal catalysts produced furfuryl alcohol (FFalc) and tetrahydrofurfuryl alcohol (THFalc) [5, 6]. The selective hydrogenolysis of furan ring in FFald, FFalc, and THFalc using supported transition metal catalysts produced a,w-diol (1,2-;1,4-;1,5-pentanediol (PeD)), which had been identified as the substituted 1,6-hexanediol (1,6-HeD) or 1,4-butanediol (1,4-BeD) in the polyester or polyurethane productions [7]. Commercially, 1,5-PeD was produced from a fossil-based precursor via multi-step reactions of glutaric acid using homogeneous catalysts [8]. Although the heterogeneous noble transition metal-based (e.g., Pt, Pd, Rh, Au, and Ir) catalysts have been intensively investigated for the synthesis of a,w-diol, the mixture of 1,5-PeD and 1,2-PeD products was inevitably obtained [9, 10, 11]. The proposed reaction pathways for the formation of a,w-diol from FFald and its derivatives are shown in Figure 1.

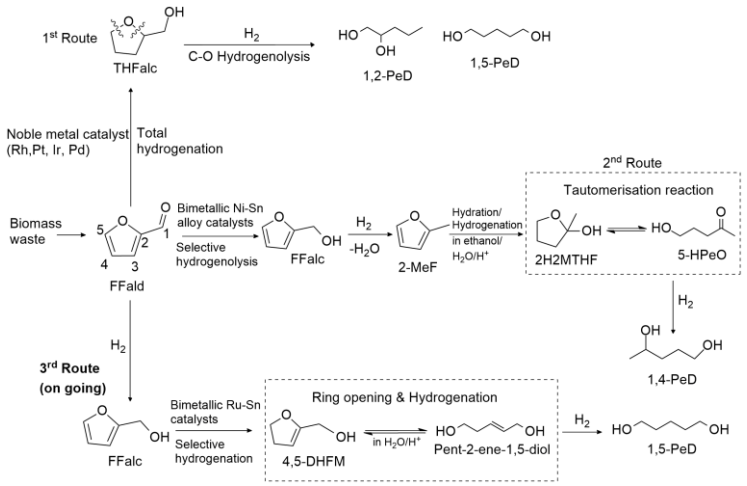

Figure 1. Proposed reaction pathways for the formation of a,w-diols from FFald using heterogeneous transition metal catalysts [12, 13, 14]

There are three proposed reaction routes for the transformation of FFald to a,w-diols. The 1st route is the common route, in which the first reaction is the hydrogenation of C=C and C=O bonds of FFald or FFalc to form THFalc under a hydrogen atmosphere. The saturated furan ring is hydrogenolysed over noble metal-based catalysts to form 1,2-PeD and 1,5-PeD, depending on the C-O bond cleavage of THFalc, reaction conditions, and catalysts. However, the selectivity of 1,5-PeD over 1,2-PeD from FFald or FFalc conversion remains inadequate.

There are three approaches for enhancing the selectivity of 1,5-PeD using catalysts; first, by addition of oxophilic metal oxides (e.g., MoO_x, Y_2O_3, or WO_x) into the active metal [15, 16], second, by the dispersion of the active metal within an acidic support and hydrothermally stable condition [17, 18], and third, the addition of an electropositive metal or promotor (e.g., Sn, In, Cu, Fe) in combination with an acidic support [13, 14]. The synergy between the active metal and the promoter is an important factor in increasing selectivity towards 1,5-PeD. For example, the Ni-Y_2O_3 catalyst system produced a 42% yield of 1,5-PeD from FFalc at 150°C, with an initial H_2 pressure of 20 bar, after 24 h [15]. The ReO_x-modified Rh/SiO_2 (Rh-ReO_x/SiO_2) catalysts selectively hydrogenolysed the C2-O bond of THFalc to produce 56% yield of 1,5-PeD at 60% conversion at 120°C, with an initial H_2 pressure of 80 bar, after 4 h [19]. Other combination catalyst systems, such as Pd-Ir-ReO_x/SiO_2, Rh-ReO_x, and Rh-Ir-ReO_x catalysts, were investigated for the conversion of FFald or FFalc to produce 1,5-PeD (78-80% yields) at 100-120°C, with an initial H_2 pressure of 60-80 bars, after 24 h [20, 21]. Another catalyst, such as an expensive metal, such as platinum (Pt) in Pt@Co^{2+} catalyst, had produced a 47% yield of a,w-diols (27% 1,5-PeD and 20% 1,2-PeD) at 100% conversion of FFalc at 150°C, initial H_2 pressure of 30 bar, and after 4 h [22].

However, most reported catalyst systems require relatively harsh reaction conditions, while achieving precise control over product selectivity remains challenging. Therefore, improving the selectivity of 1,5-PeD under milder reaction conditions is an important challenge for enhancing the sustainability of biomass-based diol production.

The 2nd route is the combination of selective-hydrolysis hydrogenation and furan ring tautomerisation reactions using bimetallic Ni-Sn alloy catalysts in ethanol/H_2O phase to produce 1,4-PeD from FFald, FFalc, or 2-methylfuran (2-MeF). The synergistic actions between RANEY®Ni-Sn and ethanol/H_2O involved the partial hydrogenation of C=C and the tautomerisation of reactions simultaneously to exclusively produce 1,4-pentanediol [23, 24]. In contrast to RANEY®Ni-Sn catalyst, bimetallic Ru-Sn catalysts have been explored as an alternative system for the selective production of 1,5-PeD from FFalc in the aqueous phase (Figure 1, 3rd route).

Bimetallic Ru-Sn catalysts supported on metal oxide supports (e.g., g-Al_2O_3, ZrO_2, TiO_2 anatase (A), TiO_2 rutile (R), and charcoal (C)), have been investigated for this reaction. Previous studies have reported that the Ru-Sn catalyst supported on various metal oxides can promote a distinct reaction route [13, 14]. In this reaction route, 4,5-dihydromethylfuran methanol (4,5-DHFM) was identified as an intermediate from partial hydrogenation on the C=C, followed by C2-O bond cleavage of the furan ring in FFalc to produce 1,5-PeD during aqueous phase reaction [13, 25]. Therefore, the formation of 1,5-PeD highlights the roles of Ru-Sn active sites and surface acidity of the support.

For instance, Ru-Sn/g-Al_2O_3-TiO_2(A) catalyst has been reported to produce high yields of 1,5-PeD (80%) at 180°C, 10 bar H_2 for 3 h [14]. Although Ru-Sn/g-Al_2O_3-TiO_2(A) afforded the highest 1,5-PeD yield, ZrO_2 is chemically distinct from g-Al_2O_3 in that it possesses amphoteric acid-base sites and stronger metal-support interactions, which have been reported to promote the hydrogenation reaction. Previous studies have demonstrated that the Ru/ZrO_2 catalyst exhibits better performance in the hydrogenation of levulinic acid into g-valerolactone in aqueous solvent [26]. Interestingly, the Ru-Sn/ZrO_2 catalyst also exhibited a high yield of 1,5-PeD (55%) at 180°C, with an initial H_2 pressure of 10 bar for 3 h, which is comparable to that of other supported bimetallic Ru-Sn catalysts [14].

In the present report, the extended investigations of ZrO_2-supported Ru-Sn catalysts for the selective hydrogenolysis of FFalc to 1,5-PeD under identical reaction conditions are described. The modification of ZrO_2 with metal oxides (e.g., TiO_2(R), TiO_2(A), g-Al_2O_3, and active carbon (C)) as the supports of bimetallic ruthenium-tin (Ru-Sn) catalysts was prepared and tested for the selective hydrogenolysis of FFalc to 1,5-PeD. The effects of support composition, calcination temperature, and reaction conditions on the yield of 1,5-PeD are also systematically discussed.

2. Experimental

2.1. Materials

$RuCl_3.xH_2O$ (Sigma-Aldrich, 99%), $SnCl_2.2H_2O$ (Sigma-Aldrich, 99%), charcoal (Sigma-Aldrich, 99%), NaOH (Sigma-Aldrich, 99%), 2-methoxy ethanol (Sigma-Aldrich, 99%), oxalic acid (Sigma-Aldrich, 99%), and ethanol (Sigma-Aldrich, 99,5%) for synthesis catalysts. TiO_2 anatase and rutile (Guangzhou Hongwu Material Technology Co., Ltd, 99%), g-Al_2O_3 (Merck Milipore, 99%), ZrO_2 monoclinic (Wako Pure Chemical, 98%) for synthesis supports. Furfuryl alcohol (Sigma-Aldrich, 99%), dodecane (Sigma-Aldrich, 99%), 1,5-pentanediol (Tokyo Chemical Industry, 97%). Furfuryl alcohol as a reactant was purified using standard procedures prior to use [27].

2.2. Catalyst Preparation

2.2.1. Preparation of Supports

The detailed procedure for synthesising ZrO_2-TiO_2 (A) support is described as follows [28][29]: ZrO_2 (0.6667 g) and TiO_2 (anatase, 0.3333 g) were mixed at room temperature, and a 10 wt% oxalic acid solution was added dropwise until a homogeneous paste was formed. The paste was then dried at 110°C for 12 h and subsequently calcined at 300°C under an N_2 flow of 100 mL/min for 2 h. The same procedure was applied to synthesize the other support.

2.2.2. Preparation of Catalysts

A typical procedure for the synthesis of Ru-Sn/ZrO_2-TiO_2 (A) (Ru= ~4 wt% and Sn = ~ 1.3 wt%) is described as follows [28][29]: $RuCl_3.xH_2O$ was dissolved in deionised water (denoted as solution A), and $SnCl_2.2H_2O$ was dissolved in ethanol and 2-methoxy ethanol (denoted as solution B) at room temperature under gentle stirring. Solutions A, B, and 1.0 g of support (ZrO_2-TiO_2 (A)) were mixed at room temperature. Then, the temperature was increased to 50°C, and the mixture was stirred for 12 h. The pH of the catalyst solutions was adjusted to 9-10 by adding an aqueous solution of NaOH (3.1 M) dropwise, and the solutions were transferred into a sealed Teflon autoclave reactor for hydrothermal processing at 150°C for 24 h. The obtained grey solid precipitate was washed with distilled water and ethanol. The precipitate was then dried *in vacuo* overnight. Prior to characterisation and catalytic reaction, Ru-Sn/ZrO_2-TiO_2 (A) was reduced with H_2 flow (100 mL/min) at 400°C for 2 h. The same procedure is used to synthesise other catalysts.

2.3. Catalyst Characterizations

The X-ray diffraction (XRD) analysis was performed using a Miniflex 600 Rigaku instrument with Cu as the monochromatic source of CuKa radiation (l = 0.1544 nm). The XRD was operated at 40 kV and 15mA with a step width of 0.02°, a scan speed at 4° min^{-1} (a1 = 0.1540 nm, a2 = 0.1544 nm), solar slit 1.25°, and a Ni kβ filter.

Ammonia temperature-programmed desorption (NH_3-TPD) was conducted on a ChemiSorb 2750 (Micromeritics). The samples were degassed at 10-200°C for 2 h to remove physisorbed gases prior to measurement. The temperature was then maintained at 350°C for 1 h while the sample was flushed with He gas. NH_3 gas was introduced at 100°C for 30 min, then evacuated with helium (He) gas for 30 min to remove physisorbed NH_3. Finally, temperature-programmed desorption was conducted at a temperature of 100-800°C, and the desorbed NH_3 was monitored by TCD.

The hydrogen temperature-programmed reduction (H_2-TPR) was performed on a Chemisorb 2920 (Micromeritics). The samples were heated at 110°C for 60 min under a N_2 stream with a flow rate of 50 mL min^{-1}, then cooled to room temperature. Before the reduction processes, the line was purged with H_2 (5% Ar gas v/v) for 30 min, then reduced with the same gas (H_2 (5% Ar v/v)) at an elevated temperature of 30-800°C with a ramp rate of 10°C min^{-1}. The H_2 uptake was calculated using the calibration curve (H_2 gas; 10% Ar gas v/v, and flow rate of 50 mL min^{-1}).

The ATR-IR analysis of adsorbed pyridine was performed using a Bruker Diamond. The catalyst sample was placed in a glass-tube reactor and heated to 150°C under N_2 flow for 1 h. Next, the spectrum of adsorbed species was obtained after the introduction of 2-3 drops of pyridine at room temperature, followed by heating at 150°C for 3 h with gentle stirring. After adsorption, the sample was evacuated to remove physisorbed pyridine and was monitored by ATR-IR spectroscopy on a Bruker Diamond at 400-4000 cm^{-1}.

2.4. Catalytic Reactions

A typical catalytic reaction procedure is described as follows [13]: Catalyst (0.05 g), FFalc (0.0020 mol), n-dodecane as the internal standard (0.0002 mol), and H_2O (3 mL) were placed in a glass reaction tube, which was fitted into a stainless-steel reactor. The reactor was flushed with H_2 at 2.5–5.0 bar approximately 30 times. After introducing an initial H_2 pressure of 10 bar at room temperature, the reactor was heated to 160°C using a silicone oil heater equipped with a magnetic stirrer. After 3 h, the reaction mixture was transferred to a sample vial, centrifuged (~5000 rpm for 5 min), and analyzed by FID-GC (PerkinElmer). The catalyst was easily separated by centrifugation and then dried overnight under vacuum at room temperature before reusability testing.

2.5. Product Analysis

Analysis of reactants (FFalc) and product (1,5-PeD) was performed on a Perkin Elmer XL-Autosystem equipped with a flame ionisation detector (FID) and with

Restek Rtx@ BAC Plus 1 capillary column (30 m, 0.32 mmID, 1.8 mdf). GC analysis was performed at detector and injector temperatures of 240°C and 200°C, respectively, with N_2 as the carrier gas (14 mL min^{-1}), and air and H_2 flow rates were 450 mL min^{-1} and 38 mL min^{-1}, respectively. The calibration curve was prepared using known concentrations of the internal standard (dodecane), the reactant, and commercially available products to determine the correct response factors, and was applied to calculate the analyte. The conversion of FFalc and the yield of the products were calculated using Equations (1) and (2).

$$Conversion = \frac{F_0 - F_t}{F_0} \times 100 \quad (1)$$

$$Yield = \frac{mol\ product}{F_0} \times conversion\ of\ FFalc \quad (2)$$

Where F_0 is the introduced mol reactant (FFalc), and F_t is the remaining mol reactant, which are all obtained from GC analysis using an internal standard technique.

3. Results and Discussion

3.1. Catalyst Characterization

The XRD patterns of three types of supported bimetallic Ru-Sn catalysts, c.a,. Ru-Sn/ZrO_2-TiO_2(A), Ru-Sn/ZrO_2-TiO_2(R), and Ru-Sn/ZrO_2-g-Al_2O_3 after reduction with H_2 at 400°C for 2 h are shown in Figure 2(A). The pristine structures of ZrO_2 are observed at 2θ = 28.2°, 31.5°, 50.1°, and 59.8° (ICDD File No. 37-1484) [29]. The presence of ruthenium, tin, or Ru-Sn species cannot be detected by XRD due to the extremely low sample amount. The XRD patterns of supported Ru-Sn on ZrO_2-TiO_2(A) obtained after calcination at 300, 400, 500, and 600°C under N_2 for 2 h are shown in Figure 1(B). Figure 1(B) shows the presence of ZrO_2-TiO_2(A) support on Ru-Sn catalyst in all samples, a series of sharp diffraction peaks of TiO_2(A) occurred at 2θ = 25.3°, 37.8°, 48.1°, 54.8°, 55.3°, and 62.9° (JCPDS card No. 21-1272) [30].

To further support the XRD data, the crystallite size of the Ru-Sn/ZrO_2-TiO_2 (A) catalyst structure with varying calcination temperatures has been calculated using the Scherrer equation, specifically the TiO_2 (A) crystallite size. Based on the diffraction peak of TiO_2 (A) at 2θ = 25.3° in all samples, these peaks became sharper as the calcination temperature increased. The crystallite size of TiO_2 (A) at calcination temperatures of 300°C, 400°C, 500°C, and 600°C was estimated to be 15 nm, 17 nm, 19 nm, and 21 nm, respectively. This phenomenon is also observed in the Pt/TiO_2-ZrO_2 catalyst [31].

The representative profile H_2-TPR of Ru-Sn/ZrO_2-TiO_2(A) with H_2 uptake of 156.5 mmol/g is shown in Figure 3. An intensity reduction peak of RuO_2 to Ru^0 was observed at 95°C, suggesting the existence of RuO_2 interacting with the supports during the preparation of the catalyst [14]. The catalyst also shows a broad reduction peak at 227°C, as reported by Luo *et al.* [32] used a Ru_3Sn_7 catalyst, indicating a shift in the reduction temperature of RuO_2 toward that of SnO_2 due to interaction between RuO_2 and SnO_2. The reduction peak at 457°C indicates the typical reduction of SnO_2 species, which interact strongly with RuO_2.

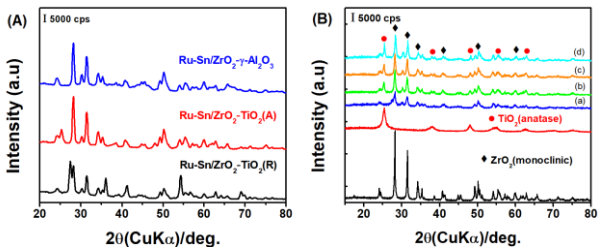

Figure 2. XRD patterns of (A) modified-ZrO_2 supported Ru-Sn, (B) supported Ru-Sn catalysts on ZrO_2-TiO_2(A) after calcination at different temperatures ((a) 300°C, (b) 400°C, (c) 500°C, and (d) 600°C)

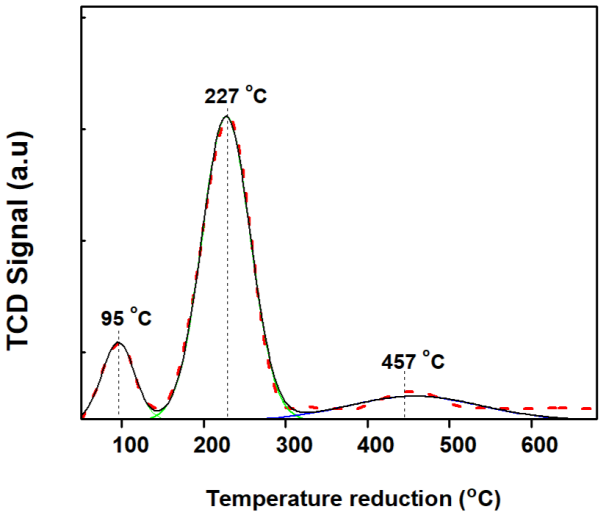

Figure 3. Representative H_2-TPR profile of Ru-Sn/ZrO_2-TiO_2(A) catalyst after calcination with N_2 at 300°C for 2 h

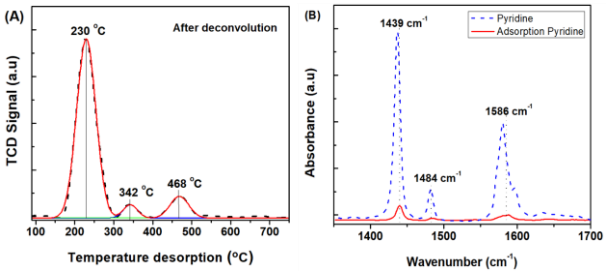

Figure 4. Representative of (A) NH_3-TPD profile, and its deconvolution peaks, and (B) pyridine adsorption of Ru-Sn/ZrO_2-TiO_2(A) catalyst after reduction with H_2 at 400°C for 2 h

The NH_3-TPD profiles were formally divided into three desorption temperature regions to denote three types of acid sites [33, 34]: (1) weak acid sites, ranging from 150-300°C, (2) medium acid sites, ranging from 300-500°C, and (3) strong acid sites, ranging from >500°C. The representative NH_3-TPD profile of the Ru-Sn/ZrO_2-TiO_2(A) catalyst is shown in Figure 3(A). The Ru-Sn/ZrO_2-TiO_2(A) catalyst is dominated by weak acid sites at 230°C with an acidity of 350 mmol NH_3 per gram, accompanied by two small desorption peaks at 342°C, and 468°C as medium acid sites with an acidity of 61 mmol NH_3 per gram. Because NH_3-TPD does not allow distinguishing Lewis and Brønsted acid sites, pyridine-ATR-IR analysis was performed on the representative of Ru-Sn/ZrO_2-TiO_2 (A) catalyst, and the results are shown in Figure 4(B) and Table 1. Coordinatively bound NH_3 pyridine on Lewis acid sites shows bands around 1439

cm^{-1} (ν_{19b}). Physisorbed or hydrogen-bonded pyridine shows a band around 1586 cm^{-1}. The band around 1490 cm^{-1} is common to vibrations due to PyH^+ (Brønsted) and coordinatively bound pyridine (Lewis) [35].

3.2. Catalytic Reaction of Furfuryl Alcohol to 1,5-pentanediol

3.2.1. Screening of Catalysts

Our previous research has shown that Ru-Sn catalysts combined with γ-Al_2O_3, TiO_2(A), and ZrO_2 can produce 1,5-PeD as the main product compared to other catalysts at 180°C, with an initial H_2 pressure of 10-30 bar for 3-5 h. Interestingly, g-Al_2O_3, TiO_2 (A), and ZrO_2 supported Ru-Sn catalysts afforded a high yield of 1,5-PeD were 69%, 55%, and 55%, respectively. In the experiment, the g-Al_2O_3 support was modified with TiO_2 (A) on the Ru-Sn catalyst, it was observed to enhance the production of 1,5-PeD by 80% at a conversion rate of 99% at 180°C, with an initial H_2 pressure of 10 bar for 5 h [14].

In our recently published work, we evaluated the screening of a modified-ZrO_2-supported bimetallic Ru-Sn catalyst in aqueous-phase hydrogenolysis of FFalc at 160°C, with an initial H_2 pressure of 10 bar for 3 h. The results are summarised in Table 2. The Ru-Sn/ZrO_2 catalysts gave 67% yield of 1,5-PeD as the main product, while yields of 4,5-DHFM (intermediate product) and levulinic acid (LA) were 28% and 5%, respectively, at 100% conversion of FFalc (Entry 1). Furthermore, using a charcoal (C)-modified ZrO_2-supported Ru-Sn catalyst slightly decreased the yields of 1,5-PeD (57%) and 4,5-DHFM (24%), but increased yields of CPO (4%) and other products (15%) (Entry 2). Furthermore, ZrO_2-g-Al_2O_3 supported Ru-Sn catalyst gave 62% yield of 1,5-PeD with small amounts of CPO (2%) and THFalc (8%) at 86% conversion of FFalc (Entry 3).

The Ru-Sn/ZrO_2-TiO_2 catalysts were also prepared using two different TiO_2 phases, anatase (A) and rutile (R), and evaluated for the same reaction. The Ru-Sn/ZrO_2-TiO_2(A) catalyst yielded 70% of 1,5-PeD and 15% of 4,5-DHFM at 98% conversion of FFalc (Entry 4). In contrast, the Ru-Sn/ZrO_2-TiO_2(R) catalyst was preferred for producing 4,5-DHFM (62%) with a lower yield of 1,5-PeD (38%) at 160°C, 10 bar H_2 for 3 h (Entry 5). Interestingly, lowering the reaction temperature to 140°C using Ru-Sn/ZrO_2-TiO_2(A) catalyst, the yield of 1,5-PeD slightly increased to 72%, accompanied by 4,5-DHFM (17%) and LA (11%) (Entry 6). Additionally, the formation of LA was mainly observed over the Ru-Sn/ZrO_2, Ru-Sn/ZrO_2-g-Al_2O_3, and Ru-Sn/ZrO_2-TiO_2(A) catalysts. Therefore, it can be concluded that the best catalyst for hydrogenolysis of FFalc was the Ru-Sn/ZrO_2-TiO_2(A) catalyst, and the reaction temperature was 140°C. This temperature will be applied for the next catalytic reaction of FFalc over Ru-Sn/ZrO_2-TiO_2(A) catalyst with different compositions of ZrO_2–TiO_2(A) and temperature of calcination.

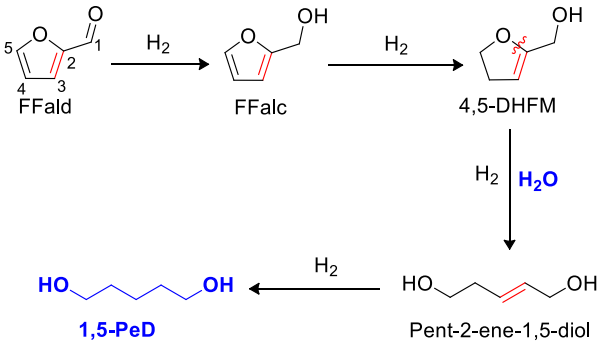

Figure 5. Proposed reaction pathways for selective hydrogenolysis of FFalc to 1,5-PeD over supported bimetallic Ru-Sn catalysts [13]

Table 1. Physico-chemical properties of the Ru-Sn/ZrO_2-TiO_2 (A) catalyst

NH_3-TPD (Acidity/μmol/g)[a]				Pyridine adsorption (band position)	
Weak (100-300°C)	Moderate (300-500°C)	Strong (>500°C)	Total acidity/ μmol/g	Lewis acid	Brønsted acid
350	61	0	411	1439 cm^{-1}	-

[a]Total acidity was derived from NH_3-TPD spectra

Table 2. Results of aqueous phase hydrogenolysis of FFalc using various modified-ZrO_2 supported Ru-Sn catalysts

Entry	Catalyst	Conv. (%)	Yields (%)					
			CPO	THFalc	4,5-DHFM	1,5-PeD	LA	Others
1	Ru-Sn/ZrO_2	100	0	0	28	67	5	0
2	Ru-Sn/ZrO_2-C	100	4	0	24	57	0	15
3	Ru-Sn/ZrO_2-g-Al_2O_3	86	2	8	5	62	4	5
4	Ru-Sn/ZrO_2-TiO_2(A)	98	0	0	15	70	4	9
5	Ru-Sn/ZrO_2-TiO_2(R)	100	0	0	62	38	0	0
6[a]	Ru-Sn/ZrO_2-TiO_2(A)	100	0	0	17	72	11	0

Reaction conditions: Cat. (0.05 g), FFalc (2.0 mmol), H_2O (3 mL), H_2 (10 bar), 160°C, 3 h. [a]The condition reaction at 140°C, 10 bar H_2 for 3 h.

Table 3. Results of aqueous phase hydrogenolysis of FFalc to 1,5-PeD, the different composition of ZrO_2-TiO_2(A) supports

Entry	Catalyst	Conv. (%)	Yields (%)				
			THFalc	4,5-DHFM	1,5-PeD	LA	Others
1	Ru-Sn/ZrO_2-TiO_2(A) (33%)	97	4	32	54	3	4
2	Ru-Sn/ZrO_2-TiO_2(A) (67%)	100	0	17	72	11	0
3	Ru-Sn/ZrO_2-TiO_2(A) (83%)	100	0	47	38	0	15

Reaction conditions: Cat. (0.05 g), FFalc (2.0 mmol), H_2O (3 mL), H_2 (10 bar), 140°C, 3 h.

Table 4. Results of aqueous phase hydrogenolysis of FFalc to 1,5-PeD, the different calcination temperatures of ZrO_2-TiO_2(A) (67%) support

Entry	Catalyst	Conv (%)	Yields (%)				
			THFalc	4,5-DHFM	1,5-PeD	LA	Others
1	Ru-Sn/ZrO_2-TiO_2(A)-300	100	0	17	72	11	0
2	Ru-Sn/ZrO_2-TiO_2(A)-400	100	2	40	27	15	16
3	Ru-Sn/ZrO_2-TiO_2(A)-500	99	0	25	65	4	5
4	Ru-Sn/ZrO_2-TiO_2(A)-600	100	0	0	0	0	100
5	Ru-Sn/ZrO_2-TiO_2(A)-300	99	0	40	40	7	12

Reaction conditions: Cat. (0.05 g), FFalc (2.0 mmol), H_2O (3 mL), H_2 (10 bar), 140°C, 3 h.

To gain insight into the interaction between FFalc and the bimetallic Ru-Sn catalyst system, a general and plausible reaction mechanism has been proposed in Figure 5 based on previous studies [13]. Previous research on Ru-Sn/g-Al_2O_3 catalysts has suggested that Ru species, Sn species, molecular water, and acidic supports play important roles in promoting partial hydrogenation of the C=C bond and cleavage of the C2-O bond of the furan ring in FFalc during aqueous-phase reactions. In the present Ru-Sn/ZrO_2-TiO_2(A) system, a similar reaction pathway is proposed for the formation of 1,5-PeD. Notably, 1,2-PeD was not detected, indicating that non-selective hydrogenation of the C-O cleavage pathways is suppressed. This phenomenon is likely associated with the interaction of Ru-Sn active sites and weak Lewis acid sites, which favor selective hydrogenation and controlled ring opening leading to 1,5-PeD. These results were also in accordance with the recent work of Rodiansono et al, who reported the screening support of Ru-Sn catalysts for one-pot hydrogenolysis of FFalc to 1,5-PeD [13, 14, 25][29].

3.2.2. Effect of ZrO_2–TiO_2(A) Composition

In order to get insight into the influence of ZrO_2-TiO_2 (A) support, three types of supported Ru-Sn/ZrO_2-TiO_2(A)(x) catalysts with different compositions (ZrO_2 to TiO_2(A)), c.a. 33 wt%, 67 wt%, and 87 wt%, were prepared and evaluated for FFalc hydrogenolysis at 140°C, initial H_2 pressure of 10 bar for 3 h. The results are summarised in Table 3.

The Ru-Sn/ZrO_2-TiO_2(A) (33%) catalyst gave 54% yield of 1,5-PeD, 4% THFA, 32% DHFM, 3% LA, and a small amount of other (typical dimer FFalc) at 97% conversion of FFalc (Entry 1). When the ZrO_2 content increased to 67 wt%, the yield of 1,5-PeD increased to 72%, while that of 4,5-DHFM increased slightly to 17% at 100% conversion of FFalc (Entry 2). Further increasing the ZrO_2 content to 83 wt% resulted in a significant decrease in the 1,5-PeD yield to 38%. On the other hand, the yields of 4,5-DHFM and others (dimer-FFalc) increased two-fold to 47% and 15%, respectively (Entry 3). The increase of ZrO_2 portion in ZrO_2-TiO_2(A) support may induce the ring opening reaction of the furan ring or dimerisation, as indicated by the increase in LA and dimer-FFalc. These products were generated due to the presence of Brønsted acid sites, as suggested by Rodiansono *et al.* [14]. Therefore, the subsequent investigation of this Ru-Sn/ZrO_2-TiO_2(A) (67%) was the effect of calcination temperatures.

3.2.3. Effect of Calcination Temperature

In an attempt to improve the yield of 1,5-PeD and to understand the ZrO_2-TiO_2(A)-x support in the catalyst system, the supported Ru-Sn catalyst was calcined with N_2 at different temperatures, c.a. 300°C, 400°C, 500°C, and 600°C for 2 h, and the XRD patterns are shown in Figure 2(B). The results of the catalytic performance of these catalysts at 140°C, initial H_2 pressure of 10 bar for 3 h, are summarised in Table 4.

The highest yield of 1,5-PeD (72%) was obtained over the Ru-Sn/ZrO_2-TiO_2-300 catalyst, while the yields of 4,5-DHFM and LA were 17% and 11%, respectively, at 100% conversion of FFalc (Entry 1). When the support was calcined at 400°C, the yield of 1,5-PeD decreased to 27%, whereas the yields of 4,5-DHFM and LA increased approximately threefold (40%) and 15%, respectively, at 100% conversion of FFalc (Entry 2). Furthermore, increasing the calcination temperature to 500°C slightly increased the yield of 1,5-PeD to 65% over the Ru-Sn/ZrO_2-TiO_2(A) catalyst after the support was calcined at 500°C.

A further increase in the calcination temperature to 600°C led to the formation of additional products, including 2-methylfuran (2-MeF), 2-pentanone (2-PeO), LA, and dimer-FFalc, with yields of 25%, 27%, 14%, and 34%, respectively (Entry 4). This phenomenon occurs

due to the increase in crystallinity of TiO_2 at higher calcination temperature, which likely enhances strong metal-support interaction (SMSI) after the reduction [36]. Previous studies have reported that higher calcination and reduction temperatures promote encapsulation of Ru nanoparticle on TiO_2, particularly for the Ru/TiO_2-R system [37]. In this study, the crystallite size of TiO_2 (A) calcined at 600°C was estimated to be 21 nm using the Scherrer equation. This increased crystallinity of TiO_2 (A) is likely to reduce metal accessibility by partially covering active Ru-Sn sites and lowering hydrogenolysis activity. In addition, the reusability test was performed on the Ru-Sn/ZrO_2-TiO_2(A)-300 catalyst, and the results are summarised in Table 4, Entry 5. The yield of 1,5-PeD was decreased to 40%, accompanied by increases in the yields of 4,5-DHFM (40%), LA (7%), and others (12%) (Entry 5). Therefore, the optimal calcination temperature for the ZrO_2-TiO_2 (A) support system was determined to be 300°C.

4. Conclusion

Modification of ZrO_2 with metal oxides such as TiO_2(R), TiO_2(A), g-Al_2O_3, and active carbon (C) as the supports of bimetallic ruthenium-tin (Ru-Sn) catalysts for the selective hydrogenolysis of furfuryl alcohol (FFalc) to 1,5-pentanediol (1,5-PeD) has been investigated systematically. The modified-ZrO_2 supports were prepared by physical mixing with oxalic acid as a binder at room temperature, followed by calcination under N_2 at 300°C (ramping rate 2.5°C min^{-1}) for 2 h. The supported Ru-Sn catalysts were synthesised by using the coprecipitation-hydrothermal method at 150°C for 24 h and reduced with H_2 at 400°C (ramping 3.3°C min^{-1}) for 2 h. The synthesised catalysts were characterised by XRD, H_2-TPR, and NH_3-TPD. The pristine structures of ZrO_2, TiO_2, and g-Al_2O_3 were maintained during the preparation of catalysts. The composition and calcination temperature of the ZrO_2-TiO_2 support significantly impacted the production of 1,5-PeD. Ru-Sn/ZrO_2-TiO_2(A) with composition of ZrO_2-TiO_2 (A) 67% and calcination temperature of 300°C gave the highest yield of 1,5-PeD (72%) at 140°C, H_2 10 bar for 3 h. The high activity and selectivity of Ru-Sn/ZrO_2-TiO_2(A) catalyst can be attributed to the synergistic effect between the high dispersion of Ru or Ru-Sn nanoparticles and the presence of Lewis/Brønsted acid sites of the catalyst system. Further investigations into the catalyst-activity relationship over these Ru-Sn/ZrO_2-TiO_2(A) catalysts for the hydrogenolysis of FFalc are in progress.

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