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Hydrogenolysis of furfuryl alcohol to 1,2-pentanediol catalyzed by first row transition metal salts

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Abstract

The growing and relatively large market share of 1,2-pentanediol (1,2-PeD) has attracted attention of researchers to find effective and economically viable catalysts. One type of catalyst that can be used for synthesizing this compound is transition-metal-based catalysts, employed in the hydrogenolysis of furfuryl alcohol (FOL). In this study, the hydrogenolysis of furfuryl alcohol were performed with 2-propanol as the hydrogen source and transition metal salts as the catalysts. The used catalysts include first-row early and late transition metals, i.e., $ZrOCl_2·8H_2O$, $VOSO_4·H_2O$, $FeSO_4·7H_2O$, $CuSO_4·5H_2O$, $NiCl_2$, $Al(NO_3)_3·H_2O$, $CoCl_2$, $FeCl_3·6H_2O$, and $Zn(NO_3)_2·6H_2O$. It was found that $ZrOCl_2·8H_2O$, $VOSO_4·H_2O$, and $FeCl_3·6H_2O$ demonstrated superior catalytic activity compared to the other catalysts. Optimal reaction conditions for these three catalysts were achieved at 150 °C for 1 hour, using 2-propanol as the hydrogen source. Under these reaction conditions, the $ZrOCl_2·8H_2O$ catalyst achieved 95.5% conversion of FOL and 30.3% yield of 1,2-PeD, while the $VOSO_4·H_2O$ catalyst attained 80.5% conversion of FOL and 36.9% yield of 1,2-PeD. Both results were obtained with a low catalyst concentration of 0.6 mmol%. Meanwhile, the $FeCl_3·6H_2O$ catalyst converted 94.9% of FOL and yielded 30.9% of 1,2-PeD, using a lower catalyst concentration of 0.4 mmol%. Kinetic studies suggested that the reactions likely follow pseudo-first-order kinetics with experimental activation energies (E_a) of 65 kJ/mol, 55 kJ/mol, and 37 kJ/mol for $ZrOCl_2·8H_2O$, $VOSO_4·H_2O$, and $FeCl_3·6H_2O$ catalysts, respectively. These findings highlight the potential of transition-metal-based catalysts in achieving high efficiency with low loading, emphasizing their suitability for industrial applications.

Keywords: $ZrOCl_2.8H_2O$; $VOSO_4.H_2O$, $FeCl_3.6H_2O$, 1,2-pentanadiol, hydrogenolysis, furfuryl alcohol

1. Introduction

The fine chemical industry is one of the industrial sectors experiencing exponential growth, given its critical role in various industrial areas [1–3]. One of the fine chemicals with high economic value is 1,2-pentanediol (1,2-PeD), a fine chemical which is widely used as a monomer of polyester, microbial agent, and moisturizing ingredient in cosmetics [4–7]. Conventionally, 1,2-PeD is produced from petroleum-based starting materials, including 1-pentene [8]. In this method, 1,2-PeD is gradually obtained from 1-pentene through the reaction with an acid catalyst to produce epoxy compounds, which are then further reacted with organic acid catalysts (such as formic acid and mineral acids). However, this method is considered less environmentally friendly due to the use of non-renewable raw materials.

In fact, 1,2-PeD can also be obtained from biomass-based raw materials, i.e., through the hydrogenolysis of furfuryl alcohol (FOL), which is derived from the hydrolysis of lignocellulose, as shown in Fig. 1 [4,7,9–11]. Most of the reaction systems employ a high pressure of hydrogen gas. However, challenges arise on C-O bond-breaking reactions with less nucleophilic reagents, such as H_2 gas, which is less effective due to the stability of these bonds [12]. The furan aromatic ring in furfuryl alcohol has a planar structure, and the π electrons delocalized throughout the furan ring. This delocalization of π electrons causes the furan ring of furfuryl alcohol to have low resonance energy, making it more stable than other non-aromatic compounds with the same number of atoms [12]. As a result, the hydrogenolysis reactions of furfuryl alcohol with H_2, as reported using a wide variety of metal-based catalysts, do not yield impressive results and reveal several weaknesses.

Several catalysts have been reported to produce 1,2-PeD via the hydrogenolysis of furfuryl alcohol (Table 1), including first row and platina group transition metals. Liu et al. (2015) reported Cu–$Mg_3AlO_{4.5}$ catalyst capable in converting 100% of

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furfuryl alcohol to give 51% yield of 1,2-PeD [13]. Other Cu-based catalysts, including Cu-Al_2O_3 and 10Cu-$LaCoO_3$, have also been reported to achieve up to 100% conversion of furfuryl alcohol and 41% yield of 1,2-PeD [14,15]. In contrast to first row transition metal catalysts, platina group catalysts demonstrated a better catalytic performance in a relatively lower hydrogen pressure (Table 1). Zhang et al. (2012) reported the selective conversion of furfuryl alcohol to 1,2-pentanediol over a Ru/MnO_x catalyst in an aqueous phase [16]. At 150 °C and 1.5 MPa of H_2, the yield of 1,2-PeD was up to 42.1% [16]. Using a different catalyst support, Yamaguchi et al. found that Ru/MgO converted 100% of furfuryl alcohol to yield 42% of 1,2-PeD at 30 atm H_2 [4]. Moreover, Tong et al. (2018) demonstrated that the crystal morphology of CeO_2 as a crystal support of Pt had a significant impact on its catalytic performance [17]. The yield of 1,2-PeD can reach up to 77% over Pt/CeO_2-nanocube catalyst but is lower over Pt/CeO_2-nanorods catalyst (48.5%) [17].

The limited abundance of the platina group catalyst as well as the complexity of the synthesis process often make them less suitable for larger 1,2-PeD production. In addition, the success of some of these catalysts has been achieved under extreme conditions, such as the use of high-pressure H_2 gas. Therefore, more effective route of hydrogenolysis of furfuryl alcohol is required. As an alternative, catalytic transfer hydrogenation (CTH) reactions are often employed to replace the use of high-pressure H_2 gas. In this method, organic compounds, such as alcohols, are commonly used as hydrogen sources [18,19]. These hydrogen donors require a catalyst that functions as a Lewis acid, capable of accepting electron pairs from the hydroxyl oxygen of the alcohol. The stronger the Lewis acid-base interaction, the more readily the hydrogen in the hydroxyl group is released. The hydrogen donor-acceptor process by organic compounds to the substrate occurs through various mechanisms, enabling effective selectivity control in this transfer process.

As an example, a hydrogenation reaction of furfural to furfuryl alcohol through CTH route by using 2-propanol as the hydrogen source was reported by Valekar et al. [20]. Zirconium-based Metal-Organic Frameworks (MOFs) were employed as catalysts. It was found that a low coordination number of zirconium cluster and surface modification of these clusters play a key role in enhancing their catalytic activity [20]. Other catalysts employed for this reaction include Fe_3O_4@C [21], Co-Al-Ru [22], and Cu-Al [23]. In addition, the hydrogenolysis of furfuraldehyde and furfuryl alcohol to 1,2-PeD via CTH route was presented by Qurbayni et al. [24]. Using a $CoWO_4$ catalyst, up to 67% yield of 1,2-PeD was achieved with 2-propanol as the hydrogen source at 160 °C for 7 hours. It is believed that the catalytic performance of the catalysts is enhanced by the presence of acid-base sites in the catalyst [18].

In this work, 1,2-PeD is proposed to be produced through the catalytic transfer hydrogenation of furfuryl alcohol, using alcohols as the hydrogen source and transition metal salts as the catalysts. Transition metal salts have the potential to be utilized as catalysts on an industrial scale. Compared to other inorganic materials whose synthesis process is often time consuming and complicated; transition metal salts are readily available. The partially filled d orbitals and the oxophilic nature of transition metals enable them to act as strong Lewis acids, forming an interaction with hydroxyl oxygen in alcohol as the hydrogen source [18]. Furthermore, anions or the oxygen atom of oxo metal cations can act as basic sites, facilitating the deprotonation process of hydrogen donor compounds. Transition metal salts used as catalysts in this study include $ZrOCl_2.8H_2O$, $VOSO_4.H_2O$, $FeSO_4.7H_2O$, $CuSO_4.5H_2O$, $NiCl_2$, $Al(NO_3).H_2O$, $CoCl_2$, $FeCl_3.6H_2O$, and $Zn(NO_3)_2.6H_2O$. The optimization of the catalytic reaction involved exploring the optimal reaction temperature, type and volume of alcohols as the hydrogen source, amount of catalyst, and reaction time. Moreover, a kinetic study was conducted using catalysts with high catalytic activity.

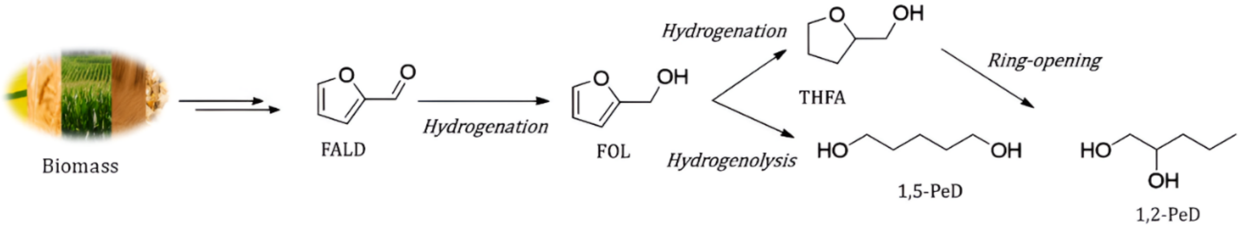

Fig. 1. Hydrogenation and hydrogenolysis of furfuraldehyde (FALD) and furfuryl alcohol (FOL)

2. Materials and Methods

2.1. Materials

The chemicals used in this study were used without further purification. These include $ZrOCl_2.8H_2O$; $VOSO_4.H_2O$; $FeSO_4.7H_2O$; $CuSO_4.5H_2O$; $NiCl_2$; $Al(NO_3).H_2O$; and $CoCl_2$ (Shandong Hanjiang Chemical Co., Ltd.). $FeCl_3.6H_2O$, furfuryl alcohol ≥98% (Merck); 2-propanol ≥99.5% (Merck); $Zn(NO_3)_2.6H_2O$ 98% and ethanol ≥99.7% (Smart-Lab); methanol ≥99.8% (Merck); Tetrahydrofurfuryl alcohol (THFA) and 1,2-pentanediol (Merck).

2.2. Methods

Gas Chromatography-Flame Ionization Detector (GC-FID) (Perkin Elmer) with a capillary column (30 m, DF = 0.25µm, 0.32 mm i.d.) was used to analyze the reaction products. The temperature program was performed as follows: initial temperature was set at 72 °C for 2 min. The temperature is then increased to 250 °C with a heating rate of 10 °C/min. Injector and detector temperature are set at 250 °C and 275 °C, respectively. Rigaku Miniflex with Cu as the X-ray source was used for Powder XRD measurement.

2.3. Catalytic test

The hydrogenolysis reactions of furfuryl alcohol were carried out in a sealed glass tube. The catalyst was added into a sealed glass tube along with furfuryl alcohol and alcohol as the hydrogen source (2-propanol, ethanol, or methanol). The temperature of the catalytic reaction was set using an oil bath on a magnetic stirrer hot plate. The catalytic reaction was performed at specified reaction temperature and time with a stirring speed of 800 rpm. In the catalyst screening stage, 0.2 mmol% of catalysts ($ZrOCl_2.8H_2O$, $VOSO_4.H_2O$, $FeSO_4.7H_2O$, $CuSO_4.5H_2O$, $NiCl_2$, $Al(NO_3).H_2O$, $CoCl_2$, $FeCl_3.6H_2O$, and $Zn(NO_3)_2.6H_2O$) were used. Then, 432 µL furfuryl alcohol (4.4 mmol) and 2.5 mL 2-propanol (32.6 mmol) were added and stirred at 100 °C for 1 hour. The reaction mixture was analyzed by GC-FID to calculate conversion of furfuryl alcohol and the yield of 1,2-PeD.

The optimization reaction was conducted by varying reaction temperatures and times, type and concentration of alcohols as the hydrogen source, and the amount of the catalyst. The reaction temperature was varied from 100 °C, 130 °C to 150 °C. This range was selected as it represents moderate to high temperatures which are suitable for studying the reaction kinetics while also ensuring optimal catalytic activity. In addition, the reactions were carried out over a 5-hour period, with monitoring conducted at 1, 3, and 5 hours to evaluate the reaction products. Prolonged reactions were avoided, as extended reaction times could lead to a decrease in the yield of 1,2-pentanediol (1,2-PeD) [14]. The amount of catalyst used in the reaction was limited to 0.6 mmol% relative to furfuryl alcohol. Higher catalyst loadings were prevented to minimize contamination of the homogeneous catalysts in the product mixture. Furthermore, the alcohol used as hydrogen sources in the catalytic reactions were limited to methanol, ethanol, and 2-propanol. Methanol and ethanol represent primary alcohol, while 2-propanol serves as an example of a secondary alcohol.

Table 1. Reported catalysts for the hydrogenolysis furfuryl alcohol to 1,2-PeD

Catalysts	Reaction conditions (°C, H_2 (atm), hour)	Conv. of FOL (%)	Yield of 1,2-PeD (%)	Ref.
Ru/MnO_x	150, 15, 4	89	42	[16]
$10Cu\text{-}Mg_3AlO_4$	140, 60, 24	>99	51	[13]
Ru/Al_2O_3	200, 100, 1	100	32	[26]
$Cu\text{-}Al_2O_3$	140, 80, 8	86	41	[14]
Ru/MgO	190, 30, 1	100	42	[4]
$10Cu\text{-}LaCoO_3$	140, 60, 1	100	15	[15]
Pt/CeO_2	165, 20, 24	100	77	[17]

Qualitative analysis of the product of the reaction was carried out by comparing the retention time of each peak that appeared on the chromatogram to the retention time of each authentic compound analyzed under the same GC method. Quantitative analysis was conducted by calculating the conversion of furfuryl alcohol and the yield of each product using the following equation.

$$\text{Conversion of FOL (\%)}= \frac{Concentration\ of\ consumed\ FOL}{Concentration\ of\ initial\ FOL} \times 100\% \quad (1)$$

$$\text{Selectivity (\%)} = \frac{Concentration\ of\ 1{,}2{-}PeD}{Concentration\ of\ consumed\ FOL} \times 100\% \quad (2)$$

$$\text{Yield of 1,2-PeD (\%)} = \text{Conversion x Selectivity} \quad (3)$$

3. Results and Discussion

The initial study began with a catalyst screening to identify transition metal salts with the highest catalytic performance in the hydrogenolysis of furfuryl alcohol. The reactions were conducted at 100 °C for 1 hour using 2-propanol as the hydrogen source. 2-Propanol was selected initially as it is reported to be the best hydrogen donor among other primary and secondary alcohols [27]. Expectedly, this reaction did not proceed in the absence of 2-propanol and catalysts (Table 2, run 10-11). Among the tested catalysts, $FeCl_3.6H_2O$, $VOSO_4.H_2O$, and $ZrOCl_2.8H_2O$ exhibited higher catalytic activity than the other six catalysts, achieving furfuryl alcohol conversion of 21.9%, 14.4%, and 17.7%, respectively (Table 2, run 1, 2 and 8). From these reactions, 1,2-PeD and an unknown product are observed. This unknown product appeared as a distinct peak in the chromatogram, with a retention time different from that of tetrahydrofurfuryl alcohol and 1,5-pentanediol (1,5-PeD). However, a higher yield of 1,2-PeD was obtained compared to the unknown product (Table 2). The absence of tetrahydrofurfuryl alcohol (THFA) products indicates that direct hydrogenation of the carbon-carbon double bonds of the furan ring is less preferred than the hydrogenolysis of the C-O bond of the furan ring. This is most likely due to a strong interaction between the oxygen of the furan ring and the metal ions of the catalyst, which weaken C-O bonds of the furan ring and facilitates the hydrogenolysis process (Fig. 2(b)).

Table 2. Catalytic hydrogenolysis of furfuryl alcohol suing various catalysts.[a]

Run	Catalysts	FOL Conversion (%)	Yield (%)	
			1,2-PeD	Unknown
1	$ZrOCl_2.8H_2O$	17.7	10.1	7.6
2	$VOSO_4.H_2O$	14.5	10.9	4.5
3	$FeSO_4.7H_2O$	1.7	1.3	0.3
4	$CuSO_4.5H_2O$	2.2	1.8	0.4
5	$NiCl_2$	1.9	1.7	0.2
6	$Al(NO_3)_3.H_2O$	2.9	2.3	0.6
7	$CoCl_2$	1.9	1.1	0.8
8	$FeCl_3.6H_2O$	21.9	11.8	10.1
9	$Zn(NO_3)_2.6H_2O$	1.3	0.8	0.5
10	$ZrOCl_2.8H_2O$[b]	-	-	-
11	Blank	-	-	-

[a]Reaction conditions: 0.2 mmol% of catalysts; 4.4 mmol of furfuryl alcohol; 2,5 ml of 2-propanol; 100 °C; 1 hour.
[b]Reaction is conducted in the absence of 2-propanol.

Comparing the tested catalyst (Table 2), it is observed that the reaction is more efficiently catalyzed by early transition metals with high oxidation states, high Lewis acidity, and oxophilicity. This is further supported by the fact that $FeSO_4.7H_2O$ catalyst (Table 2, run 3) only resulted 1.7% of furfuryl alcohol conversion and 1.3% yield of 1,2-PeD, which is lower than the results obtained with the $FeCl_3.6H_2O$ catalyst under the same reaction conditions (21.9% of furfuryl alcohol conversion and 11.8% yield of 1,2-PeD). The difference in the oxidation state of iron ions significantly influences the catalytic performance. The Fe(II) ion in $FeSO_4.7H_2O$ has a lower oxidation state than that for the Fe(III) ions in $FeCl_3.6H_2O$, resulting in reduced Lewis acidity for Fe(II) ions. A stronger Lewis acid-base interaction between the catalyst and the oxygen atom of the hydroxyl group in the alcohol facilitates easier deprotonation of the alcohol molecule [18,28,29]. Notably, such deprotonation is well-established, even in the absence of a hydrogen acceptor [29,30]. In this context, Zr(IV), V(IV) and Fe(III) ions can form stronger interactions with 2-propanol compared to that of Cu(II), Fe(II), Ni(II), and Co(II) ions, facilitating easier deprotonation process. Furthermore, the presence of basic species in the catalysts, such as the oxygen atoms in ZrO^{2+} and VO^{2+} ions, plays a role in catalyzing this reaction, i.e., by weakening the O-H bond on the donor alcohol through an interaction with its hydrogen (Fig. 2(a)) [18,28]. Additionally, Lewis acid catalysts strongly interact with the substrate, furfuryl alcohol, promoting its activation and subsequent transfer hydrogenation reactions (Fig. 2(b)).

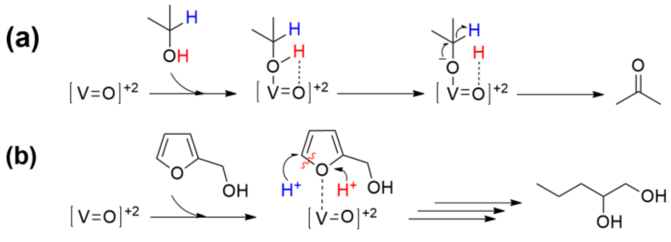

Fig. 2. (a) Proposed dehydrogenation of 2-propanol and (b) transfer hydrogenation reaction of furfuryl alcohol

The catalytic activity of $FeCl_3.6H_2O$, $VOSO_4.H_2O$, and $ZrOCl_2.8H_2O$ under these reaction conditions is considerably better than some other reported catalysts in yielding 1,2-PeD. For example, Ru/Al_2O_3, Ru/MgO, Ru/CeO_2, or Ru/H-ZSM-5 catalysts yields a relatively low amounts of 1,2-PeD under more extreme conditions (>10 bar H_2, 130 °C, 1h) [4]. This is attributed to the ability of homogeneous catalysts to interact on a molecular level, which eliminate the contact boundaries between the active sites of the catalysts and the substrates [18]. This interaction could accelerate the rate of the deprotonation step of proton donor or the hydrogen transfer step [20].

The hydrogenolysis reaction route of furfuryl alcohol with transition metal salt catalysts is proposed to follow the reaction mechanism outlined by Wijaya et al., as shown in Fig. 2 [25]. In this reaction, the selectivity to the 1,2-PeD product is influenced by the tendency of hydrogen atoms to attack the specific bonds in furfuryl alcohol. If the hydrogen atoms first attack the C5-O bond, the lysis stage occurs, leading to the formation of 1,2-PeD as the final product [25]. However, the formation of 1,5-pentanediol formation is favored when hydrogen atoms attack the carbon-carbon double bond of the furfuryl alcohol, leading to the formation of tetrahydrofurfuryl alcohol (THFA). This is related to the stability of the secondary carbanion, which is more likely to form [31].

To increase the yield of 1,2-PeD, the reaction conditions were optimized by varying the reaction parameters.

Initial optimization was conducted by varying reaction temperature with $FeCl_3.6H_2O$, $VOSO_4.H_2O$, and $ZrOCl_2.8H_2O$ used as the catalysts. As shown in Fig. 3(a), all the reactions with these catalysts show a similar trend; the higher the reaction temperature, the higher the conversion of furfuryl alcohol and the yield of 1,2-PeD. At the highest tested reaction temperature of 150 °C, $ZrOCl_2.8H_2O$ and $FeCl_3.6H_2O$ catalysts converted 36% and 34% of furfuryl alcohol, respectively. Meanwhile, the reaction catalyzed by $VOSO_4.H_2O$ catalyst showed a superior catalytic activity compared to the other two catalysts, achieving 51% conversion of furfuryl alcohol. According to Shafaghat et al. (2019), the increase in reaction temperature provides the activation energy necessary for the dehydrogenation of 2-propanol [32]. The best yield of 1,2-PeD for all three catalysts was obtained at 150 °C: 16% for $ZrOCl_4 \cdot 8H_2O$, 27% for $VOSO_4 \cdot H_2O$, and 18% for $FeCl_3 \cdot 6H_2O$ (Fig. 1(a)).

The types of alcohol used as hydrogen sources were varied to study their role in catalytic performance and selectivity control. As shown in Table 3, methanol and ethanol (primary alcohols) exhibited very low selectivity towards 1,2-PeD (<10%) for all three catalysts tested (Table 3, runs 1-2, 6-7, and 11-12). In contrast, 2-propanol (a secondary alcohol) demonstrated high selectivity towards 1,2-PeD, achieving up to 52% selectivity (Table 3, runs 3, 8, and 13). A similar finding was reported by Qurbayni et al. (2024) [24], where primary alcohols (methanol and ethanol) showed higher conversion value, but lower selectivity compared to the secondary alcohol (2-propanol). Examination of the hydrogen donors revealed that 2-propanol, with its lower reduction potential, provided higher proton availability than ethanol. Additionally, its shorter alkyl chain resulted in a weaker spatial effect, contributing to optimal catalytic activity [27].

As in the catalyst screening stage, most of the reactions conducted with 2-propanol yielded three different products; 1,2-PeD, tetrahydrofuran (THFA) and an unknown product. These reaction products appeared as distinct peaks in chromatograms, with no formation of 1,5-pentanediol. THFA is produced via hydrogenation of the double bonds in the furan ring of furfuryl alcohol. In contrast, while reactions conducted in ethanol also produce THFA, both methanol and ethanol reactions yield multiple unknown peaks, indicating the formation of additional reaction products.

In addition to varying the types of alcohol, different amounts of alcohol were also tested as hydrogen sources to determine the optimal reaction conditions. 2-Propanol, identified as the best hydrogen donor for producing 1,2-PeD, was selected for this study. As shown in Table 3, increasing the amount of 2-propanol in the reaction tends to decrease both the catalytic conversion and the yield of 1,2-PeD. This is observed in all reactions catalyzed by $ZrOCl_2.8H_2O$ (Table 3, run 3-5), $VOSO_4.H_2O$ (Table 3, run 8-10), and $FeCl_3.8H_2O$ (Table 3, run 13-15). The use of 1 mL of 2-propanol provided optimal results, yielding 18% of 1,2-PeD for the reaction with $ZrOCl_2.8H_2O$ catalyst, 28.5% for the reaction with $VOSO_4.H_2O$ catalyst, and 30.6% for the reaction with $FeCl_3.8H_2O$ catalyst. This suggests that a lower ratio of catalyst or furfuryl alcohol to 2-propanol as the hydrogen source enhances catalytic performance.

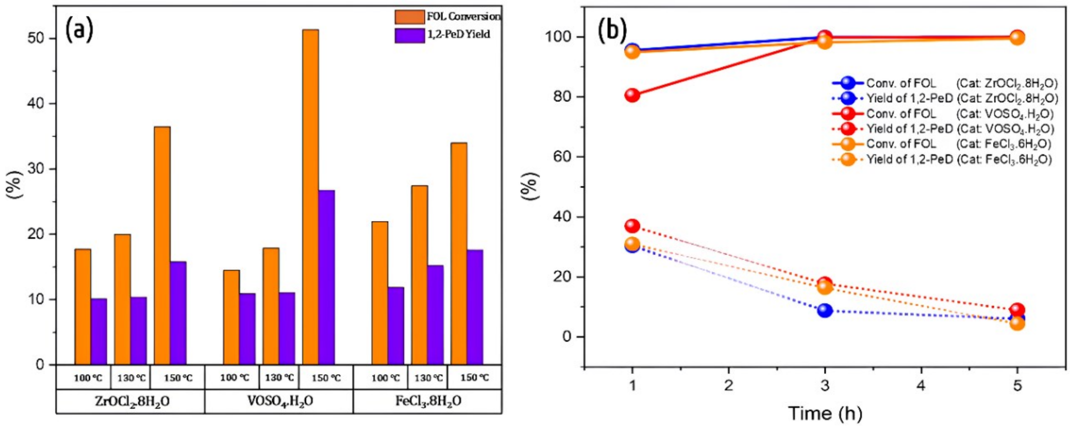

Fig. 3. (a) Catalytic hydrogenolysis of furfuryl alcohol at various reaction temperatures (0.2 mmol% of catalysts, 2,5 ml of 2-propanol, 1 h); (b) Catalytic hydrogenolysis of furfuryl alcohol at various reaction time (1 ml of 2-propanol, 0.6 mmol % of catalyst for $ZrOCl_2.8H_2O$ and $VOSO_4$. H_2O and 0.4 mmol% for $FeCl_3.6H_2O$, 1 h, 150 °C)

Table 3. Catalytic hydrogenolysis of furfuryl alcohol using different type and concentration of alcohols.[a]

Run	Hydrogen source	Volume (mL)	FOL Conv. (%)	Yield (%)			1,2-PeD Selectivity (%)
				1,2-PeD	THFA	Unknown	
$ZrOCl_2.8H_2O$							
1	Methanol	2.5	85	1.2	-	83.9	1.4
2	Ethanol	2.5	>99	2.6	34.7	60.6	2.6
3	2-Propanol	2.5	36.4	15.8	-	20.7	43.4
4	2-Propanol	1	53.2	18.0	-	35.2	33.8
5	2-Propanol	4	24.3	10.0	-	14.3	41.2
$VOSO_4.H_2O$							
6	Methanol	2.5	87.3	6.1	1.5	79.7	7.0
7	Ethanol	2.5	53.5	-	29.0	24.5	0
8	2-Propanol	2.5	51.3	26.7	-	24.6	52.0
9	2-Propanol	1	75.2	28.5	2.9	43.8	37.9
10	2-Propanol	4	35.5	16.0	-	19.5	45.1
$FeCl_3.6H_2O$							
11	Methanol	2.5	74.6	1.5	-	73.1	2.0
12	Ethanol	2.5	95.3	3.7	10.1	81.5	3.9
13	2-Propanol	2.5	34.0	17.6	-	16.4	51.8
14	2-Propanol	1	87.2	30.6	-	56.7	35.1
15	2-Propanol	4	26.7	12.0	-	14.7	44.9

[a]Reaction conditions: 0.2 %mmol of catalysts; 4,4 mmol of furfuryl alcohol; 150 °C; 1 hour.

Table 4. Catalytic hydrogenolysis of furfuryl alcohol using various amount of catalysts.[a]

Run	Catalyst (mmol%)	FOL Conv. (%)	Yield (%)				Select. 1,2-PeD (%)
			1,2-PeD	THFA	FALD	Unknown	
$ZrOCl_2.8H_2O$							
1	0.2	53.2	18.0	-	-	35.2	33.8
2	0.4	76.4	25.6	-	-	50.8	33.5
3	0.6	95.5	30.3	-	-	65.2	31.7
$VOSO_4.H_2O$							
4	0.2	75.2	28.5	2.9	-	43.8	37.9
5	0.4	82.9	33.8	-	-	49.1	40.8
6	0.6	80.5	36.9	-	-	43.6	45.8
$FeCl_3.8H_2O$							
7	0.2	87.2	30.6	-	-	56.7	35.1
8	0.4	94.9	30.9	2.7	-	61.3	32.6
9	0.6	>99	10.3	-	2.3	87.4	10.3

[a]Reaction conditions: 4,4 mmol of FOL; 1 mL of 2-Propanol; 150 °C; 1 hour

This finding is supported by the fact that an increase in catalyst concentration leads to a higher conversion of furfuryl alcohol, as shown in Table 4. An increase in catalyst concentration raises the number of active sites capable of catalyzing the hydrogenolysis of furfuryl alcohol. $ZrOCl_2.8H_2O$ and $VOSO_4.H_2O$ catalysts achieved the highest furfuryl alcohol conversions (95.5% & 80.5%) and 1,2-PeD yields (30.3% & 36.9%) at the catalyst concentration of 0.6 mmol% (Table 4, run 3 and 6). Meanwhile, the reaction catalyzed by 0.6 mmol% $FeCl_3.8H_2O$ resulted in the lowest yield of 1,2-PeD (10.3%) despite the furfurylalcohol conversion exceeding 99%. In this reaction, a dark brown solid was obtained. P-XRD analysis (Fig. 4) confirmed that the solid is an amorphous phase, indicating that it is a product of furfuryl alcohol polymerization rather than an iron compound. A similar brown polymer product has also been observed in similar reactions catalyzed by Ru/AC (activated carbon), Ru/TiO_2, Ru/ZrO_2, $CuCr_2O_4$ and $Ni\text{-}Y_2O_3$ catalysts [16,25].

In sought the optimum reaction time, the catalytic reactions were conducted at three different reaction times, i.e., 1, 3, and 5 hours. As shown in Fig. 3(b), although the conversion of furfuryl alcohol increases with reaction time, the yield of 1,2-PeD decreases. It is observed for all reactions catalyzed by $ZrOCl_2.8H_2O$, $VOSO_4.H_2O$, and $FeCl_3.6H_2O$. Similar observation was reported by Liu at al. (2016), where prolonged reaction times resulted in a decrease in the yield of 1,2-PeD [14]. This reduction may be due to further reactions of 1,2-PeD, leading to the formation of other derivative products. Wijaya et al. (2017) found that the 1,2-PeD product underwent further reaction to form 1-butanol at a longer time [25]. Hence at given reaction conditions, 1 hour is the optimum reaction time to produce the highest yield of 1,2-PeD.

The kinetic order of the reaction was determined by monitoring changes in furfuryl alcohol concentration over time. The kinetic parameters were derived from reactions using 0.6 mol% of the catalysts, 4,4 mmol of furfuryl alcohol, and 1 ml of 2-propanol. A plot of 1/[furfuryl alcohol] against time gives a less linear curve compared to a plot of $\ln[\text{product}]_\infty\text{-}[\text{product}]$ against time (Fig. 5(a-b)). It indicates that the reactions follow pseudo-first-order kinetics. The pseudo first-order kinetic profile indicates that the reaction requires an induction period at temperature lower than 150 °C. Moreover, the rate constant (k_{obs}) tends to increase as the reaction temperature rises, as it is observed for all reactions catalyzed by $ZrOCl_2.8H_2O$, $VOSO_4.H_2O$, and $FeCl_3.6H_2O$ (Table 5 & Fig. 5(c-e)). The increase in k_{obs} with rising reaction temperature indicates a higher reaction rate at elevated temperature. Comparing the three tested catalysts, the calculated k_{obs} for reaction catalyzed by $FeCl_3.6H_2O$ is higher than those reactions catalyzed by $VOSO_4.H_2O$ (1.65 vs 1.57 at 373 K, respectively). Meanwhile, the reactions catalyzed by $ZrOCl_2.8H_2O$ have the lowest value of k_{obs} (1.18 at 373 K).

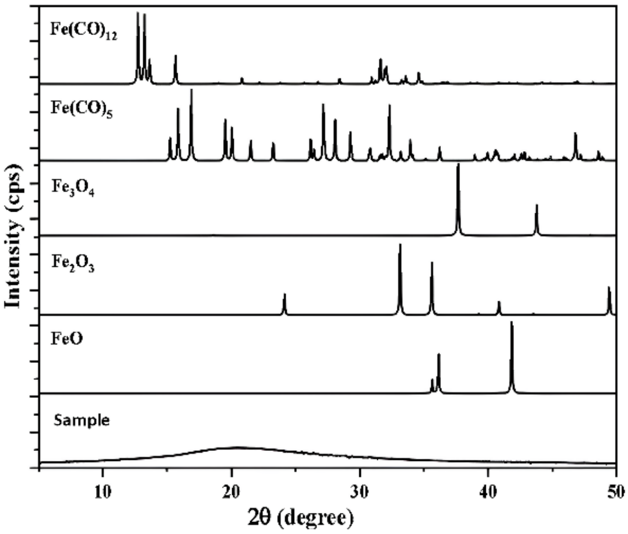

Fig. 4. PXRD diffractograms of dark brown solid (sample) compared to some iron compound standards

This is consistent with the calculated activation energy (E_a), determined using the Arrhenius equation.By plotting the values of k_{obs} at temperatures of 100, 130, and 150 °C against 1/T. The experimental E_a for reactions catalyzed by $ZrOCl_2.8H_2O$, $VOSO_4.H_2O$ and $FeCl_3.6H_2O$ were found to be 65, 55, 37 kJ/mol, respectively (Fig. 5(f-h)). This result indicates that the activation energy is lower for the reaction catalyzed by $FeCl_3.6H_2O$, suggesting the rate of the reaction should be higher (Table 5).

In addition, the thermodynamic study related to the Gibbs free energy of activation ($\Delta G^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$), and entropy of activation ($\Delta S^\ddagger$) were determined using the Eyring equation. As tabulated in Table 5, The hydrogenolysis reaction of furfuryl alcohol towards 1,2-PeD has a positive enthalpy ($\Delta H^\ddagger > 0$), meaning that the reaction requires energy from the environment to proceed. Furthermore, the spontaneity of the reaction is further reduced due to a decrease in entropy ($\Delta S^\ddagger < 0$), indicating the system becomes more ordered. During hydrogenolysis, certain bonds in furfuryl alcohol are broken and new bonds are formed with hydrogen atoms, restricting the motion of atoms within the molecules. This leads to fewer possible conformations and a lower entropy value. The combination of positive enthalpy and negative entropy results in a positive Gibbs free energy ($\Delta G^\ddagger > 0$), which signals that the reaction will not occur spontaneously and requires external energy input for it to proceed.

Tabel 5. Activation parameters of hydrogenolysis of furfuryl alcohol to 1,2 PeD

Catalysts	*k_{obs}*			Activation Energy/ E_a (kJ/mol)	Activation Parameters		
	373 K	403 K	423 K		$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (kJ.K/mol)	$\Delta G^\ddagger$ (kJ/mol)
$ZrOCl_2.8H_2O$	1.18	2.31	3.77	65	62	-70	23
$VOSO_4.H_2O$	1.57	2.69	2.94	55	52	-92	31
$FeCl_3.6H_2O$	1.65	3.08	3.75	37	33	-142	49

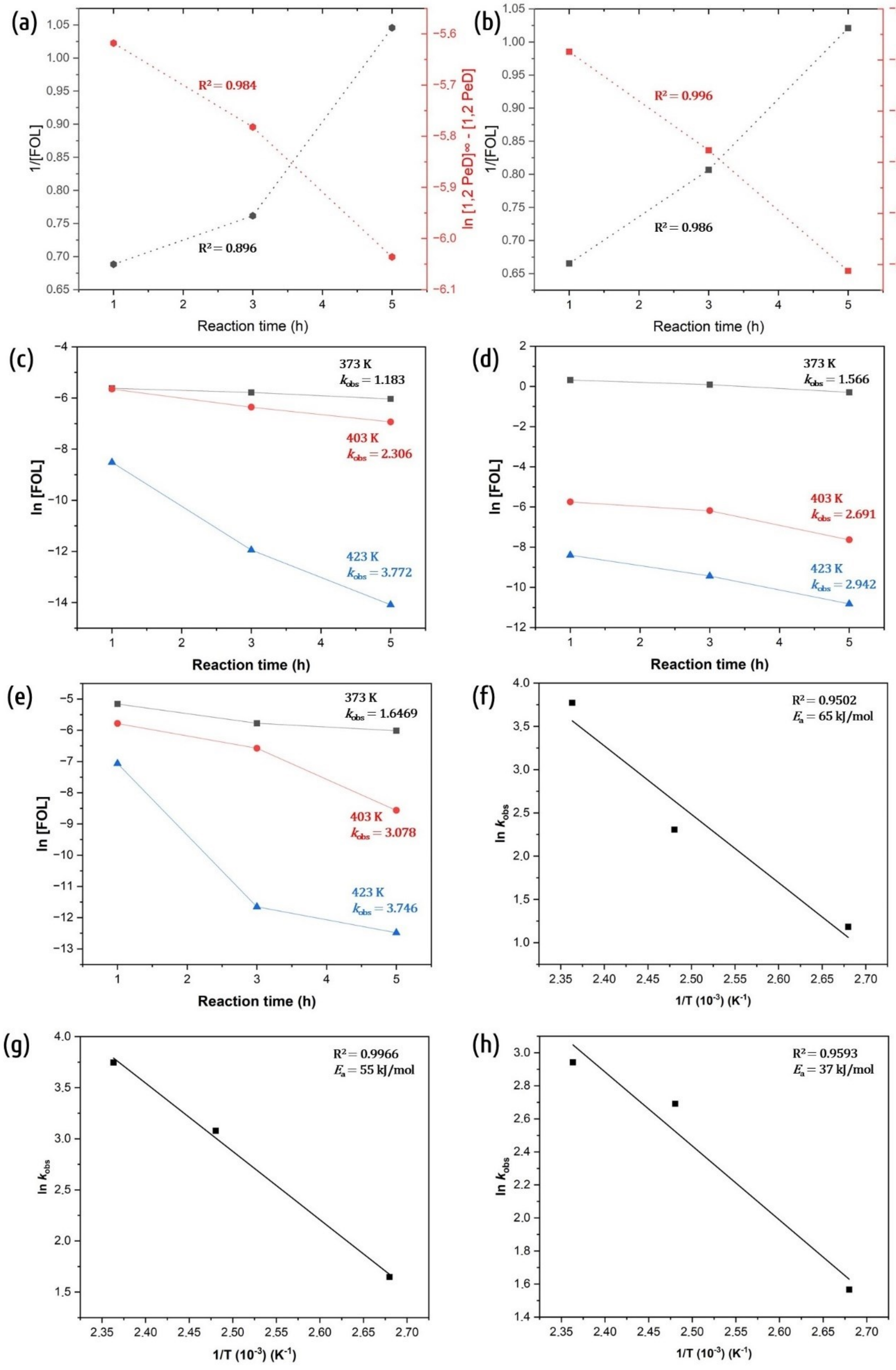

Fig. 5. Plots of 1/[FOL] vs reaction time and ln[C]$_\infty$ - [C] vs reaction time at 100°C for the reaction catalyzed by (a) $ZrOCl_2.8H_2O$ and (b) $VOSO_4.H_2O$; k_{obs} pseudo first-order of FOL hydrogenolysis at 100, 130 and 150 °C for the reaction catalyzed by (c) $ZrOCl_2.8H_2O$, (d) $VOSO_4.H_2O$, and (e) $FeCl_3.6H_2O$ ([C] is the product concentration); Arrhenius plot of hydrogenolysis of FOL catalyzed by (f) $ZrOCl_2.8H_2O$, (g) $VOSO_4.xH_2O$, and (h) $FeCl_3.6H_2O$

4. Conclusion

The catalysts $FeCl_3·6H_2O$, $VOSO_4·H_2O$, and $ZrOCl_2·8H_2O$ demonstrated superior catalytic activity in the hydrogenolysis of furfuryl alcohol compared to $FeSO_4·7H_2O$, $CuSO_4·5H_2O$, $NiCl_2$, $Al(NO_3)_3·H_2O$, $CoCl_2$, and $Zn(NO_3)_2·6H_2O$ catalysts. Using only 0.2 mmol% of these catalysts, a 1,2-PeD yield exceeding 10% was achieved at 100 °C in 1 hour. The optimal reaction condition with these three catalysts to produce 1,2-PeD was reached at 150 °C for 1 h using 1 ml of 2-propanol as the hydrogen source. Under this condition, the $ZrOCl_2.8H_2O$ catalyst was able to convert 95.5% furfuryl alcohol with a selectivity of 31.7% for 1,2-PeD. Meanwhile, the $VOSO_4.H_2O$ catalyst achieved 80.5% conversion of furfuryl alcohol with 45.8% selectivity for 1,2-PeD. Both results were obtained with only 0.6 mmol% catalyst. Meanwhile, 0.4 mmol% of $FeCl_3.6H_2O$ catalyst converted 94.9% of furfuryl alcohol with 32.6% selectivity for 1,2-PeD. Kinetic studies suggest that the reactions likely follow pseudo-first-order kinetics, with experimental activation energies (E_a) of 65 kJ/mol, 55 kJ/mol, and 37 kJ/mol for reactions catalyzed by $ZrOCl_2.8H_2O$, $VOSO_4.H_2O$ and $FeCl_3.6H_2O$, respectively. The hydrogenolysis reaction of furfuryl alcohol towards 1,2-PeD has a positive enthalpy ($\Delta H^{\ddagger} > 0$), a negative entropy ($\Delta S^{\ddagger} < 0$), and a positive Gibbs free energy ($\Delta G^{\ddagger} > 0$). This implies the reaction will not occur spontaneously and requires external energy input for it to proceed.

Declaration

Ethical Approval

Not applicable

Competing interests

The authors declare no competing interests

Authors' contributions

Hendra J. Situmorang, Muhammad R. Pratama, Istifhamy Irnanda: Investigation, Formal Analysis, Visualization and initial manuscript writing. Siti Hartinah Qurbayni: Investigation, Formal Analysis. Yessi Permana, Husni W Wijaya: Resources, Review & Editing. Ubed Sonai Fahruddin Arrozi: Conceptualization, Methodology, Investigation, Validation, Supervision, Review & Editing, Resources, Funding Acquisition, and Project Administration.

Availability of data and materials

The data presented in this article will be available on request from the corresponding author

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