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Mechanism of the hydrogenolysis of ethers over silica-supported rhodium catalyst modified with rhenium oxide

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ABSTRACT

The Rh–ReO_x/SiO_2 (Re/Rh = 0.5) exhibited high activity in the hydrogenolysis of ethers with an OH group. The C—O bond neighboring —CH_2OH group was selectively dissociated: The hydrogenolysis of tetrahydro-5-methyl-2-furfuryl alcohol and 2-isopropoxyethannol gave 1,5-hexanediol and ethanol + isopropanol, respectively. This tendency suggests the regioselective C—O dissociation mechanism via anion intermediate formed by the attack of hydride and the subsequent protonation of the anion.

1. Introduction

Catalytic conversion of renewable biomass resources, as feedstock for the chemical industry, becomes more and more important because of the worldwide and serious energy and environmental problems [1,2]. Furan derivatives, such as furfural and 5-hydroxymethylfurfural (5-HMF), can be produced from renewable biomass resources by acid-catalyzed dehydration of pentoses and hexoses, respectively. These compounds have the potential to be sustainable substitutes for building blocks derived from petrochemical in the production of plastics and fine chemicals [3,4]. Tetrahydrofurfuryl alcohol (THFA) is manufactured by total hydrogenation of furfural via furfuryl alcohol [5–7]. THFA is widely used as a "green" solvent for fats and resin in industry applications because of its relatively benign nature and very low toxicity [5]. In addition, THFA is also able to be used in the production of 1,5-pentanediol, which can be used as a monomer for the production of polyesters and polyurethanes [8]. Schniepp and Geller have proposed the multistep method for the production of 1,5-pentanediol from THFA [9]. However, this method required the isolation and purification of intermediates, and the yield of 1,5-pentanediol was 70% [9].

Recently, we reported that Rh–ReO_x/SiO_2 [10], Rh-MoO_x/SiO_2 [11], and Rh–ReO_x/C [12] are effective for the hydrogenolysis of THFA. These catalysts can produce 1,5-pentanediol from THFA in high yield (Rh–ReO_x/SiO_2: 86%, Rh–MoO_x/SiO_2: 85%, Rh–ReO_x/C: 94%). In addition, catalyst characterization suggested that Rh metal particles directly modified with corresponding oxide species are formed. From these results, it is thought that the interface between metal oxide species and Rh metal surface can play an important role on the catalysis in the hydrogenolysis. However, the reaction mechanism is not elucidated. In this article, the activity and product distribution of Rh–ReO_x/SiO_2 (Re/Rh = 0.5) and Rh/SiO_2 were investigated in the hydrogenolysis of various cyclic ethers and non-cyclic ethers in order to elucidate the reaction mechanism of the THFA hydrogenolysis to 1,5-pentanediol. The kinetic analysis of the THFA hydrogenolysis was also carried out for the understanding of the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

A Rh–ReO_x/SiO_2 catalyst was prepared by sequentially impregnating SiO_2 with aqueous solutions of $RhCl_3{\cdot}3H_2O$ (Soekawa Chemical Co., Ltd.) and NH_4ReO_4 (Soekawa Chemical Co., Ltd.). First, a $RhCl_3{\cdot}3H_2O$ aqueous solution was impregnated to SiO_2 (Fuji Silysia Chemical Ltd., G-6, BET surface area 535 m^2/g). Second, it was dried at 383 K for 12 h. Then, an NH_4ReO_4 aqueous solution was impregnated to Rh/SiO_2 after the drying procedure. After the impregnation procedure and another drying at 383 K for 12 h, it was calcined in air at 773 K for 3 h. The loading amount of Rh was 4 wt.%. The catalyst with Re/Rh = 0.5 gave the best performance

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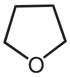
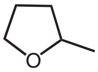
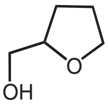
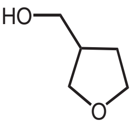
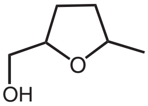
in catalysts with various Re amount and was used throughout this study. Catalysts were used in powdery form with granule size of <100 mesh. A Pd/C (Pd: 5 wt.%) catalyst was purchased from Wako Pure Chemical Industries, Ltd. and was used for acetol hydrogenation as references.

2.2. Activity test

Catalytic testing was performed in a 190-ml stainless steel autoclave with an inserted glass vessel. An aqueous solution of THFA (Wako Pure Chemical Industries Ltd.) was placed into the autoclaves with a Teflon-coated magnetic spinner with a rugby-boll shape and an appropriate amount of catalysts. After sealing the reactors, their air content was purged by flushing thrice with 1 MPa hydrogen (99.99%; Takachiho Trading Co. Ltd.). Autoclaves were then heated to 393 K and pressurized to 1 MPa for the reduction pretreatment. The temperature was monitored using a thermocouple inserted in the autoclave. After 1 h, the H_2 pressure was increased to appropriate pressure at reaction temperature. During the experiment, the stirring rate was fixed at 500 rpm (magnetic stirring). After an appropriate reaction time, the reactors were cooled down and all the gases were collected in a gas bag. The autoclave contents were transferred to vials, and the catalysts were separated by centrifugation and filtration. The standard conditions for the reaction were as follows: 393 K reaction temperature, 8.0 MPa initial hydrogen pressure, 4 h reaction time, 5 wt.% THFA aqueous solution, and 50 mg supported metal catalyst. The parameters were changed appropriately in order to investigate the effect of reaction conditions. Details of the reaction conditions are described in each result. The products were analyzed using a gas chromatography (GC-17A; Shimadzu Corp.) equipped with FID. A Rtx®-1 PONA capillary column (diameter 0.25 mmϕ, 100 m) was used for the separation. Products were also identified using GC–MS (QP5050, Shimadzu). The conversion and the selectivity were determined by the external standard method using an aqueous solution of each product with known concentration. The mass balance was checked by comparing between amount of products and that of unreacted reactants, and the difference was within 5% in all experiments. The agreement in terms of the mass balance indicated that polymeric by-products were not formed. The hydrogenolysis of tetrahydrofuran (Wako Pure Chemical Industries Ltd.), 2-methyltetrahydrofuran (Wako Pure Chemical Industries Ltd.), tetrahydro-3-furan methanol (Aldrich Chemical Co. Inc.), 2-ethoxyethanol (Wako Pure Chemical Industries Ltd.), 2-butoxyethanol (Wako Pure Chemical Industries Ltd.), 2-isopropoxyethanol (Wako Pure Chemical Industries Ltd.), and tetrahydro-5-methyl-2-furfuryl alcohol synthesized by hydrogenation of 5-methyl-2-furfural (Wako Pure Chemical Industries Ltd.) with Raney Ni [13] was also tested in the similar way to the case of THFA. In each test, 20 ml of 5 wt.% aqueous solution of the substrate was used. Selectivities were calculated in carbon basis. The C—C cracking products are summarized as “Others” in the results. The hydrogenation of acetol (Wako Pure Chemical Industries Ltd.) was also tested in the similar way to the case of THFA. Because of the high reactivity of acetol, the reduction and reaction temperatures were lowered to 353 K. The reaction of dihydropyran (Wako Pure Chemical Industries Ltd.) was also tested in the similar way to the case of THFA. The hydrogenolysis of THFA under the coexistent product was also tested in almost the same way to the case of THFA, and 3-methyl-1,5-pentanediol (Wako Pure Chemical Industries Ltd.) and 1-butanol (Wako Pure Chemical Industries Ltd.) were used as additive products in this reaction. To check the absence of diffusion control in the kinetics, we examined the effect of the stirring rate in this reaction (Supplementary information Table S1). The change in the stirring rate did not affect the reaction when the rate was higher than 50 rpm, indicating that the diffusion rate of H_2 was much higher than the reaction rate in the standard conditions (500 rpm).

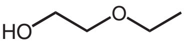
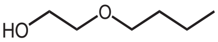
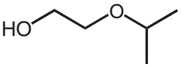
Table 1
Catalytic performance in the hydrogenolysis of various cyclic ethers over Rh–ReO_x/SiO_2 (Re/Rh = 0.5) and Rh/SiO_2.[a]

Entry	Substrate (amount (mmol))		Catalyst	Conversion (mmol)	Amount of products (mmol) [selectivity/%]						TOF (h^{-1})
					1-BuOH						
1		(14)	Rh–ReO_x/SiO_2	0.2	0.2 [>99]						15
2			Rh/SiO_2	1.3	1.3 [>99]						43
					1-PeOH	2-PeOH	Others				
3		(12)	Rh–ReO_x/SiO_2	0.1	0.0	0.1 [90]	0.0 [10]				8
4			Rh/SiO_2	0.7	0.0	0.6 [90]	0.1 [10]				23
					1,5-PeD	1,2-PeD	1-PeOH	2-PeOH	2-MTHF	Others	
5		(9.8)	Rh–ReO_x/SiO_2	5.6	5.3 [94]	0.0	0.2 [4]	0.0	0.1 [1]	0.0	420
6			Rh/SiO_2	0.6	0.1 [18]	0.3 [62]	0.1 [6]	0.0	0.0	0.1 [14]	20
					2-M-1,4-BuD	2-E-1,3-PrD	3-MTHF	Others			
7		(9.8)	Rh–ReO_x/SiO_2	0.3	0.1 [45]	0.0	0.1 [31]	0.1 [24]			23
					1,5-HxD	1,2-HxD	2,5-DMTHF	2-HxOH	1-HxOH	Others	
8		(8.5)	Rh–ReO_x/SiO_2	4.0	3.8 [92]	0.0	0.0 [1]	0.1 [3]	0.0	0.1 [4]	300

PeD = pentanediol, PeOH = pentanol, 2-MTHF = 2-methyltetrahydrofuran, 1-BuOH = 1-butanol, 2-M-1,4-BuD = 2-methyl-1,4-butanediol, 2-E-1,3-PrD = 2-ethyl-1,3-propanediol, 3-MTHF = 3-methyltetrahydrofuran, 2,5-DMTHF = 2,5-dimethyltetrahydrofuran.

[a] Reaction conditions: 5 wt.% reactant aqueous solution 20 ml, catalyst 50 mg (2 mg Rh), reaction temperature 393 K, initial H_2 pressure 8.0 MPa, reaction time 4 h.

Table 2
Catalytic performance in the hydrogenolysis of various ethylene glycol ethers over Rh–ReO_x/SiO_2 (Re/Rh = 0.5).[a]

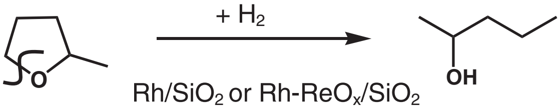
Entry	Substrate (amount (mmol))	Conversion (mmol)	Amount of products (mmol) [selectivity/%]			TOF (h^{-1})
1	(11) 	3.6	Ethanol 7.2 [100]	Others 0.0		270
2	(8.3) 	4.9	1-BuOH 4.9 [64]	Ethanol 4.9 [33]	Others 0.1 [2]	368
3	(9.6) 	4.0	Ethanol 4.0 [40]	2-Propanol 4.0 [60]		300

[a] Reaction conditions: 5 wt.% reactant aqueous solution 20 ml, catalyst 50 mg (2 mg Rh), reaction temperature 393 K, initial H_2 pressure 8.0 MPa, reaction time 4 h. 1-BuOH = 1-butanol.

3. Results and discussion

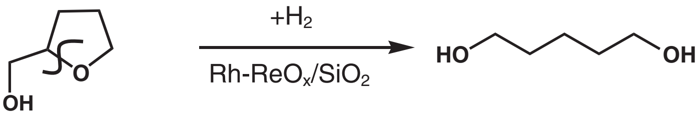
3.1. Catalytic performance in the hydrogenolysis of cyclic ethers over Rh–ReO_x/SiO_2 and Rh/SiO_2

Table 1 lists the results of hydrogenolysis of cyclic ethers over Rh–ReO_x/SiO_2 (Re/Rh = 0.5) and Rh/SiO_2, and the turnover frequency (TOF) was calculated on the basis of the CO adsorption amount. The CO adsorption amount of Rh–ReO_x/SiO_2 (Re/Rh = 0.5) and Rh/SiO_2 was CO/Rh = 0.17 and 0.39, respectively [10], where the CO adsorption amount represents the number of surface Rh atoms because the ReO_x species do not adsorb CO [14–16]. In the hydrogenolysis of tetrahydrofuran (Entries 1 and 2), Rh/SiO_2 and Rh–ReO_x/SiO_2 gave 1-butanol selectively. The amount of 1-butanol on Rh/SiO_2 was much larger than that on Rh–ReO_x/SiO_2, and the TOF of Rh/SiO_2 was higher than that of Rh–ReO_x/SiO_2. In the hydrogenolysis of 2-methyltetrahydrofuran (Entries 3 and 4), both catalysts gave 2-pentanol as a main product as shown below.

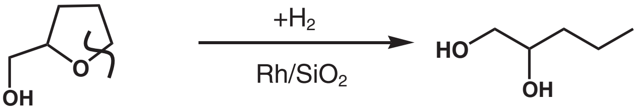


(1)

It is characteristic that the activity of both Rh–ReO_x/SiO_2 and Rh/SiO_2 in the hydrogenolysis of 2-methyltetrahydrofuran became about half of that in the hydrogenolysis of tetrahydrofuran. The decrease in the activity shows that the presence of methyl group lowers the reactivity of the C—O bond connecting the methyl group in 2-methyltetrahydrofuran.



(2)

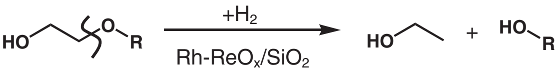


(3)

In the case of the THFA hydrogenolysis (Entries 5 and 6), Rh–ReO_x/SiO_2 gave 1,5-pentanediol with high selectivity, and another important point is that the TOF of the THFA hydrogenolysis was much higher than that of the hydrogenolysis of tetrahydrofuran and 2-methyltetrahydrofuran. In contrast, Rh/SiO_2 gave 1,2-pentanediol as a main product, and the TOF of the THFA hydrogenolysis was comparable to that of 2-methyltetrahydrofuran. This means that the presence of —CH_2OH group can interfere with the hydrogenolysis of tetrahydrofuran ring (Entry 6) similarly to the case of methyl group (Entry 4) over Rh/SiO_2, and the decrease in the reactivity by both —CH_2OH and methyl group is probably due to the steric hindrance judging from the product distribution. Another important point is that the hydrogenolysis of tetrahydro-3-furan-methanol hardly proceeds on Rh–ReO_x/SiO_2 (Entry 7). This result indicates that the position of —CH_2OH group is very important for the hydrogenolysis of the tetrahydrofuran ring. The hydrogenolysis of tetrahydro-5-methyl-2-furfuryl alcohol with a similar molecular structure to THFA gave 1,5-hexanediol, and the TOF of this reaction is comparable to that of THFA (Entry 8).

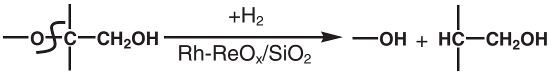
3.2. Application of Rh–ReO_x/SiO_2 to the hydrogenolysis of non-cyclic ethers such as ethylene glycol mono-ethers

Table 2 lists the results of hydrogenolysis of ethylene glycol mono-ethers. In the case of 2-ethoxyethanol and 2-buthoxyethanol (Entries 1 and 2), it is characteristic that the TOF in the hydrogenolysis of these ethers was comparable to that in the hydrogenolysis of THFA and tetrahydro-5-methyl-2-furfuryl alcohol (Table 1). Another important point is the product distribution, and two mono-alcohols were selectively formed, and the formation of ethylene glycol was not detected at all. These behaviors are represented by the reaction scheme as below.



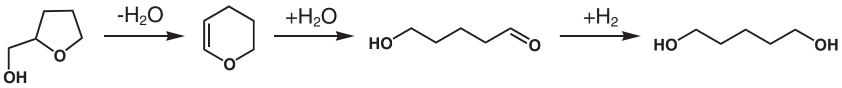
(R = CH_2CH_3, $CH_2CH_2CH_2CH_3$, $CH(CH_3)_2$) (4)

A common structure in THFA, tetrahydro-5-methyl-2-furfuryl alcohol, and these ethylene glycol ethers is —O—C—CH_2OH. And it is thought that Rh–ReO_x/SiO_2 recognizes this structure and catalyzes the hydrogenolysis of the C—O bond as shown below.


$$-O-C-CH_2OH \xrightarrow[Rh\text{-}ReO_x/SiO_2]{+H_2} -OH + HC-CH_2OH \qquad (5)$$

3.3. Reaction scheme of the THFA hydrogenolysis over Rh–ReO_x/SiO_2

A reaction scheme of the multistep conversion of THFA to 1,5-pentanediol via dihydropyran and δ-hydroxyvaleraldehyde as shown below has been reported [9].



(6)

According to the previous report, the yield of 1,5-pentanediol was increased to 70% by the purification of reaction intermediates [9]. In order to check the contribution of this reaction route, we evaluated the reaction of dihydropyran over Rh–ReO_x/SiO_2 under the presence of H_2.

Under the reaction conditions of dihydropyran 12 mmol, H_2O 19 mL, 8.0 MPa H_2, 0.05 g Rh–ReO_x/SiO_2, 393 K and 4 h, 9.4 mmol 1,5-pentanediol, and 1.3 mmol tetrahydropyran were formed. This result indicates that the formation of 1,5-pentanediol should accompany the tetrahydropyran formation. However, the formation of tetrahydropyran was actually below the detection limit in the THFA hydrogenolysis over Rh–ReO_x/SiO_2. The reaction route over Rh–ReO_x/SiO_2 is different from that via dihydropyran reported previously. Under the same conditions of the reaction of dihydropyran except that the catalyst was not used, 7.7 mmol δ-hydroxyvaleraldehyde was formed. This result suggests that the formation of 1,5-pentanediol from dihydropyran over Rh–ReO_x/SiO_2 consists of non-catalytic conversion of dihydropyran to δ-hydroxyvaleraldehyde and hydrogenation of δ-hydroxyvaleraldehyde to 1,5-pentanediol catalyzed by Rh–ReO_x/SiO_2.

Table 3
Effect of addition of sulfuric acid for hydrogenolysis of THFA over Rh–ReO_x/SiO_2 (Re/Rh = 0.5).[a]

H^+/Re	Conversion (%)	Selectivity (%)				
		1,5-PeD	1,2-PeD	1-PeOH	2-MTHF	Others
0	57	94	0.0	4.6	0.4	1.0
1	62	97	0.0	2.4	0.2	0.4
2	66	97	0.0	2.2	0.1	0.7
3	63	97	0.0	2.7	0.1	0.2
10	63	96	0.0	2.8	0.3	0.9

PeD = pentanediol, PeOH = pentanol, 2-MTHF = 2-methyltetrahydrofuran.
[a] Reaction conditions: 5 wt.% THFA aqueous solution 20 ml, catalyst 50 mg (2 mg Rh), reaction temperature 393 K, initial H_2 pressure 8.0 MPa, reaction time 4 h.

It has been reported that the hydrogenolysis of glycerol to propanediols proceeds in the dehydration catalyzed by acid catalysts and subsequent hydrogenation catalyzed by metal catalysts, which has been regarded as an indirect reaction route [17–25]. In this indirect reaction route, the role of acid catalysts for the dehydration is important. In addition, if THFA can be converted to dihydropyran, the subsequent reaction to 1,5-pentanediol can proceed as mentioned above, and the reaction rate of dihydropyran was much higher than the hydrogenolysis of THFA over the Rh–ReO_x/SiO_2 catalyst. This tendency indicates that the conversion of THFA to dihydropyran can be a rate-determining step in the reported reaction route, where the conversion of THFA to dihydropyran is catalyzed by acid catalysts. Therefore, the effect of addition of H_2SO_4 to the THFA hydrogenolysis over Rh–ReO_x/SiO_2 (Re/Rh = 0.5) (Table 3) was investigated. The conversion and product distribution were not influenced by the presence of H_2SO_4. These tendencies also indicate that the reported reaction route via dihydropyran and δ-hydroxyvaleraldehyde does not contribute at all in the THFA hydrogenolysis over Rh–ReO_x/SiO_2. Here, we propose the direct route of the THFA hydrogenolysis.

3.4. Reaction kinetics of the hydrogenolysis of THFA

For the elucidation of the elementary steps in the direct THFA hydrogenolysis, a kinetic study was carried out. Table 4 shows the effect of the THFA concentration on the catalyses of Rh–ReO_x/SiO_2 (Re/Rh = 0.5) and Rh/SiO_2. In these experiments, the concentration of THFA was varied by changing the H_2O amount at the constant amount of THFA. Reaction rate was calculated from the

Table 4
Effect of the concentration of THFA in the hydrogenolysis of THFA over Rh–ReO_x/SiO_2 (Re/Rh = 0.5)[a] and Rh/SiO_2.[b]

Catalyst	Concentration of THFA (%)	Conversion (%)	Selectivity (%)						Reaction rate (mmol g-cat^{-1} h^{-1})
			1,5-PeD	1,2-PeD	1-PeOH	2-PeOH	2-MTHF	Others	
Rh–ReO_x/SiO_2	20	11	98	0.0	2.0	0.0	0.0	0.0	67
	30	11	98	0.0	1.5	0.0	0.5	0.3	62
	40	14	98	0.0	2.0	0.0	0.0	0.0	80
	50	13	98	0.0	1.9	0.0	0.3	0.3	74
	60	13	97	0.0	3.0	0.0	0.0	0.0	77
Rh/SiO_2	10	2.8	14	68	5.3	0.0	3.9	8.7	2.7
	20	4.1	20	68	3.3	0.0	2.0	6.5	4.0
	40	4.7	23	62	3.9	0.2	4.2	7.6	4.6
	60	5.6	20	65	4.4	0.3	4.4	6.6	5.5

PeD = pentanediol, PeOH = pentanol, 2-MTHF = 2-methyltetrahydrofuran.
[a] Reaction conditions: THFA 6 g (58 mmol), catalyst 50 mg (2 mg Rh), reaction temperature 393 K, initial H_2 pressure 8.0 MPa, reaction time 2 h.
[b] Reaction conditions: THFA 3 g(29 mmol), catalyst 150 mg (6 mg Rh), reaction temperature 393 K, initial H_2 pressure 8.0 MPa, reaction time 2 h.

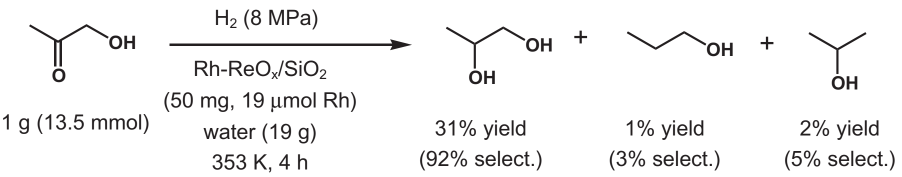
Table 5
Effect of H_2 pressure on the THFA hydrogenolysis over $Rh–ReO_x/SiO_2$ (Re/Rh = 0.5).[a]

H_2 pressure (MPa)	Conversion (%)	Selectivity (%)						Reaction rate (mmol g-cat^{-1} h^{-1})
		1,5-PeD	1,2-PeD	1-PeOH	2-PeOH	2-MTHF	Others	
2.0	3.5	97	0.0	1.9	0.0	0.2	0.0	20
4.0	6.7	96	0.0	2.7	0.0	0.3	0.0	39
6.0	11	98	0.0	1.6	0.0	0.3	0.0	65
8.0	13	97	0.2	1.6	0.0	0.3	0.2	77

PeD = pentanediol, PeOH = pentanol, 2-MTHF = 2-methyltetrahydrofuran.

[a] Reaction conditions: 60 mass% aqueous solution of THFA 10 mL, catalyst 50 mg (2 mg Rh), reaction temperature 393 K, reaction time 2 h.

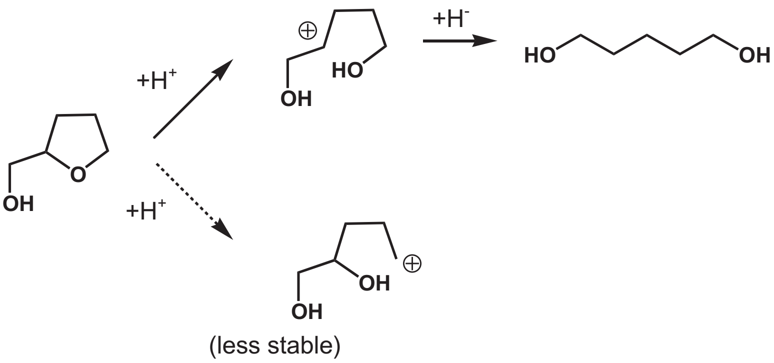
converted amount of THFA divided by the reaction time and the catalyst amount at low conversion (<15%) of THFA. The reaction rate over $Rh–ReO_x/SiO_2$ was almost constant in the THFA concentration between 20% and 60%; on the other hand, the rate over Rh/SiO_2 increased gradually with increasing THFA concentration. The reaction order with respect to the THFA concentration over $Rh–ReO_x/SiO_2$ and Rh/SiO_2 was estimated to be zero and 0.4, respectively. In particular, the reaction order indicated that $Rh–ReO_x/SiO_2$ more strongly adsorbs THFA than Rh/SiO_2. Therefore, it is suggested that ReO_x species is responsible for the strong adsorption of THFA on $Rh–ReO_x/SiO_2$.



(7)

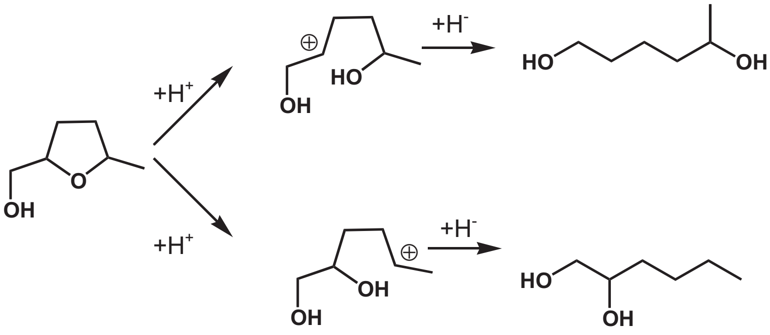
Table 5 shows the effect of H_2 pressure on the THFA hydrogenolysis over $Rh–ReO_x/SiO_2$ (Re/Rh = 0.5). In this reaction, the H_2 pressure during the reaction was almost constant because THFA conversion was relatively low. The THFA conversion increased linearly with increasing H_2 pressure, and the reaction order with respect to H_2 pressure was calculated to be +1. The first reaction order with respect to H_2 pressure in the THFA hydrogenolysis over $Rh–ReO_x/SiO_2$ determined from the results in Table 5 means that the activation of H_2 is an important step. Based on the results, ReO_x/SiO_2 without Rh showed very low hydrogenolysis activity [10], and Rh can play a role on H_2 activation. Generally, H_2 molecule is dissociated to two hydrogen atoms on the metal surface ($H_2 \rightarrow 2H$). In this case, it is known that the reaction order with respect to H_2 pressure is 1/2 in the Langmuir–Hinshelwood mechanism. Another possible H_2 activation is heterolytic activation ($H_2 \rightarrow H^+ + H^-$) [26]. The nature of the active hydrogen species was also investigated using ketone hydrogenation, which has been known to proceed by hydride transfer [27,28]. The $Rh–ReO_x/SiO_2$ showed high catalytic activity in the acetol hydrogenation and gave 1,2-propanediol as a main product (Eq. (7)). Small amounts of 1- and 2-propanols were also produced by the hydrogenolysis of produced 1,2-propanediol.

On the other hand, Pd/C, which is known to activate H_2 to two hydrogen atoms [29], has no activity in the same reaction conditions [17], and Rh/SiO_2 also showed very low activity in the hydrogenation of acetol. From the results of acetol hydrogenation, it was suggested that one hydride species and one proton are formed by heterolytic activation of H_2 over $Rh–ReO_x/SiO_2$ catalyst. In the case that the hydrogenolysis reaction can proceed by the attack of proton and/or hydride, the product selectivity is strongly influenced by the stability of cation and anion reaction intermediates. One typical reaction route is S_N1-type one that consists of protonation of oxygen atom, dissociation of C—O bond to form carbocation intermediate, and hydride transfer (proton → hydride mechanism). In the THFA hydrogenolysis, this proton → hydride mechanism can explain the product distribution. As shown below, 1,5-pentanediol is formed via more stable secondary carbocation.



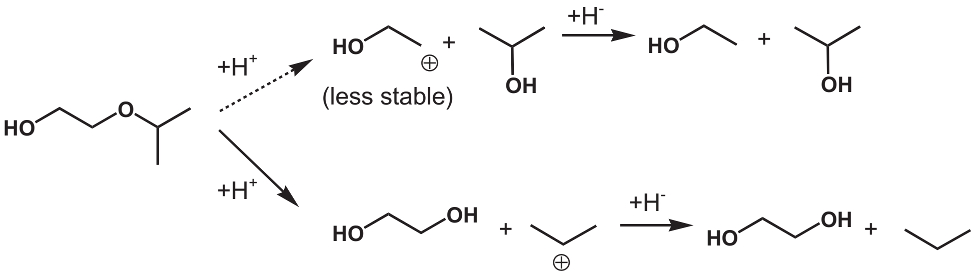
(8)

However, in fact, this proton → hydride mechanism cannot explain the product distribution in the hydrogenolysis of tetrahydro-5-methyl-2-furfuryl alcohol (Table 1, Entry 8) and 2-isopropoxyethanol (Table 2, Entry 3). In the case of tetrahydropyran-5-methyl-2-furufuryl alcohol, the carbocations formed by the proton attack are both secondary ones, suggesting the formation of both 1,5-hexanediol and 1,2-hexanediol in the scheme below.



(9)

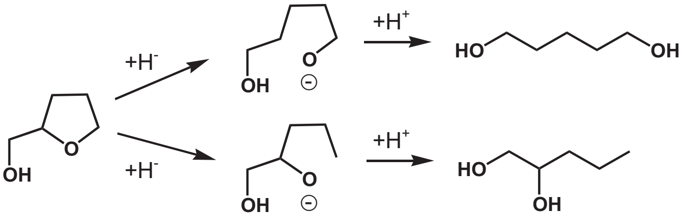
However, in fact, the formation of 1,2-hexanediol is not detected (Table 1, Entry 8). Furthermore, in the hydrogenolysis of 2-isopropoxyethanol by the proton attack, the formation of ethylene glycol and propane could be more preferable than that of ethanol and 2-propanol judging from the secondary cation intermediate as below.



(10)

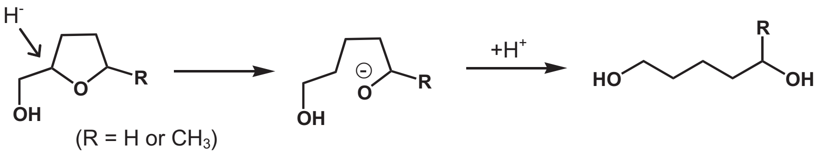
This is completely opposite to the experimental result that Rh–ReO$_x$/SiO$_2$ catalyzed the selective hydrogenolysis of 2-isopropoxyethanol to ethanol and 2-propanol (Table 2, Entry 3). This discussion denies the proton → hydride mechanism. In addition, the small effect of the acidity on the hydrogenolysis catalysis (Table 3) also indicates that the hydrogenolysis mechanism over Rh–ReO$_x$/SiO$_2$ is not the proton → hydride mechanism and suggests that the proton-transfer step is located after the rate-determining step.

Next, we consider the mechanism via the anion intermediate formed by the attack of hydride and subsequent protonation of the anion (hydride → proton mechanism).

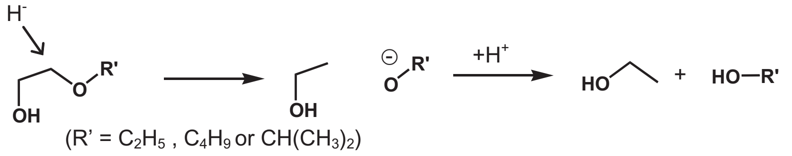


(11)

In the case of the THFA hydrogenolysis, the difference in the stability of two anion intermediates is thought to be small, and the product distribution is not determined by the stability of the anion intermediates. One possible explanation is the regioselective hydride attack. If hydride attacks the reactant from the side of —CH$_2$OH group, all the product distribution in the hydrogenolysis of THFA, tetrahydro-5-methyl-2-furfuryl alcohol, and ethylene glycol ethers can be explained as below.

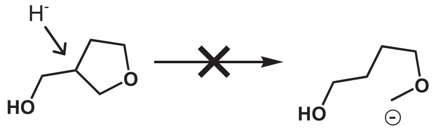


(12)



(13)

In addition, the regioselective hydride attack mechanism also explains the almost no reactivity of tetrahydro-3-furan methanol over Rh–ReO$_x$/SiO$_2$ because of the less stability of carboanion as shown below.



(14)

3.5. Kinetic modeling

Based on the proposed regioselective hydride attack mechanism of Rh–ReO$_x$/SiO$_2$-catalyzed hydrogenolysis, we carried out the kinetic modeling using a Langmuir–Hinshelwood type (L–H) one. In the THFA hydrogenolysis over the Rh–ReO$_x$/SiO$_2$ catalyst, the synergy between Rh and ReO$_x$ is incorporated into the present model based on the L–H mechanism using two different sites, including Rh for H$_2$ activation and ReO$_x$ for the THFA adsorption. The first order of H$_2$ and the zero order of THFA also support two different adsorption sites because the competitive adsorption of H$_2$ and THFA may give strong negative reaction order with respect to THFA. We have characterized the Rh–ReO$_x$/SiO$_2$ catalyst after the reduction at 393 K by TEM, XRD, CO adsorption, TPR, and EXAFS. The results showed the structure where Rh metal particles are covered with ReO$_x$ clusters with Re valence of 2–3 [10,30,31]. We also verified that the structure was almost unchanged after the catalytic use [10,30,31].

The proposed regioselective hydride attack mechanism of Rh–ReO$_x$/SiO$_2$-catalyzed hydrogenolysis of THFA is shown in Fig. 1a. First, THFA is adsorbed on ReO$_x$ cluster to form alkoxide species (i). Next, H$_2$ is activated on Rh metal surface, and adsorbed hydride species and proton are formed (ii). The substrate bound on the interface between Rh and ReO$_x$ reacts with the adsorbed hydride species (iii). Reactions of the produced alkoxide with proton and another substrate release products (iv). The step (iv) also produces the alkoxide of substrate, followed by step (ii) of the next cycle. Based on this reaction scheme in Fig. 1a, the elemental steps are represented as below.

$$\mathrm{THFA} + \sigma_{\mathrm{Re}} \overset{K_{\mathrm{THFA}}}{\rightleftarrows} (\mathrm{THFA})_{\mathrm{Re}} \tag{15}$$

$$1{,}5\text{-PeD} + \sigma_{\mathrm{Re}} \overset{K_{1,5\text{-PeD}}}{\rightleftarrows} (1{,}5\text{-PeD})_{\mathrm{Re}} \tag{16}$$

$$\mathrm{H_2} + \sigma_{\mathrm{Rh}} \overset{K_{\mathrm{H2}}}{\rightleftarrows} \mathrm{H^+} + (\mathrm{H^-})_{\mathrm{Rh}} \tag{17}$$

$$(\mathrm{THFA})_{\mathrm{Re}} + (\mathrm{H^-})_{\mathrm{Rh}} \xrightarrow{k_1} (a-1,5-\mathrm{PeD})_{\mathrm{Re}} + \sigma_{\mathrm{Rh}} \tag{18}$$

$$(a-1,5-\mathrm{PeD})_{\mathrm{Re}} + H^+ \xrightarrow{k_2} 1,5-\mathrm{PeD} + \sigma_{\mathrm{Re}} \tag{19}$$

Here, (A)$_M$ means the adsorbed species of compound A on M (M = Rh, Re) involved in the catalysis. σ_M represents the vacant site or the site occupied by the solvent of M. a-1,5-PeD represents the deprotonated anion of 1,5-PeD. It is suggested that Rh plays a role on the H$_2$ activation, where Rh metal tends to activate H$_2$ to two H atoms. Judging from much lower activity of Rh/SiO$_2$ than that of Rh–ReO$_x$/SiO$_2$, the H atom activated on Rh metal surface has low reactivity. Therefore, a different active hydrogen species can be formed on Rh–ReO$_x$/SiO$_2$, and the hydride species is suggested

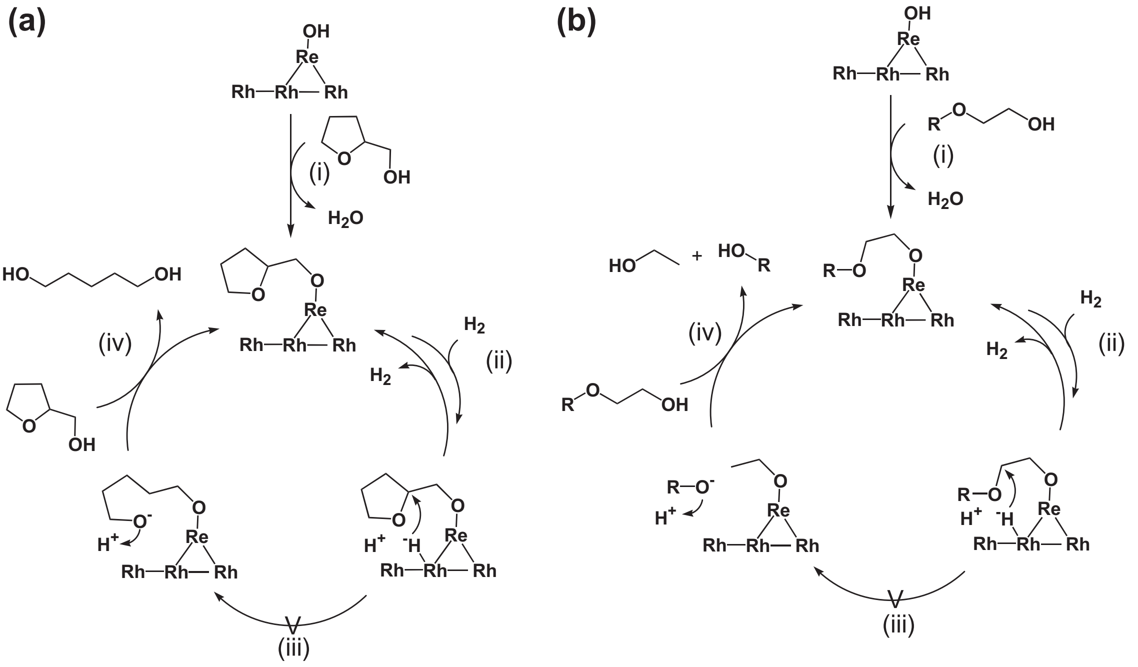
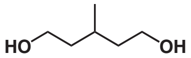
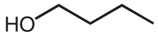


Fig. 1. Proposed mechanism of THFA (a) and ethylene glycol ethers (b) hydrogenolysis over Rh–ReO$_x$/SiO$_2$.

Table 6
Effect of the copresence of di- and mono-ols in the hydrogenolysis of THFA over Rh–ReO_x/SiO_2 (Re/Rh = 0.5)[a].

Additive	Conversion (%)	Selectivity (%)					Reaction rate (mmol g-cat^{-1} h^{-1})
		1,5-PeD	1,2-PeD	1-PeOH	2-MTHF	Others	
None	25	98	0.0	1.3	0.0	0.2	74
	8.5	97	0.0	2.1	0.3	0.9	25
	14	95	0.0	1.6	0.1	2.9	41

PeD = pentanediol, PeOH = pentanol, 2-MTHF = 2-methyltetrahydrofuran.

[a] Reaction conditions: THFA 3 g (29 mmol), additive 29 mmol, solvent: water (total 10 mL), catalyst 50 mg (2 mg Rh), reaction temperature 393 K, initial H_2 pressure 8.0 MPa, reaction time 2 h.

from the product selectivity in the hydrogenolysis of cyclic and non-cyclic ethers. The formation of this hydride species can be induced by the presence of ReO_x, although ReO_x itself has low ability to activate hydrogen. It is thought that Rh metal species activate H_2 to two H atoms, which move to the interface of Rh and ReO_x, and two H atoms are converted to a proton in the aqueous solution and a hydride adsorbed on Rh atom at the interface of Rh and ReO_x. This hydrogen activation step is represented by Eq. (17)

According to the effect of the THFA concentration (Table 4), it is suggested that the THFA can be adsorbed on Rh–ReO_x/SiO_2 strongly. In particular, —CH_2OH group in THFA can interact with ReO_x species on the catalyst. In this case, the product 1,5-pentanediol can also interact with the catalyst since 1,5-pentanediol has two —CH_2OH group. In order to investigate the effect of the coexistent product on the reaction rate of the THFA hydrogenolysis, we carried out the activity test in the presence of 3-methyl-1,5-pentanediol or 1-butanol. Here, 3-methyl-1,5-pentanediol and 1-butanol are models of 1,5-pentanediol and 1-pentanol which are the products of the THFA hydrogenolysis, where it is easy to measure the formation rate of 1,5-pentanediol and 1-pentanol and the conversion rate of 3-methyl-1,5-pentanediol and 1-butanol simultaneously. The results are listed in Table 6. The conversion rate of 3-methyl-1,5-pentanediol and 1-butanol was much lower than the conversion rate of THFA, and it can be assumed that the amount of 3-methyl-1,5-pentanediol and 1-butanol is constant during the reaction. When equimolar amount of 3-methyl-1,5-pentanediol to THFA was added, the reaction rate became 1/3 times as low as without the addition. On the other hand, when 1-butanol (1-butanol/THFA = 1) was added, the reaction rate became half. Therefore, the reaction rate can be determined by the ratio of THFA to the total amount of OH groups, suggesting that each —CH_2OH group in the reaction media can competitively interact with the catalyst surface. According to the previous report, adsorbed methoxy species is formed by the interaction between methanol and Re species [32]. The strong interaction between —CH_2OH group and the catalyst surface suggests the formation of alkoxide species on ReO_x sites. This result is connected to the Eq. (20), where $K_{1,5-\mathrm{PeD}} = 2K_{\mathrm{THFA}}$ and $K_{1-\mathrm{PeOH}} = K_{\mathrm{THFA}}$

$$\mathrm{ROH} + \sigma_{\mathrm{Re}} \overset{K_{\mathrm{Alcohol}}}{\rightleftarrows} (\mathrm{ROH})_{\mathrm{Re}} \tag{20}$$

It is assumed that the surface reaction between the adsorbed THFA on Re site $(\mathrm{THFA})_{\mathrm{Re}}$ and adsorbed hydride on Rh site $(H^-)_{Rh}$ is the rate-determining step (Eq. (18)). The quasi-equilibrium expressions representing adsorption on the Re and Rh surface are

$$K_{\mathrm{THFA}} = \theta_{\mathrm{THFA,Re}}/C_{\mathrm{THFA}}\theta_{\mathrm{v,Re}} \tag{21}$$

$$K_{1,5-\mathrm{PeD}} = 2K_{\mathrm{THFA}} = \theta_{1,5-\mathrm{PeD,Re}}/C_{1,5-\mathrm{PeD}}\theta_{\mathrm{v,Re}} \tag{22}$$

$$K_{\mathrm{H_2}} = \theta_{\mathrm{H^-,Rh}}C_{\mathrm{H^+}}/P_{\mathrm{H2}}\theta_{\mathrm{v,Rh}} \tag{23}$$

where $\theta_{\mathrm{A,M}}$, $\theta_{\mathrm{v,M}}$, and C_{A} mean the surface coverage of A on M, the vacant site of M, and the concentration of A, respectively. $P_{\mathrm{H_2}}$ represents the partial pressure of hydrogen. The concentration of proton can be assumed to be the constant because the proton produced by heterolytic activation of H_2 can be much smaller than that in the liquid phase, which is originated from the weak acidity of the Rh–ReO_x catalyst. The weak acidity was confirmed by the NH_3-TPD (Supplementary information Fig. S1). Therefore, $K_{\mathrm{H_2}}/C_{\mathrm{H}}$ can be replaced by $K'_{\mathrm{H_2}}$. Expression for $\theta_{\mathrm{THFA,Re}}$, $\theta_{1,5\text{-}\mathrm{PeD,Re}}$, and $\theta_{\mathrm{H^-,Rh}}$ can be obtained from Eqs. (21)–(23) as follows:

$$\theta_{\mathrm{THFA,Re}} = K_{\mathrm{THFA}}C_{\mathrm{THFA}}\theta_{\mathrm{v,Re}} \tag{24}$$

$$\theta_{1,5-\mathrm{PeD,Re}} = 2K_{\mathrm{THFA}}C_{1,5-\mathrm{PeD}}\theta_{\mathrm{v,Re}} \tag{25}$$

$$\theta_{\mathrm{H^-,Rh}} = K'_{\mathrm{H_2}}P_{\mathrm{H2}}\theta_{\mathrm{v,Rh}} \tag{26}$$

Using the site balance, the following expressions for the fractional surface coverage on Re and Rh sites are obtained:

$$\theta_{\mathrm{THFA,Re}} + \theta_{\mathrm{v,Re}} + \theta_{1,5-\mathrm{PeD,Re}} = 1 \tag{27}$$

$$\theta_{\mathrm{v,Rh}} + \theta_{\mathrm{H^-Rh}} = 1 \tag{28}$$

Using Eqs. (24)–(28), the fractional surface coverage of reactants can be expressed as follows:

$$\theta_{\mathrm{THFA,Re}} = K_{\mathrm{THFA}}C_{\mathrm{THFA}}/(K_{\mathrm{THFA}}C_{\mathrm{THFA}} + 2K_{\mathrm{THFA}}C_{1,5-\mathrm{PeD}} + 1) \tag{29}$$

$$\theta_{\mathrm{H^-,Rh}} = K'_{\mathrm{H_2}}P_{\mathrm{H_2}}/(K'_{\mathrm{H_2}}P_{\mathrm{H_2}} + 1) \tag{30}$$

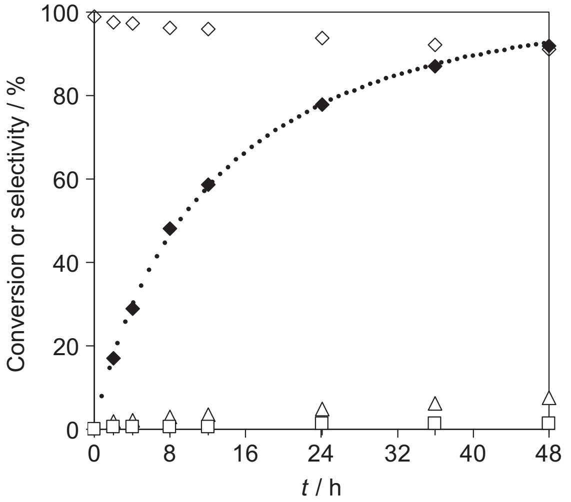


Fig. 2. Time course of the THFA hydrogenolysis over Rh–ReO_x/SiO_2. ◆, conversion; ◇, selectivity to 1,5-pentanediol; △, selectivity to 1-pentanol; □, selectivity to other products. Open circles and closed circles represent the calculated conversion values based on Eqs. (4) and (5), respectively. Reaction conditions: 60 mass% aqueous solution of THFA 20 mL, catalyst 100 mg (4 mg Rh), reaction temperature 393 K, initial H_2 pressure 8.0 MPa.

The overall rate of the hydrogenolysis of THFA is expressed using Eqs. (18), (29), and (30):

$$
\begin{aligned}
r &= k_1 \theta_{\mathrm{THFA,Re}} \theta_{\mathrm{H^-,Rh}} \\
&= k_1 \{K_{\mathrm{THFA}} C_{\mathrm{THFA}} / (K_{\mathrm{THFA}} C_{\mathrm{THFA}} + 2K_{\mathrm{THFA}} C_{1,5-\mathrm{PeD}} + 1)\} \\
&\quad \times \{K'_{\mathrm{H_2}} P_{\mathrm{H_2}} / (K'_{\mathrm{H_2}} P_{\mathrm{H_2}} + 1)\} \qquad (31)
\end{aligned}
$$

where k_1 is the rate constant of Eq (18).

The first-order kinetics on P_{H_2} (Table 5) indicates $K'_{\mathrm{H_2}} P_{\mathrm{H_2}} \ll 1$, and the zero-order kinetics on THFA concentration (Table 4) indicates $K_{\mathrm{THFA}}(C_{\mathrm{THFA}} + 2C_{1,5\text{-PeD}}) \gg 1$. These can give the reaction rate as below.

$$
r = k_1 K'_{\mathrm{H2}} P_{\mathrm{H2}} C_{\mathrm{THFA}} / (C_{\mathrm{THFA}} + 2C_{1,5-\mathrm{PeD}}) \qquad (32)
$$

Fig. 2 shows the reaction time dependence of the THFA hydrogenolysis over Rh–ReO$_x$/SiO$_2$ (Re/Rh = 0.5). The THFA conversion increased almost linearly at the initial stage; however, the increase became smaller at longer reaction time. Based on the results at 2 h, the rate constant $k_1 K'_{\mathrm{H_2}}$ was determined to be 0.025 MPa^{-1} h^{-1} g-cat^{-1}. It is possible to calculate the conversion curve using this obtained reaction rate constant and the Eq. (32). The reaction time dependence of the calculated conversion is also plotted in Fig. 2 (Closed circles). The decrease in H_2 pressure during the reaction (initial 8.0 MPa → 6.5 MPa at 94% conv.) was also considered in the calculation. The agreement indicates the validity of the Eq. (32) and the reaction step including the adsorbed THFA on Re species attached by the hydride species. In addition, Fig. 1b shows the reaction scheme of ethylene glycol ethers, which is similar to the case of THFA (Fig. 1a). The C—O bond neighboring the —CH$_2$ORe group is attacked in the hydrogenolysis of both THFA and ethyleneglycol ethers. The regioselectivity of hydride attack can be caused by the site of the hydride formation. The regioselectivity can also be induced by the formation of a six-membered ring transition state (—H$^-$—Rh—Re—O—CH$_2$—C—).

In the hydrogenolysis of THFA over Rh–ReO$_x$/SiO$_2$, water is the most suitable solvent, and the reaction rate of the THFA hydrogenolysis in other solvents such as 1,4-dioxane was much smaller than that in water. This behavior agreed well with the solvent effect on the glycerol hydrogenolysis as previously reported [30]. One explanation is that H_2O can contribute to the construction of Rh–ReO$_x$ surface structure, such as Re hydroxide species, and further investigation on the effect of H_2O is necessary.

4. Conclusions

1. Rh–ReO$_x$/SiO$_2$ (Re/Rh = 0.5) catalyzed the hydrogenolysis of tetrahydrofuran ring only with —CH$_2$OH group located at the 2-position. The C—O bond neighboring the —CH$_2$OH group is selectively dissociated. The catalyst was also applicable to the hydrogenolysis of ethylene glycol ethers where —CH$_2$OH group is connected to the ether C—O bond.
2. The reaction scheme of the THFA hydrogenolysis to 1,5-pentanediol is different from that via dihydropyran and δ-hydroxyvaleraldehyde as reported previously on the basis of no additive effect of H_2SO_4 to the THFA hydrogenolysis over Rh–ReO$_x$/SiO$_2$ and tetrahydropyran formation in the reaction of dihydropyran.
3. Product distribution in the hydrogenolysis of tetrahydro-5-methyl-2-furfuryl alcohol and 2-isopropoxyethanol suggests that the mechanism of Rh–ReO$_x$/SiO$_2$-catalyzed hydrogenolysis includes the formation of anion intermediate by the attack of hydride and subsequent protonation of the anion (hydride → proton mechanism), where hydride and proton are formed by heterolytic activation of H_2.
4. The kinetic analysis of the THFA hydrogenolysis indicates the first and zeroth reaction order with respect to the H_2 pressure and THFA concentration, respectively. Combined with the catalyst characterization results showing that Rh–ReO$_x$/SiO$_2$ has the Rh metal particles modified with ReO$_x$ clusters, it is suggested that the hydride species formed at the interface between Rh metal surface and ReO$_x$ cluster can attack the carbon atom neighboring the —CH$_2$OH group adsorbed on ReO$_x$ clusters. In addition, the presence of 1,5-pentanediol decreased the activity of the THFA hydrogenolysis because of the strong interaction between OH groups and the catalyst surface. Based on the regioselective hydride attack mechanism of Rh–ReO$_x$/SiO$_2$-catalyzed hydrogenolysis, the Langmuir–Hinshelwood type (L–H) kinetic modeling agreed with the reaction time dependence very well.

Acknowledgment

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.03.018.

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