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Research Note

Promoting effect of Mo on the hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol over Rh/SiO_2

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ABSTRACT

Addition of Mo to Rh/SiO_2 promoted the hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol drastically. Addition of Re and W to Rh/SiO_2 was also effective, but the promoting effect of Mo was more remarkable in terms of catalyst stability and high activity even at low reactant concentrations. Characterization of $Rh–MoO_x/SiO_2$ suggests that a partially reduced Mo species is attached to the surface of Rh metal particles. The synergy between the MoO_x and the Rh metal surface results in a high chemoselectivity and activity in the hydrogenolysis of tetrahydrofurfuryl alcohol.

1. Introduction

The development of the transformations of non-food biomass to (petro) chemicals is an important sustainability issue [1]. Furanic compounds are promising intermediates in the production of non-petroleum-derived chemicals because other biomass-related raw materials usually have a much higher oxygen content. One of the basic non-petroleum chemicals accessible from biomass resources is furfural produced by the acid-catalyzed dehydration of pentoses [2]. Furfural is the starting material for the manufacture of tetrahydrofurfuryl alcohol (THFA) by hydrogenation, which is an environmentally acceptable, biodegradable furan chemical and is widely used as a green solvent for fats and resin [3]. Another potential utilization of THFA is in the production of 1,5-pentanediol, which can be used as a monomer for the production of polyesters and polyurethanes [4]. Two methods have been reported for the conversion of THFA to 1,5-pentanediol [5,6]. A multi-step method requiring the isolation and purification of intermediates has been proposed to give 70% yield of 1,5-pentanediol [5]. A simple and one-step method would be the direct hydrogenolysis of THFA to 1,5-pentanediol. However, the selectivity to 1,5-pentanediol was low, and the main product was 1,2-pentanediol over conventional catalysts such as Cu-chromite [6]. Therefore, it is necessary to develop more effective catalysts. We recently reported that the modification of Rh/SiO_2 with Re species is effective for the hydrogenolysis of THFA [7], however this system has only limited catalyst stability. Here, we report the discovery that Rh/SiO_2 modified with Mo species is an active, selective, and stable catalyst for the hydrogenolysis of THFA to 1,5-pentanediol.

2. Experimental

A Rh/SiO_2 catalyst was prepared by impregnating SiO_2 (Fuji Silysia Chemical Ltd., BET surface area 535 m^2/g) with an aqueous solution of $RhCl_3 3H_2O$. The preparation method and conditions were described in the previous report [7]. $Rh–MoO_x/SiO_2$ catalysts were prepared by impregnating Rh/SiO_2 after the drying procedure with an aqueous solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Wako Pure Chemical Industries Ltd.). They were calcined in air at 773 K for 3 h after drying at 383 K for 12 h. The loading amount of Rh was 4 wt%, and that of Mo was in the range of 0.03–0.5 by the molar ratio of Mo to Rh. As a reference, MoO_x/SiO_2 was also prepared by a method similar to the case of $Rh–MoO_x/SiO_2$. The preparation methods of $Rh–ReO_x/SiO_2$ and $Rh–WO_x/SiO_2$ were described in the previous reports [7,8].

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Catalytic testing was performed in a 190-ml stainless steel autoclave with an inserted glass vessel. An aqueous tetrahydrofurfuryl alcohol solution of various concentrations was placed into the autoclaves together with an appropriate amount of catalysts (see Tables 1 and 2 for actual reaction conditions) and stirring bar. After sealing the reactors, their air contents were purged by flushing thrice with 1 MPa hydrogen (99.99%; Takachiho Chemical Industrial Co. Ltd.). Autoclaves were then heated to the required temperature and pressurized to 1 MPa for the reduction pretreatment. After 1 h, the H_2 pressure was increased to 8 MPa. During the experiment, the stirring rate was fixed at 500 rpm. After an appropriate reaction time, the reactors were cooled down, and the gas-phase products were collected in a gas bag. The autoclave contents were transferred to vials, and the catalysts were separated by centrifugation and filtration.

In the hydrogenolysis of THFA, 1,5-pentanediol (1,5-PeD), 1,2-pentanediol (1,2-PeD), and 1-pentanol (1-PeOH) were produced. The reaction scheme for the hydrogenolysis of THFA is shown in Scheme 1. Additionally, 2-methyltetrahydrofuran, 2-pentanol (2-PeOH), and various products resulting from the cracking of carbon-carbon bond in the molecule were also detected. A small amount of methane was detected as a gaseous product. Consequently, the sum of the cracking products, 2-methyltetrahydrofuran, 2-pentanol, and gaseous product is integrated as “Others” in the results. The analysis method for the products was described in detail in the previous report [7].

Catalysts were characterized by measurement of CO adsorption and by using transmission electron microscope (TEM, JEM 2010; JEOL) operated at 200 kV. The methods were as detailed in the previous report [7]. Mo *K*-edge EXAFS spectra were measured at the BL01B1 station at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal No. 2008B1235). The storage ring was operated at 8.0 GeV. A Si (1 1 1) single crystal was used to obtain a monochromatic X-ray beam. Measurements were carried out in a way similar to that described in Ref. [9]. For the curve fitting analysis, the empirical phase shift and the amplitude function for the Mo–O bond were extracted from the data of Na_2MoO_4. Theoretical functions for the Mo–Rh bond were calculated using the FEFF8.2 program [10]. Analyses of EXAFS data were performed using a computer program (REX2000 Ver. 2.3.3; Rigaku Corp.).

3. Results and discussion

The activity of Rh–MoO_x/SiO_2 catalysts in the hydrogenolysis of tetrahydrofurfuryl alcohol (THFA) is influenced by the amount of Mo added to Rh, and the optimum was determined to be Mo/Rh = 0.13 in terms of both the THFA conversion and turnover frequency (TOF) of 1,5-PeD formation (Table 1, entries 1–5). Without the addition of Mo, Rh/SiO_2 showed much lower activity and the main product was 1,2-PeD (Table 1, entry 6). As reported previously, Rh–ReO_x/SiO_2 was effective in this reaction, and the optimum amount of Re/Rh was 0.5 (Table 1, entries 7–9) [7]. At a ratio of Re/Rh = 0.13, which is the same as the case of the optimum Mo/Rh, the promoting effect of Re was not as pronounced as that of Mo (Table 1, entries 3 and 7). According to the previous reports on the hydrogenolysis of glycerol, the combination of H_2WO_4 with Rh catalysts was effective [11,12]. Therefore, the additive effect of W was also investigated, and it was found that the optimum amount of W was W/Rh = 0.13 (Table 1, entry 10), although the details of these results are not shown. The promoting effect of W also was not as pronounced as that of Mo (Table 1, entries 3 and 10). In order to maximize the yield of 1,5-PeD, the reaction temperature was changed to 373 K and longer reaction times were applied. The maximum 85% yield of 1,5-PeD on Rh–MoO_x/SiO_2 (Mo/Rh = 0.13) was attained at 24 h reaction time (Table 1, entry 12). In contrast, the maximum yield of 86% on Rh–ReO_x/SiO_2 (Re/Rh = 0.5) was attained at 36 h (Table 1, entry 16). While the activity of Rh–MoO_x/SiO_2 was slightly lower than that of Rh–ReO_x/SiO_2 when the conversion level was not high (Table 1, entries 3 and 8), the reaction time for the highest yield of 1,5-PeD was shorter on Rh–MoO_x/SiO_2. This can be explained by much higher activity of Rh–MoO_x/SiO_2 than that of Rh–ReO_x/SiO_2 in very low concentration of THFA (Table 1, entries 17 and 18). The catalyst also worked effectively in higher concentration of THFA. The results of the activity test in 60 wt% THFA aqueous solution over Rh–MoO_x/SiO_2 (Mo/Rh = 0.13) and Rh–ReO_x/SiO_2 (Re/Rh = 0.5) are listed out in Table 2. In addition, the catalysts were reused repeatedly in order to evaluate the catalyst stability. The Rh–ReO_x/SiO_2 gave higher activity than Rh–MoO_x/SiO_2, but the stability was lower probably due to the leaching of Re [7].

In order to elucidate the promoting mechanism of the Mo addition, the interaction between Rh and Mo species in the catalyst

Table 1
Results of the hydrogenolysis of tetrahydrofurfuryl alcohol.

Entries	Catalyst	M/Rh (M = Mo, Re, W)	CO/Rh	Catalyst amount (g)	Temp. (K)	Time (h)	THFA concentration (wt%)	Conv. (%)	Selectivity of products (%)				TOF[a] (h^{-1})
									1,5-PeD	1,2-PeD	1-PeOH	Others	
1	Rh–MoO_x/SiO_2	0.03	0.38	0.05	393	4	5	20.2	82.3	3.3	10.0	4.5	55
2		0.06	0.34					40.3	93.4	0.0	4.9	1.7	139
3		0.13	0.29					50.1	95.5	0.0	3.8	0.7	208
4		0.25	0.25					39.2	94.7	0.0	4.1	1.2	187
5		0.5	0.18					21.3	89.1	0.0	8.1	2.8	132
6	Rh/SiO_2	–	0.39	0.05	393	4	5	5.7	18.0	61.7	6.2	14.1	3
7	Rh–ReO_x/SiO_2	0.13	0.28	0.05	393	4	5	26.2	84.0	0.0	10.8	5.2	99
8		0.5	0.17					56.9	94.2	0.0	4.4	1.3	397
9		1	0.06					48.3	92.3	0.0	6.0	1.7	936
10	Rh–WO_x/SiO_2	0.13	0.30	0.05	393	4	5	30.4	84.7	0.0	5.8	9.5	108
11	Rh–MoO_x/SiO_2	0.13	0.29	0.10	373	12	5	74.6	85.4	0.0	12.7	1.9	46
12						24		94.2	90.3	0.0	8.7	0.9	–
13						36		95.7	66.0	0.0	30.4	3.6	–
14	Rh–ReO_x/SiO_2	0.5	0.17	0.10	373	12	5	75.2	94.9	0.0	4.1	1.0	88
15						24		89.6	92.0	0.0	6.4	1.6	–
16						36		95.7	89.8	0.0	8.3	1.9	–
17	Rh–MoO_x/SiO_2	0.13	0.29	0.10	373	4	1	60.3	94.4	0.0	4.8	0.7	25
18	Rh–ReO_x/SiO_2	0.5	0.17	0.10	373	4	1	23.5	97.6	0.0	2.4	0.0	17
19	$Rh/SiO_2 + MoO_x/SiO_2$[b]	0.13	–	0.05 + 0.05	393	4	5	16.8	85.4	1.3	9.0	4.3	–

Reaction conditions: 8.0 MPa initial H_2 pressure. 20 ml, aqueous solution of tetrahydrofurfuryl alcohol, PeD = pentanediol, PeOH = pentanol.

[a] Turnover frequency (TOF) in hydrogenolysis is calculated on the basis of 1,5-pentanediol formation rate and the amount of CO adsorption at room temperature.

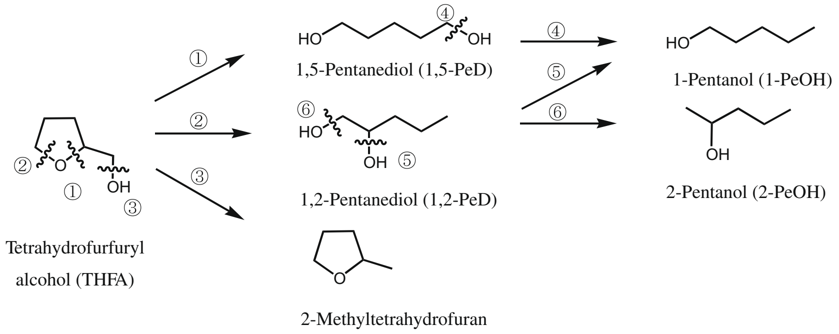
[b] Loading amount of Mo on MoO_x/SiO_2 is the same as that of Rh–MoO_x/SiO_2 (Mo/Rh = 0.13).

Table 2
Results of the life test in the hydrogenolysis of tetrahydrofurfuryl alcohol over Rh–MoO_x/SiO_2 and Rh–ReO_x/SiO_2.

Catalyst	M/Rh (M = Mo, Re)	CO/Rh	Usage time	Conv. (%)	Selectivity (%)				TOF[a] (h^{-1})
					1,5-PeD	1,2-PeD	1-PeOH	Others	
Rh–MoO_x/SiO_2	0.13	0.29	1st	53.5	93.7	0.0	5.0	1.3	218
			3rd	53.2	94.1	0.0	4.8	1.0	218
			5th	53.0	94.9	0.0	4.2	0.9	218
Rh–ReO_x/SiO_2	0.50	0.17	1st	79.0	93.6	0.0	5.3	1.1	548
			3rd	68.3	94.1	0.0	4.8	1.2	476
			5th	64.5	95.4	0.0	3.9	0.7	456
Rh/SiO_2	–	0.39	1st	11.1	18.1	66.0	4.5	11.4	6

Reaction conditions: 8.0 MPa initial H_2 pressure, 393 K, 12 h, 0.2 g-cat, 20 ml aqueous solution of 60 wt% THFA.

[a] Turnover frequency (TOF) in hydrogenolysis is calculated on the basis of 1,5-pentanediol formation rate and the amount of CO adsorption at room temperature.



Scheme 1. Reaction scheme of tetrahydrofurfuryl alcohol hydrogenolysis.

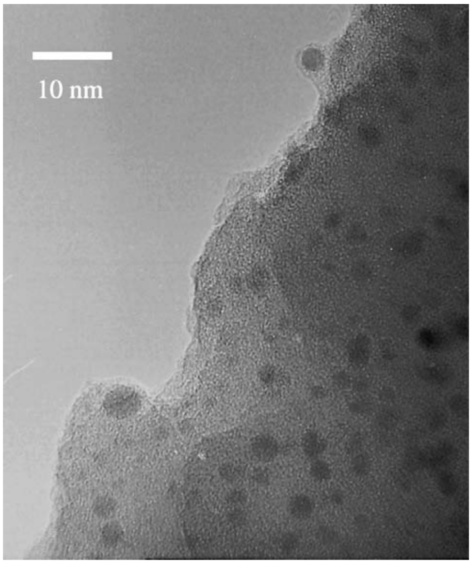


Fig. 1. TEM image of Rh–MoO_x/SiO_2 (Mo/Rh = 0.13) after the reaction.

should be characterized. The average particle size of Rh–MoO_x/SiO_2 (Mo/Rh = 0.13) was determined to be 3.2 ± 0.3 nm by TEM observation (Fig. 1), i.e., it was almost the same as that of Rh/SiO_2 [13]. In addition, the crystal size of Rh metal determined by X-ray diffraction was 3.6 ± 0.3 nm for Rh–MoO_x/SiO_2, which supports the TEM result. The CO adsorption on Rh–MoO_x/SiO_2 (Mo/Rh = 0.13; CO/Rh = 0.29) was significantly lower than that of Rh/SiO_2 (CO/Rh = 0.39), although the average metal particle sizes of the two catalysts were similar. This behavior indicates that the CO adsorption is suppressed by the presence of MoO_x. The suppressed amount of CO adsorption (CO/Rh = 0.1) agreed with the additive amount of Mo (Mo/Rh = 0.13), and this suggests that one Mo atom inhibits the adsorption of approximately one CO molecule. This behavior agreed well with the previous report that CO is adsorbed more preferably on the surface Rh atom than MoO_x species [14]. Table 3 lists out the curve fitting result of Mo *K*-edge EXAFS of Rh–MoO_x/SiO_2 (Mo/Rh = 0.13) after the reaction. The detailed spectra are described in Figure S1 (Supplementary Information). The EXAFS result shows the presence of the Mo–O and Mo–Rh (or –Mo) bonds, but in the EXAFS analysis, it is theoretically impossible to distinguish between Rh and Mo as a backscattering atom [15]. However, judging from the suppression of CO adsorption by Mo addition, it is suggested that the Mo species directly interacts with

Table 3
Curve fitting results of Mo *K*-edge EXAFS of Rh–MoO_x/SiO_2 after the hydrogenolysis of tetrahydrofurfuryl alcohol.

Catalyst	Molar ratio Mo/Rh	Shells	CN[a]	R (10^{-1} nm)[b]	σ (10^{-1} nm)[c]	ΔE_0 (eV)[d]	R_f (%)[e]
Rh–MoO_x/SiO_2	0.13	Mo–O	1.1	2.08	0.061	−2.8	0.8
		Mo–Rh (or–Mo)	3.0	2.64	0.077	−5.9	

[a] Coordination number.

[b] Bond distance.

[c] Debye–Waller factor.

[d] Difference in the origin of photoelectron energy between the reference and the sample.

[e] Residual factor. Fourier filtering range: 0.129–0.276 nm.

Rh metal particle. In the case of the EXAFS analysis of Rh–ReO_x/SiO_2 (Re/Rh = 0.5), the Re–Re and Re–Rh bonds as well as the Re-O bond were observed [7]. The coordination number (CN) of the Re–Re and Re–Rh bonds was 2.6 and 3.6, respectively [7]. This indicates that ReO_x clusters are formed on the surface of Rh metal particles over Rh–ReO_x/SiO_2. In contrast, the CN of the Mo–Rh (or –Mo) bond is comparable to that of Re–Rh bond. This suggests that the MoO_x species adsorbed on the surface of Rh metal particles are spatially well-defined and isolated. The structure difference between MoO_x and ReO_x on Rh metal particles can be related to the different optimum amount of the modifiers. The isolated Mo species can give larger interface between Rh metal and MoO_x species than the cluster. Another different property is that the excessive Mo species decreased the TOF and the excessive Re increased the TOF. It is difficult to explain this different behavior from the present data. The difference in the ability of H_2 activation may explain the tendency. Further investigations are necessary for the elucidation. In addition, the CN of the Mo–O bond is much smaller than the precursor, indicating that the Mo species is partially reduced. Based on the no activity of MoO_x/SiO_2, the promoting effect of MoO_x addition to Rh/SiO_2 is caused by the synergy between MoO_x and Rh species. For comparison, $Rh/SiO_2 + MoO_x/SiO_2$ (Mo/Rh = 0.13) physical mixture catalyst was also tested. The addition of MoO_x/SiO_2 also enhanced the conversion and the selectivity of 1,5-PeD (Table 1, entry 19), however, the effect is not so remarkable as the case of Rh–MoO_x/SiO_2. This can be explained by the transfer of a small amount of Mo species from MoO_x/SiO_2 to Rh/SiO_2 during the procedure of the reaction test via the solution and/or the solid state reaction, since the $Rh/SiO_2 + MoO_x/SiO_2$ (Mo/Rh = 0.13) seems to be similar to Rh–MoO_x/SiO_2 (Mo/Rh = 0.03) (Table 1, entry 1) in the results of the activity test. As a result, it is found that the high performance of Rh–MoO_x/SiO_2 is caused by the direct interaction between Rh and MoO_x. In particular, it has been established that Mo oxides catalyze the oxidation of alcohol, and alcohol molecules can be adsorbed on Mo oxide to form Mo–alkoxide species [16]. The interaction between Rh and MoO_x can be related to the cooperative function as follows: tetrahydrofurfuryl alcohol is adsorbed on MoO_x species via the OH group and the hydrogenolysis of the C–O bond catalyzed by neighboring Rh surface. A similar mechanism is also suggested on Rh–ReO_x/SiO_2 [7]. The addition of H_2WO_4 to Rh catalysts such as $Rh(CO)_2(acac)_2$ and Rh/C in the hydrogenolysis of glycerol has also been reported to be effective [11,12]. In these cases, H_2WO_4 was separated from the Rh species, and the additive amount ratio of W to Rh was W/Rh = 6.9 [11] and 10 [12], and no direct interaction was demonstrated at all. In the present case, the additive effect of Mo is pronounced in spite of the very small amount of additive used. We hypothesize that this is due to the direct interaction between MoO_x species and Rh metal particles as suggested by the catalyst characterization.

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