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Synthesis of α-Hydroxy Ketones from Vicinal Diols by Selective Dehydrogenation over Ir–ReO_x/SiO_2 Catalyst

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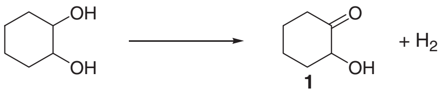
Rhenium oxide-modified Ir/SiO_2 (Ir–ReO_x/SiO_2) catalyst shows high activity and selectivity for the dehydrogenation of *trans*-1,2-cyclohexanediol to 2-hydroxycyclohexanone in water solvent under Ar. Linear vicinal diols bearing two secondary hydroxy groups or both a primary hydroxy group and a secondary hydroxy group can also be transformed to the corresponding α-hydroxy ketones in high selectivities. Ir–ReO_x/SiO_2 can be reused at least four times without loss of activity and selectivity.

α-Hydroxy ketones are valuable in organic chemistry because these compounds are important intermediates for syntheses of natural products and fine chemicals such as fragrances, agrochemicals, and medicines.[1] As conventional methods, acyloin condensation of diesters or benzoin condensation of aldehydes are very well known for the synthesis of α-hydroxy ketones. However, these reaction systems have serious drawbacks such as use of hazardous reagents like sodium metal or cyanide compounds and production of metal salts by neutralization after the reaction. To overcome these problems, various methods for preparation of α-hydroxy ketones such as dihydroxylation of enol ethers,[2] oxidation of silylenol ethers[3] or epoxides,[4] α-oxidation of ketones,[5] oxidation of olefins,[6] and selective transformation of vicinal diols[7–13] have been developed. Among these methods, selective transformation of diols is promising from the viewpoints of availability of substrates because diols can be easily produced from biomass and biomass-derived compounds.[14] However, selective transformation of diols to α-hydroxy ketones is a quite challenging reaction because of poor chemoselectivity caused by competitive C–C cleavage, over-oxidation, and dehydration. Among various diols, 1,2-cyclohexanediol (1,2-CHD) is frequently used as a motif of sugars.[9a] Various transformation methods of 1,2-CHD to 2-hydroxycyclohexanone (**1**) with stoichiometric dioxiranes,[7] organotin,[8] $NaBrO_3/NaHSO_3$,[9] Pd complex,[10] Cu catalyst,[11] and electrocatalyst[12] have been reported. From the viewpoints of green chemistry and energy consumption, direct and selective dehydrogenation of diols by a catalyst will be the most preferable because only H_2 is produced in the reaction.



(1)

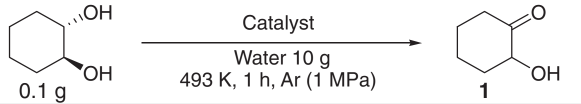
There is only one report for dehydrogenation of 1,2-CHD by a heterogeneous catalyst, the system of which consists of a Cu catalyst.[11] However, this catalyst system suffers from high reaction temperature (≥533 K). Therefore, development of a new heterogeneous catalyst for selective dehydrogenation of diols to α-hydroxy ketones is desirable.

In our previous studies[15] on hydrogenolysis of polyols or hydrogenation of aldehydes, Ir–ReO_x/SiO_2 catalyst showed high activity for these reactions. The high activity can arise from the high ability for heterolytic H_2 activation. Considering the same dissociation mechanism of C–H bonds as that of H–H bonds in coordination chemistry, Ir–ReO_x/SiO_2 catalyst will be active for heterolytic dissociation of C–H. Therefore, Ir–ReO_x/SiO_2 catalyst may be a new catalyst for dehydrogenation of alcohols because dissociation of C–H is a key step in dehydrogenation of alcohols. In this communication, we demonstrated that Ir–ReO_x/SiO_2 catalyst is an effective heterogeneous catalyst for the selective dehydrogenation of diols in water under Ar.

Ir–ReO_x/SiO_2 catalyst was prepared by a sequential impregnation method using SiO_2, $H_2[IrCl_6]$(aq), and NH_4ReO_4(aq), followed by drying at 383 K and calcination at 773 K. The loading amount of Ir was 4 wt %, and the molar ratio of Re to Ir was 2. Carbon-supported noble metal (5 wt %) catalysts (Pd/C, Ru/C, Rh/C, and Pt/C) are commercially available. For the pretreatment of these catalysts, a catalyst in water was heated at 473 K with 8 MPa H_2 for 1 h in an autoclave. After the pretreatment, the autoclave was cooled down, and H_2 was removed from the autoclave. *trans*-1,2-CHD was put into the autoclave, and the autoclave was heated to 493 K under Ar. Products were analyzed by GC and GC-MS. The isomerization product, *cis*-1,2-CHD, was excluded in the calculation of conversion and selectivity because *cis*-1,2-CHD can be converted to **1** at the same reactivity (Table S1).[16] Conversion and selectivity were defined as follows: conversion (%) = 100 × [1 − {produced *cis*-1,2-CHD (mol) + unreacted *trans*-1,2-CHD (mol)}/*trans*-1,2-CHD before the reaction (mol)] and selectivity (%) = 100 × product (mol)/{*trans*-1,2-CHD before the reaction (mol) − produced *cis*-1,2-CHD (mol) − unreacted *trans*-1,2-CHD (mol)}. The details of the experimental method are described in the Supporting Information.[16]

The dehydrogenation of *trans*-1,2-CHD to **1** was examined over various catalysts (Table 1). Compared with the conventional carbon-supported hydrogenation catalysts such as Pd/C, Ru/C, Rh/C and Pt/C, Ir–ReO_x/SiO_2 catalyst showed higher selectivity to **1** and higher or similar conversion (Entries 2 and 5–8), resulting in providing higher yield of **1**. In the case of carbon-supported catalysts, the selectivities to phenol and linear alkanes were relatively high, indicating that dehydrogenation of cyclohexane and C–C bond cleavage easily take place. On the other hand, the selectivity of copper oxide was as high as that of Ir–ReO_x/SiO_2, however, the activity was much lower (Entry 9). It should be noted that the activity of Ir–ReO_x/SiO_2 catalyst was much higher than that of Ir/SiO_2 (Entry 3) and ReO_x/SiO_2 (Entry 4). As above, Ir–ReO_x/SiO_2 catalyst is the most effective for dehydrogenation of *trans*-1,2-CHD to **1** in water under Ar.

Table 1. Production of 2-hydroxycyclohexanone (**1**) by dehydrogenation of *trans*-1,2-CHD over various catalysts[a]



Entry	Catalyst	*t* /h	Conv. /%	Yield of **1** /%	Selectivity/%						*cis*/*trans* ratio of 1,2-CHD
					2-Hydroxy-cyclohexanone (**1**)	Cyclohexanone	Cyclohexanol	Phenol	Linear alkanes	Others[b]	
1	Ir–ReO$_x$/SiO$_2$	0[c]	25.8	19.8	78.4	12.3	7.6	0.0	1.3	0.5	0.2
2		1	35.8	24.7	68.9	16.9	8.8	1.6	1.1	2.8	0.4
3	Ir/SiO$_2$	1	19.3	17.0	85.8	7.2	4.5	0.6	1.3	0.5	0.1
4	ReO$_x$/SiO$_2$	1	1.1	0.8	71.5	6.2	6.6	0.0	13.9	1.8	0.0
5	Pd/C	1	12.7	8.2	63.8	13.5	6.1	2.6	2.2	11.8	0.1
6	Ru/C	1	38.1	16.0	42.5	8.6	10.2	18.4	10.2	10.0	0.6
7	Rh/C[d]	1	36.9	15.8	42.1	22.2	17.0	15.2	0.0	3.5	0.5
8	Pt/C[e]	1	40.7	13.0	31.5	24.6	24.8	16.0	0.1	3.1	0.6
9	CuO	1	5.0	3.7	72.4	10.4	10.0	2.5	4.5	0.2	0.0

[a]Reaction conditions: Ir–ReO$_x$/SiO$_2$ 0.1 g, *trans*-1,2-CHD 0.5 g, water 10 g, $T = 493$ K, $P_{Ar} = 1$ MPa. [b]Others: cyclohexane + benzene + cyclopentanecarbaldehyde + 1,2-cyclohexanedione. [c]The reaction was stopped when the temperature was raised to 493 K. [d]Rh/C 50 mg. [e]Pt/C 20 mg.

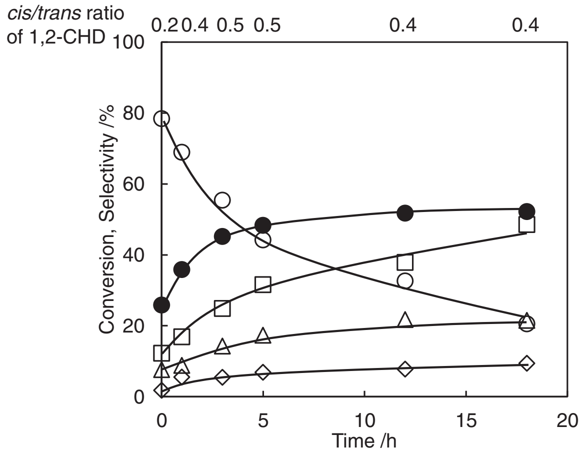
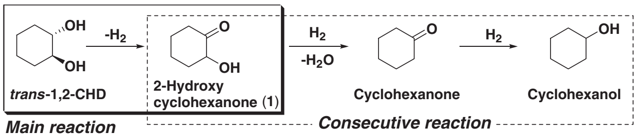


Figure 1. Time-course of dehydrogenation of *trans*-1,2-CHD over Ir–ReO$_x$/SiO$_2$ catalyst (●: conversion; ○: selectivity to **1**; □, selectivity to cyclohexanone; △, selectivity to cyclohexanol; ◇, selectivity to others). Reaction conditions: Ir–ReO$_x$/SiO$_2$ 0.1 g, *trans*-1,2-CHD 0.5 g, water 10 g, $T = 493$ K, $P_{Ar} = 1$ MPa. Others: phenol + linear alkanes + cyclohexane + benzene + cyclopentanecarbaldehyde + 1,2-cyclohexanedione.



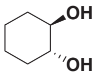
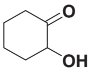
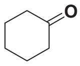
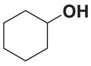
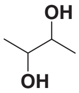
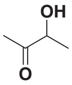
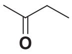
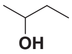
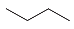
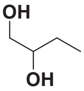
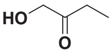
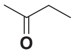
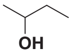
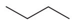
Scheme 1. Reaction pathway for dehydrogenation of *trans*-1,2-CHD over Ir–ReO$_x$/SiO$_2$ catalyst.

The time-course of the *trans*-1,2-CHD dehydrogenation over Ir–ReO$_x$/SiO$_2$ was examined as shown in Figure 1. At the initial stage, the selectivity to **1** was very high (78% at 0 h). The selectivity to **1** gradually decreased with increasing the reaction time, and those to cyclohexanone and cyclohexanol increased simultaneously. These results indicate that cyclohexanone and cyclohexanol are formed by the consecutive reactions of **1** (Scheme 1): cyclohexanone was produced by hydrogenolysis of the hydroxy group of **1**, and cyclohexanol was produced by hydrogenation of cyclohexanone.[15g] On the other hand, after 5 h reaction time, dehydrogenation of *trans*-1,2-CHD hardly proceeded and the conversion was saturated at about 50%, however, the consecutive hydrogenolysis reaction proceeded. These results suggest that the active site for dehydrogenation is different from that for hydrogenolysis, and the active site for dehydrogenation will be decomposed or covered by the products as the reaction proceeds. To clarify the cause of deactivation of Ir–ReO$_x$/SiO$_2$, the catalyst after the reaction was characterized by TG-DTA (Figure S1).[16] The TG-DTA profile showed two signals at 330 and 560 K, which are assigned to water and products, respectively. The sample for TG-DTA was obtained by flashing the recovered catalyst with ethanol. Therefore, the products detected at 560 K will be strongly adsorbed on the catalyst, resulting in a poison for the catalyst.

Next, effects of concentration of *trans*-1,2-CHD and the reaction temperature were investigated (Figures S2 and S3).[16] Effect of concentration of *trans*-1,2-CHD was examined within the range from 3.2 to 9.0 wt % of *trans*-1,2-CHD. The concentration of *trans*-1,2-CHD was adjusted by addition of water (5–15 g) to the fixed amount of *trans*-1,2-CHD (0.5 g). The conversion was almost constant in the above range. However, the selectivity to **1** was decreased with increasing the concentration of *trans*-1,2-CHD, and those to cyclohexanone and linear alkanes were increased. The hydrogenolysis of **1** must readily take place at the high concentration of the substrate because concentration dependence of the reaction rate in hydrogenation is positive (reaction order: +0.7).[15g] Therefore, lower concentration of *trans*-1,2-CHD is more preferable. Effect of the reaction temperature was investigated within the range from 433 to 533 K. The conversion was increased with increasing the reaction temperature. The selectivity to **1** was almost the same in the range from 433 to 493 K, but the selectivity was drastically decreased at 533 K. Taking into consideration that the yield of cyclohexanone was increased, the consecutive hydrogenolysis reaction of **1** will proceed at the temperature.

The scope of diols in dehydrogenation at 453 K over Ir–ReO$_x$/SiO$_2$ catalyst was examined (Table 2). 2,3-Butanediol,

Table 2. Dehydrogenation of various diols over Ir–ReO_x/SiO_2[a]

Entry	Substrate	Conv./%	Selectivity/%			
1		17.1	 56.2	 16.5	 20.9	Others[b] 6.3
2		19.1	 84.9	 13.9	 0	 1.2
3		12.6	 83.0	 8.2	 7.2	 1.5

[a]Reaction conditions: Ir–ReO_x/SiO_2 0.1 g, substrate 4.3 mmol, water 10 g, $T = 453$ K, $t = 1$ h, $P_{Ar} = 1$ MPa. [b]Others: phenol + linear alkanes + cyclohexane + benzene + cyclopentanecarbaldehyde + 1,2-cyclohexanedione.

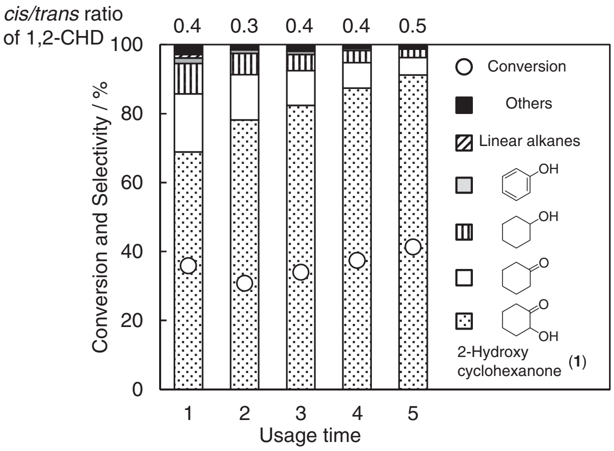


Figure 2. Reusability of Ir–ReO_x/SiO_2 for dehydrogenation of *trans*-1,2-CHD. Reaction conditions: Ir–ReO_x/SiO_2 0.1 g, *trans*-1,2-CHD 0.5 g, water 10 g, $T = 493$ K, $t = 1$ h, $P_{Ar} = 1$ MPa. Others: cyclohexane + benzene + cyclopentanecarbaldehyde + 1,2-cyclohexanedione.

which has two secondary hydroxy groups, reacted to afford 3-hydroxy-2-butanone in high selectivity (Entry 2). 1,2-Butanediol, which has one primary hydroxy group and one secondary hydroxy group, was also converted to 1-hydroxy-2-butanone in high selectivity (Entry 3). These results indicate that dehydrogenation of the secondary hydroxy group is more preferable. The reactivities were almost the same as that of *trans*-1,2-CHD. However, the selectivities of linear vicinal diols to the corresponding α-hydroxy ketones were higher than that of *trans*-1,2-CHD to 2-hydroxycyclohexanone. This result is probably because the linear α-hydroxy ketones have no ring strain and the structures are more stable than that of 2-hydroxycyclohexanone.

Reusability of the catalyst is very important from an industrial viewpoint. We evaluated the reusability of Ir–ReO_x/SiO_2 catalyst for the selective dehydrogenation of *trans*-1,2-CHD (Figure 2). The catalyst can be easily retrieved from the reaction mixture by filtration. For each successive use, the catalyst was washed with 10 mL of ethanol and dried at 383 K for 12 h. After the treatment, the recovered catalyst was reused at least four times without loss of its high catalytic performance, and the selectivity was rather improved with increasing the reuse time. From XRD and XAFS analyses of the catalysts before and after the reaction, the structure of Ir–ReO_x/SiO_2 was hardly changed during the course of the reaction (Figures S4–S7 and Tables S2 and S3).[16] This phenomenon is of great interest, however, the details remain unclear. Further investigation is necessary to clarify this behavior of Ir–ReO_x/SiO_2 catalyst.

In summary, Ir–ReO_x/SiO_2 catalyst acted as an efficient catalyst for the dehydrogenation of diols to the corresponding α-hydroxy ketones in water under Ar. Ir–ReO_x/SiO_2 catalyst can be reused at least four times without loss of activity or selectivity.

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