

## Selective Hydrogenation of Crotonaldehyde to Crotyl Alcohol over Metal Oxide Modified Ir Catalysts and Mechanistic Insight

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**Supporting Information** 

**ABSTRACT:** The scope of metal oxide modified noble metal (M +M'O<sub>x</sub>) catalysts was scrutinized in the hydrogenation of crotonaldehyde to crotyl alcohol as a model reaction under mild reaction conditions (303 K, 0.8 MPa, water solvent), demonstrating that  $MoO_{xy}$   $NbO_{xy}$   $FeO_x$  and  $ReO_x$  are effective metal oxides for Ir/SiO<sub>2</sub> to enhance both the activity and selectivity, although the optimized (metal oxide)/(Ir metal) molar ratio depends on the metal oxide.  $MoO_x$  modified Ir/SiO<sub>2</sub> catalyst (Ir- $MoO_x/SiO_2$  (Mo/Ir = 1)) was the most efficient, providing a high yield of crotyl alcohol (90%) and a high TOF (217 h<sup>-1</sup>). The catalytic activity under such mild reaction conditions is the highest among the reported heterogeneous catalysts. These results showed that modification of active metals with an appropriate amount of metal oxides is an effective method for the development of efficient catalysts for selective hydrogenations. The



reaction mechanism over the metal oxide modified Ir catalysts was investigated using Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) as a model catalyst by means of FTIR studies on H<sub>2</sub>/D<sub>2</sub> adsorption, crotonaldehyde adsorption, and temperature-programmed desorption of crotonaldehyde, and kinetic studies on effects of H<sub>2</sub> pressure and crotonaldehyde concentration, isotopic effect of hydrogen  $(V_{H2}/V_{D2})$ , and comparison of reactivities between the aldehyde group and olefin group using various substrates. The reaction proceeds via four steps: (i) adsorption of crotonaldehyde on ReO<sub>x</sub> species, (ii) generation of hydride species from H<sub>2</sub> on Ir metal species, (iii) hydride attack to the crotonaldehyde adspecies, and (iv) desorption of the produced crotyl alcohol, and the third step is the rate-determining step. Ir metal plays a role in the generation of hydride (H<sup>-</sup>) species from H<sub>2</sub>, leading to the high selectivity to crotyl alcohol, and ReO<sub>x</sub> plays a role in promotion of crotonaldehyde adsorption, leading to the proximity of crotonaldehyde to the active site and activation of the aldehyde group, which results in high activity and further improvement in the selectivity.

KEYWORDS: selective hydrogenation, heterogeneous catalysis, iridium, unsaturated aldehyde, unsaturated alcohol

## ■ INTRODUCTION

Selective hydrogenation of unsaturated aldehydes to unsaturated alcohols is a challenging reaction, since hydrogenation of C=C bonds is easier than that of C=O bonds thermodynamically and kinetically.<sup>1</sup> Crotonaldehyde is often used as a model substrate for unsaturated aldehydes because selective hydrogenation of crotonaldehyde to crotyl alcohol is comparatively difficult among the unsaturated aldehydes, due to the absence of directing groups in the structure (Scheme 1). Conventionally, metal hydrides<sup>2</sup> such as LiAlH<sub>4</sub> and NaBH<sub>4</sub> are used for





the selective hydrogenation of aldehyde groups. It was also reported that transfer hydrogenation using alcohol reagents can be applied to the reaction.<sup>3</sup> However, H<sub>2</sub> is preferable as a hydrogen source to metal hydride and alcohols because it is a clean and cheap resource. Some homogeneous catalyst systems<sup>4</sup> using RuCl<sub>2</sub>[(*R*)-binap](dmf)<sub>n</sub>, [RuH(CO)-(CH<sub>3</sub>CN)(TPPMS)<sub>3</sub>][BF<sub>4</sub>], and [H<sub>2</sub>Ir(phosphine)<sub>4</sub>]<sup>+</sup> are effective for the reaction because the hydrogenation reaction can be caused by ionic hydrogen species, which are known to be efficient for polarized double bonds such as carbonyl groups;<sup>5</sup> however, heterogeneous catalysts are unfavorable for the reaction mainly because of the difficulty in generating the ionic hydrogen species over the heterogeneous catalysts. In fact, conventional heterogeneous hydrogenation catalysts such as

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Pd, Rh, Ni, and Pt/C provide butanal or 1-butanol in the hydrogenation of crotonaldehyde (Scheme 1).<sup>6</sup>

From environmental and economic viewpoints, heterogeneous catalysts are more preferable than metal hydrides and homogeneous catalysts, and hence, heterogeneous catalysts for the reaction have been intensely investigated.<sup>7</sup> Effective heterogeneous catalysts are summarized in Table S1 in the Supporting Information. Among the reported heterogeneous catalysts for hydrogenation of crotonaldehyde,<sup>7a-r</sup> Ag or Au supported heterogeneous catalysts are effective in providing high yield and selectivity to crotyl alcohol,<sup>7a-d</sup> and in particular, AgNp@CeO2 nanocomposite catalyst achieved a high yield of 98%.<sup>7a</sup> However, these catalysts suffer from high temperature ( $\geq$ 333 K), high H<sub>2</sub> pressure ( $\geq$ 2.0 MPa), use of organic solvent, and/or low catalytic activity per total metal (turnover number (TOF) < 10  $h^{-1}$ ). Recently, Pt<sub>3</sub>Sn alloy or Ru–Ir bimetallic catalysts were reported to be efficient for the reaction to afford a high yield of crotyl alcohol;<sup>8</sup> however, these catalysts also suffer from high  $H_2$  pressure ( $\geq 2.0$  MPa), high temperature ( $\geq$ 333 K), use of organic solvent, and/or low activity (TOF  $< 10 h^{-1}$ ). Modification of hydrogenation-active metals with other metal species often decreases the original activity of the hydrogenation-active metals.7e,f,l,9 Therefore, development of effective heterogeneous catalysts without loss of the activity of the main hydrogenation-active metal species under mild reaction conditions has been desirable.

We previously reported preliminary results on the selective hydrogenation of unsaturated aldehydes to unsaturated alcohols, where  $\text{ReO}_{x}$ -modified  $\text{Ir}/\text{SiO}_{2}$  (Ir- $\text{ReO}_{x}/\text{SiO}_{2}$ ) catalyst is effective for the reaction, providing a high yield of various unsaturated alcohols (70-99%).<sup>10</sup> Modification of ReO<sub>x</sub> species on Ir metal dramatically enhanced both the activity and selectivity, which can make the reaction conditions milder such as a low temperature of 303 K, a low H<sub>2</sub> pressure of 0.8 MPa, and water solvent. The additive effect on  $Ir-ReO_x/SiO_2$  is quite characteristic, considering that the hydrogenation activity of metal species in other catalyst systems is often sacrificed to obtain high selectivity.<sup>7e,f,l,9</sup> On the other hand, it has been reported that metal oxide  $(M'O_x)$  modified noble metal (M)catalyst (M+M'O<sub>x</sub> catalyst) systems, including Ir-ReO<sub>x</sub>/SiO<sub>2</sub> and Ir-MoO<sub>x</sub>/SiO<sub>2</sub>, are efficient for the hydrogenolysis of polyols<sup>11</sup> or ethers,<sup>12</sup> hydrogenation of carboxylic acids,<sup>13</sup> and hydrodeoxygeneation of diols,<sup>14</sup> where the activity and selectivity were often simultaneously improved in comparison with only noble-metal catalysts without metal oxide modification. Therefore, modification of noble metals with metal oxides will be a promising strategy to realize both high selectivity and high activity in selective hydrogenation of unsaturated aldehydes to unsaturated alcohols, and clarification of the reaction mechanism will provide a clue for development of effective heterogeneous catalysts for selective hydrogenation reactions.

Herein, we investigate the scope of M+M'O<sub>x</sub> catalysts in the hydrogenation of crotonaldehyde to crotyl alcohol as a typical model reaction, and a reaction mechanism is proposed on the basis of kinetics and spectroscopy using Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst as a model catalyst.

#### RESULTS AND DISCUSSION

Catalyst Screening in the Selective Hydrogenation of Crotonaldehyde. In order to select effective metal oxide modifiers,  $Ir/SiO_2$  catalysts modified with various metal oxides such as  $ReO_{xy}$  MoO<sub>xy</sub> WO<sub>xy</sub> NbO<sub>xy</sub> FeO<sub>xy</sub> CoO<sub>xy</sub> VO<sub>xy</sub> and  $MnO_x$  were applied to the hydrogenation of crotonaldehyde to crotyl alcohol (Table 1). The main products were crotyl

# Table 1. Hydrogenation of Crotonaldehyde over Various Catalysts<sup>a</sup>

			selectivity (%)		
entry	catalyst	conversion (%)	crotyl alcohol	butanal	1-butanol
1	Ir-ReO <sub>x</sub> /SiO <sub>2</sub>	43.3	95.0	3.4	1.3
2	$Ir-MoO_x/SiO_2$	78.9	94.2	1.0	4.1
3	$Ir-WO_x/SiO_2$	14.0	87.8	8.7	2.0
4	Ir-NbO <sub>x</sub> /SiO <sub>2</sub>	10.1	85.0	10.3	0.0
5	$Ir-FeO_x/SiO_2$	1.4	69.3	30.8	0.0
6	$Ir-CoO_x/SiO_2$	46.3	38.5	41.2	19.9
7	$Ir-VO_x/SiO_2$	<0.1			
8	$Ir-MnO_x/SiO_2$	<0.1			
9	Ir/SiO <sub>2</sub>	10.9	86.9	8.2	3.1
<sup>a</sup> React	ion conditions:	crotonaldehvde	3.0 mmol.	H <sub>2</sub> O 3.0	ø. catalvst

(M'/Ir = 1) 50 mg, 303 K, 1 h, H<sub>2</sub> 0.8 MPa.

alcohol, butanal, and 1-butanol, while a small amount of butane was also produced as a byproduct. Ir-ReO<sub>x</sub>/SiO<sub>2</sub>, Ir-MoO<sub>x</sub>/ SiO<sub>2</sub>, Ir-WO<sub>x</sub>/SiO<sub>2</sub>, and Ir-NbO<sub>x</sub>/SiO<sub>2</sub> catalysts showed high selectivity to crotyl alcohol (85.0-95.0%), which is similar to or higher than the selectivity over  $Ir/SiO_2$  (Table 1, entries 1–4 and 9); among these catalysts, Ir-MoO<sub>x</sub>/SiO<sub>2</sub> provided the highest conversion of 78.9% (Table 1, entry 2) with a high selectivity of 94.2%. Ir-FeO<sub>x</sub>/SiO<sub>2</sub> showed a moderate selectivity of 69.3%, although the conversion was very low (Table 1, entry 5). Ir-CoO<sub>x</sub>/SiO<sub>2</sub> (Table 1, entry 6) showed much lower selectivity to crotyl alcohol than  $Ir/SiO_2$ . Ir-VO<sub>r</sub>/  $SiO_2$  and Ir-MnO<sub>x</sub>/SiO<sub>2</sub> showed almost no activity (Table 1, entries 7 and 8). These results indicate that  $CoO_{xy}$  VO<sub>xy</sub> and MnO<sub>x</sub> are unfavorable modifiers for the selective hydrogenation of crotonaldehyde to crotyl alcohol. Therefore, modification of Ir metal with the appropriate metal oxide species drastically enhanced the activity of Ir/SiO2 catalyst and improved the selectivity over Ir/SiO<sub>2</sub> catalyst. In terms of the selectivity to crotyl alcohol (>60%), Ir-ReO<sub>x</sub>/SiO<sub>2</sub>, Ir-MoO<sub>x</sub>/SiO<sub>2</sub>, Ir-WO<sub>x</sub>/ SiO<sub>2</sub>, Ir-NbO<sub>x</sub>/SiO<sub>2</sub>, and Ir-FeO<sub>x</sub>/SiO<sub>2</sub> catalysts were selected as catalyst candidates for the selective hydrogenation of unsaturated aldehydes.

According to previous literature,<sup>15</sup> the optimized molar ratio of  $M'O_x/M$  ((metal oxide)/(noble metal)) for achieving high selectivity and activity strongly depends on the metal oxide modifiers. The effect of M'/Ir atomic ratio was investigated using Ir-MoO<sub>x</sub>/SiO<sub>2</sub>, Ir-WO<sub>x</sub>/SiO<sub>2</sub>, Ir-NbO<sub>x</sub>/SiO<sub>2</sub>, and Ir- $FeO_{x}/SiO_{2}$  catalysts (Table 2). The optimized Re/Ir atomic ratio of Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst was reported to be 1 in our previous work<sup>10</sup> (Table 2, entry 21). Ir-MoO<sub>x</sub>/SiO<sub>2</sub> catalysts showed the maximum conversion at an Mo/Ir atomic ratio of 1 (78.9%, Table 2, entry 5), and the atomic ratio of M'/Ir is the same as that of Ir-ReO<sub>x</sub>/SiO<sub>2</sub>. The selectivity was maintained over 90% at any Mo/Ir ratios (Table 2, entries 1-7). On the other hand, Ir-WO<sub>x</sub>/SiO<sub>2</sub>, Ir-NbO<sub>x</sub>/SiO<sub>2</sub>, and Ir-FeO<sub>x</sub>/SiO<sub>2</sub> catalysts showed higher conversion and selectivity at a smaller atomic ratio of M'/Ir, and the conversion and selectivity decreased with an increase in the amount of M'O<sub>x</sub> species. At the atomic ratio of M'/Ir = 0.1,  $Ir-WO_x/SiO_2$ ,  $Ir-NbO_x/SiO_2$ , and Ir-FeO<sub>x</sub>/SiO<sub>2</sub> catalysts (Table 2, entries 8, 13, and 17) showed high conversion and selectivity (conversion 31-50%, selectivity 92–94%), which is similar to those over Ir-ReO<sub>r</sub>/

Table 2. Effect of M'/Ir Atomic Ratio in Hydrogenation of
Crotonaldehyde over Ir-M'O./SiO2 Catalysts <sup>a</sup>

				selectivity (%)		
entry	catalyst	M'/Ir	conversion (%)	crotyl alcohol	butanal	1- butanol
1	$Ir-MoO_x/SiO_2$	0.1	35.0	92.7	3.1	3.2
2		0.3	46.8	94.6	2.1	2.8
3		0.5	57.4	94.1	1.7	3.4
4		0.8	62.2	95.9	1.0	2.7
5		1	78.9	94.2	1.0	4.1
6		1.3	52.0	92.8	3.3	3.4
7		2	45.2	93.8	2.7	2.5
8	Ir-WO <sub>x</sub> /SiO <sub>2</sub>	0.1	31.0	94.3	2.8	2.2
9		1	14.0	87.8	8.7	2.0
10		3	17.5	84.1	12.3	0.0
11		5	17.6	82.1	11.8	2.2
12		7	11.2	77.8	15.9	0.0
13	Ir-NbO <sub>x</sub> /SiO <sub>2</sub>	0.1	44.0	92.3	4.0	2.5
14		0.5	14.7	87.0	8.0	2.0
15		1	10.1	85.0	10.3	0.0
16		2	10.4	86.1	9.5	0.0
17	Ir-FeO <sub>x</sub> /SiO <sub>2</sub>	0.1	49.8	93.7	2.3	3.8
18		0.5	6.8	89.3	7.4	2.4
19		1	1.4	69.3	30.8	0.0
20		2	1.2	50.8	49.2	0.0
21	Ir-ReO <sub>x</sub> /SiO <sub>2</sub>	1	43.3	95.0	3.4	1.3
$^{^{3}}Reaction$ conditions: crotonal dehyde 3.0 mmol, H_2O 3.0 g, catalyst 50 mg, 303 K, 1 h, H_2 0.8 MPa.						

 $SiO_2$  (Re/Ir = 1) (Table 2, entry 21). The conversion was slightly lower than that over  $Ir-MoO_x/SiO_2$  (Mo/Ir = 1), while the selectivities were almost the same (Table 2, entries 5, 8, 13, and 17). Among Ir-M'O<sub>x</sub>/SiO<sub>2</sub> catalysts, Ir-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/ Ir = 1) catalyst showed about 2 times higher activity than the other optimized Ir-M'Ox/SiO2 catalysts, and the TOF was calculated to be 227  $h^{-1}$  under mild reaction conditions such as 303 K, 0.8 MPa H<sub>2</sub>, and water solvent. The TOF was calculated by the following equation: TOF  $(h^{-1}) = (converted)$ crotonaldehyde (mmol))/((total Ir metal amount (mmol))-(reaction time (h))). In addition, TOF per the surface Ir metal sites, TOFs, was calculated by using the adsorbed CO amount (CO/(total Ir) = 0.07), giving a value of 3200 h<sup>-1</sup>. The catalytic activity for the selective hydrogenation of crotonaldehyde is the highest among the reported catalysts under such mild reaction conditions (Table S1 in the Supporting Information).

As mentioned in the Introduction, overhydrogenation of the produced unsaturated alcohols to saturated alcohols will decrease the selectivity to unsaturated alcohols. In order to obtain the maximum yield of crotyl alcohol, the time course in the hydrogenation of crotonaldehyde was investigated using the optimized catalysts: Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1), Ir-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Ir = 1), Ir-FeO<sub>x</sub>/SiO<sub>2</sub> (Fe/Ir = 0.1), Ir-NbO<sub>x</sub>/SiO<sub>2</sub> (Nb/Ir = 0.1), and Ir-WO<sub>x</sub>/SiO<sub>2</sub> (W/Ir = 0.1) (Figure 1). The reactions proceeded smoothly over all of the catalysts, and the selectivities to crotyl alcohol gradually decreased with the reaction time. A 90% selectivity to crotyl alcohol was maintained over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) and Ir-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Ir = 1) catalysts even at >99% conversion, providing

![](_page_2_Figure_6.jpeg)

**Figure 1.** Time courses in hydrogenation of crotonaldehyde: (a) Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1); (b) Ir-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Ir = 1); (c) Ir-FeO<sub>x</sub>/SiO<sub>2</sub> (Fe/Ir = 0.1); (d) Ir-NbO<sub>x</sub>/SiO<sub>2</sub> (Nb/Ir = 0.1); (e) Ir-WO<sub>x</sub>/SiO<sub>2</sub> (W/Ir = 0.1). Reaction conditions: crotonaldehyde 3.0 mmol, H<sub>2</sub>O 3.0 g, catalyst 50 mg, 303 K, H<sub>2</sub> 0.8 MPa. Legend: ( $\bullet$ ) conversion; (O) selectivity to crotyl alcohol; ( $\Box$ ) selectivity to butanal; ( $\Delta$ ) selectivity to 1-butanol.

high crotyl alcohol yields of 90% (Figure 1a, 8 h) and 92% (Figure 1b, 8 h), respectively. In contrast, the selectivities at high conversion were below 90% in the case of the catalysts Ir-FeO<sub>x</sub>/SiO<sub>2</sub> (Fe/Ir = 0.1) (Figure 1c, 5 h), Ir-NbO<sub>x</sub>/SiO<sub>2</sub> (Nb/Ir = 0.1) (Figure 1d, 8 h), and Ir-WO<sub>x</sub>/SiO<sub>2</sub> (W/Ir = 0.1) (Figure 1e, 5 h). On the other hand, in the case of the catalyst Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) the selectivity to crotyl alcohol was drastically decreased after 100% conversion of crotonaldehyde (Figure 1a, 24 h), which implies that the reactivity of crotyl alcohol depends on the presence of crotonaldehyde. The change in reactivity is discussed in the following section. We selected ReO<sub>x</sub> as a model modifier in the following experiments.

The support often influences the performance of catalysts due to its acid/base properties or redox properties.<sup>15a,16</sup> The effect of supports was investigated using various metal oxides as supports (Table 3). In comparison with Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1), Ir-ReO<sub>x</sub>/Nb<sub>2</sub>O<sub>5</sub> (Re/Ir = 1) (Table 3, entry 2) showed slightly higher conversion (54.2%) with high selectivity (91.2%), which is slightly lower than the selectivity of Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) (Table 3, entry 1, 95.0%). Other catalysts (Table 3, entries 3–9) showed comparable or lower activity and lower selectivity in comparison with Ir-ReO<sub>x</sub>/SiO<sub>2</sub>

# Table 3. Effect of Supports in $Ir-ReO_x$ Catalysts for Hydrogenation of Crotonaldehyde<sup>*a*</sup>

			selectivity (%)		
entry	catalyst	conversion (%)	crotyl alcohol	butanal	1-butanol
1	$Ir-ReO_x/SiO_2$	43.3	95.0	3.4	1.3
2	Ir-ReO <sub>x</sub> /Nb <sub>2</sub> O <sub>5</sub>	54.2	91.2	4.2	4.2
3	$Ir-ReO_x/TiO_2$	43.2	85.3	7.4	6.5
4	$Ir-ReO_x/ZrO_2$	38.7	89.6	4.7	4.9
5	$Ir-ReO_x/Al_2O_3$	25.2	82.4	12.0	5.2
6	$Ir-ReO_x/CeO_2$	20.8	86.1	6.7	6.2
7	$Ir-ReO_x/Fe_2O_3$	12.8	83.4	12.5	3.4
8	$Ir-ReO_x/Y_2O_3$	11.9	69.0	25.4	4.9
9	Ir-ReO <sub>x</sub> /MgO	7.4	70.6	23.7	5.0
<sup>a</sup> React	ion conditions.	crotonaldehyde	3.0 mmol	H.O. 30	r catalyst

(Re/Ir = 1) 50 mg, 303 K, 1 h,  $H_2$  0.8 MPa.

(Re/Ir = 1). In particular, strong base metal oxides such as  $CeO_2$ ,  $Y_2O_3$ , and MgO showed low conversion and selectivity (Table 3, entries 6, 8, and 9), indicating that base sites will be unfavorable for the reaction. This result can be related to the previous result, where a basic additive is unfavorable for Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) catalyst in the hydrogenolysis of glycerol.<sup>17</sup> MO<sub>x</sub> species will not be able to approach the Ir metal surface on basic supports because MO<sub>x</sub> species can be easily adsorbed on the supports, which decreases the active sites, the interface between Ir metal and metal oxide species (discussed in the following sections). In addition, the basic sites of the supports can stabilize IrO<sub>2</sub> to suppress the formation of Ir metal, which will also decrease the interface sites. Therefore, supports without basic sites are preferable for the reaction.

In our previous work on the selective hydrogenation of unsaturated aldehydes,<sup>10</sup> carbon supported noble-metal catalysts (Pt/C, Ru/C, Rh/C, Pd/C) and M-ReO<sub>x</sub>/SiO<sub>2</sub> (M = Pt, Ru, Rh, Pd; Re/M = 0.5) had been applied to the reaction at a high H<sub>2</sub> pressure of 8 MPa, giving low selectivities to crotonaldehyde of <10% and <35%, respectively. In order to ascertain that Ir metal is a truly effective metal species for the reaction, SiO<sub>2</sub> supported ReO<sub>x</sub> modified noble-metal (M- $\text{ReO}_{x}/\text{SiO}_{2}$ , M = Pt, Ru, Rh, Pd) catalysts with various Re/M atomic ratios (0.1, 0.5, 1) were applied to the hydrogenation of unsaturated aldehydes at a low H<sub>2</sub> pressure of 0.8 MPa (Table S2 in the Supporting Information), because the amount of metal oxide species drastically influences the selectivity and activity as discussed above. M-ReO<sub>x</sub>/SiO<sub>2</sub> catalysts showed much lower selectivity to crotyl alcohol ( $\leq$ 30%) than Ir-ReO<sub>*x*</sub>/  $SiO_2$  (Re/Ir = 1) catalyst, although the selectivity was slightly improved in Ru-ReO<sub>x</sub>/SiO<sub>2</sub> catalysts in comparison with Ru/C. These results indicate that Ir metal is an effective metal species for the selective hydrogenation reaction among the tested metal species.

From the above results, it can be concluded that Ir metal is intrinsically effective for the reaction and that modification of Ir metal with metal oxides is an efficient strategy to obtain high activity and selectivity at the same time.

**Catalyst Structure and Stability.** The catalyst Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) had been characterized by XRD, XAFS, TEM, and CO adsorption analyses in our previous work on the hydrogenation of crotonaldehyde.<sup>10</sup> The state of Ir and ReO<sub>x</sub> species and the structure of Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) have been proposed as follows: Ir is in the metallic state, and the particle size is about 2–3 nm. ReO<sub>x</sub> species are in the oxidized

state, and the valence of Re is about +3. Ir metal particles are partially covered with  $\text{ReO}_x$  species.<sup>10</sup> These results agree well with the structure of  $\text{Ir-ReO}_x/\text{SiO}_2$  (Re/Ir = 1) catalyst in hydrogenolysis of polyols.<sup>18</sup> In addition,  $\text{Ir-ReO}_x/\text{SiO}_2$  (Re/Ir = 1) catalyst can be reused without loss of activity and selectivity, and the stability of the catalyst during the reaction was also confirmed by various analyses such as XRD, BET, and CO adsorption using Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) before and after the reaction.<sup>10</sup> ICP analysis and the leaching test demonstrated that Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) works as a heterogeneous catalyst.<sup>10</sup>

 $Ir-MoO_x/SiO_2$  (Mo/Ir = 1) catalyst after the reduction and reaction was also characterized by XRD (Figure S1 in the Supporting Information), TEM (Figure S2 in the Supporting Information), and XAS (Figures S3–S5 in the Supporting Information and Tables 3 and 4) analyses. XRD analysis of Ir-

Table 4. Comparison of Reactivities of Various Substrates<sup>a</sup>

Entry	Substrate	Product	<i>t</i> (h)	Conv. (%)	Selec. (%)	TOF <sup>b</sup> (h <sup>-1</sup> )
1	~~~ <sup>0</sup>	OH	1	43.3	95.0	$(125)^{c}$
2	~~~ <sup>0</sup>	∕OH	1	53.1	94.8	(153) <sup>c</sup>
3	~~~^°	~~^°	H0.25	15.4	91.1	178
4	~~~~¢ <sup>0</sup>	~~~^0	<sup>H</sup> 0.25	33.6	95.7	388
5	$\sim \sim \sim$	$\sim \sim \sim$	1	43.0	>99.9	(124) <sup>c</sup>
6	√∕ОН	∽∽ОН	1	16.7	82.8	48

<sup>*a*</sup>Reaction conditions: substrate 3.0 mmol, H<sub>2</sub>O 3.0 g, Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) 50 mg, 303 K, H<sub>2</sub> 0.8 MPa. <sup>*b*</sup>TOF was calculated by the following equation: TOF (h<sup>-1</sup>) = (converted substrate (mmol))/ ((total Ir metal amount (mmol))(reaction time (h))). <sup>*c*</sup>The calculation of the TOF was tentative because of the high conversion of substrate.

 $MoO_r/SiO_2$  (Mo/Ir = 1) after the reaction showed the signal due to Ir metal, and the particle size of Ir metal was estimated to be 2.5 nm (Figure S1 in the Supporting Information). On the other hand, no signals due to Mo species were observed, indicating that Mo species were highly dispersed on the catalyst. TEM analysis of  $Ir-MoO_x/SiO_2$  (Mo/Ir = 1) provided a particle size of 3.3 nm, which is assigned to Ir metal (Figure S2 in the Supporting Information). Ir L<sub>3</sub>-edge EXAFS of Ir- $MoO_r/SiO_2$  (Mo/Ir = 1) after the reduction and reaction showed that Ir was in the metallic state and that the Ir-Ir CN of ~10.5 was smaller than 12 (Figure S3 and Table S3 in the Supporting Information), which is due to the small Ir metal particles as shown in TEM analysis (Figure S2 in the Supporting Information). Mo K-edge XANES analysis of Ir- $MoO_r/SiO_2$  (Mo/Ir = 1) after the reduction and reaction showed that the shape of the spectra of  $Ir-MoO_{x}/SiO_{2}$  (Mo/Ir = 1) seems to be close to that of  $MoO_2$ , indicating that Mo species of  $Ir-MoO_r/SiO_2$  (Mo/Ir = 1) were partially reduced (Figure S4 in the Supporting Information). Mo K-edge EXAFS analysis of  $Ir-MoO_x/SiO_2$  (Mo/Ir = 1) after the reduction and reaction provided the presence of Mo-O and Mo-Ir bonds (Figure S5 and Table S4 in the Supporting Information). The presence of a Mo-O bond indicates that Mo species were not fully reduced to the metallic state, which is also supported by the result of Mo K-edge XANES analysis (Figure S4 in the Supporting Information). In addition, the state of Ir and  $MoO_r$ species in Ir-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Ir = 1) was not changed before and after the reaction in XAS analyses, which suggests that Ir- $MoO_x/SiO_2$  (Mo/Ir = 1) was stable under the reaction conditions. In order to estimate the surface Ir metal amount, CO adsorption was also carried out using Ir-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/

Ir = 1). The adsorption amount of CO was calculated to be 14.5  $\mu$ mol/(g of cat.), which is about half as small as that of Ir/SiO<sub>2</sub> (31.4  $\mu$ mol/(g of cat.)). Considering that the Ir particle size of Ir/SiO<sub>2</sub> (3.6 nm<sup>18b</sup>) is almost the same as that of Ir-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Ir = 1), the Ir metal surface will be partially covered by MoO<sub>x</sub> species. From these results, the state of Ir metal over Ir-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Ir = 1) is similar to that of Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1),<sup>10,18</sup> and the structure is also similar to that of Ir-metal surface was partially covered by the metal oxide species.

With regard to other catalysts, catalysts similar to  $Ir-NbO_x/$  $SiO_2$ , Ir-FeO<sub>x</sub>/SiO<sub>2</sub>, and Ir-VO<sub>x</sub>/SiO<sub>2</sub> were reported in hydrogenation or hydrogenolysis reactions such as Ir/NbO<sub>x</sub>-SiO<sub>2</sub>, (Ir 1 wt %, Nb/Ir = 2.3, reduction 473 K, 1 h) in hydrogenation of citral,<sup>19</sup> Ir-FeO,/SiO<sub>2</sub> (Ir 3 wt %, Fe/Ir = 5, reduction 573 K, 1 h) in hydrogenation of cinnamaldehyde<sup>20</sup> and Ir-VO,  $/SiO_2$  (Ir 4 wt %, V/Ir = 0.2, reduction 473 K, 2 h) in hydrogenolysis of tetrahydrofurfuryl alcohol.<sup>12a</sup> In these reports, Ir was in the metallic state and the particle size of Ir metal was about 3-5 nm. The detailed structure formed from Ir metal and metal oxide species was not described, although the interface between Ir metal and metal oxide species was proposed to be active sites by part of these reports.<sup>12a,20</sup> In addition, we previously reported that the reaction behavior of  $Ir-WO_x/SiO_2$  is similar to that of  $Ir-MoO_x/SiO_2$  in hydrogenolysis of glycerol,<sup>18b</sup> which suggests that the state of Ir metal of  $Ir-WO_x/SiO_2$  will be similar to that of  $Ir-MoO_x/SiO_2$ . On consideration of these results and facts, the state of Ir metal will be almost the same in these  $M+M'O_r/SiO_2$  catalysts, although the state of metal oxides depends on the properties of the metal oxides. Therefore, the state of metal oxides, particularly the reducibility of metal oxides, will be a key factor in the formation of the active sites. The relationship between the reducibility of metal oxides and the formation of the active sites will be discussed in the last section.

We selected  $\text{Ir-ReO}_x/\text{SiO}_2$  (Re/Ir = 1) as a model catalyst in the following experiments for clarification of the reaction mechanism.

Kinetic Studies. From the time course of hydrogenation of crotonaldehyde over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) catalyst (Figure 1a), two competitive reactions take place (Scheme 1): (i) hydrogenation to crotyl alcohol and (ii) hydrogenation to butanal. At the initial stage of the reaction over  $Ir-ReO_x/SiO_2$ (Re/Ir = 1) (1 h, Figure 1a), the crotyl alcohol/crotonaldehyde selectivity ratio is 15 (95%/5%), meaning that the reactivity of the aldehyde group in crotonaldehyde is about 15-fold higher than that of the olefin group, because 1-butanol, an overhydrogenated product of crotyl alcohol or butanal, was almost not observed. In order to ascertain whether the difference in the reactivity between the aldehyde group and olefin group in crotonaldehyde is derived from the original reactivities of an aldehyde group and olefin group, reactions using a simple aldehyde and olefin as model substrates were carried out (Table 4). Since it is difficult to handle butanal or butene owing to their low boiling points, model compounds with higher boiling points such as heptanal and 3-heptene were selected to ensure the reliability of the data (Table 4, entries 4 and 5). At first, the effect of the main alkyl chain length in  $\alpha_{,\beta}$ -unsaturated aldehydes was investigated (Table 4, entries 1-3). The influence of the alkyl chain length on the reactivity is very small, and the selectivities were also similar. Heptanal, a simple aldehyde, reacted to afford 1-heptanol with high selectivity, and the reactivity is about 2 times higher than that of 2-heptenal

(Table 4, entries 3 and 4). On the other hand, 3-heptene, a simple internal alkene, reacted to afford *n*-heptane quantitatively, but the reactivity is slightly lower than that of 2-heptenal (Table 4, entries 3 and 5). These results indicate that the catalyst  $Ir-ReO_r/SiO_2$  (Re/Ir = 1) originally showed higher activity to the aldehyde group than the olefin group. The reactivity ratio of the simple aldehyde group to the simple olefin group is calculated to be about 3 (Table 4, entries 4 and 5), which is much lower than that in the case of unsaturated aldehydes as discussed above (about 15-fold). These results indicate that the reactivity of the olefin group in  $\alpha_{\beta}$ unsaturated aldehydes drastically decreased by conjugation between the aldehyde group and olefin group. In general, electron-withdrawing groups at the  $\alpha$ -position of the olefin group weakens the coordination of the olefin to metal species by reduction of the electron density in the olefin group via the conjugation between the aldehyde group and olefin group, which may be related to a decrease in the reactivity of the olefin group. In addition, the adsorption state of crotonaldehyde can also influence the reactivity of these functional groups. If the adsorption of the aldehyde group on the catalyst  $Ir-ReO_x/SiO_2$ (Re/Ir = 1) is stronger than that of the olefin group, hydrogenation of the aldehyde group will be more preferred to that of the olefin group. The adsorption of these functional groups is discussed later.

From the time course of the reaction over  $Ir-ReO_r/SiO_2$ (Re/Ir = 1), the high selectivity (>90%) of crotyl alcohol was maintained even at high conversion (99%), but the selectivity drastically decreased after the conversion reached 100%. The TOF in the case of crotyl alcohol as a substrate is about 48 h<sup>-1</sup> (Table 4, entry 6), which is half or one-third lower than that of  $\alpha_{\beta}$ -unsaturated aldehydes (Table 4, entries 1–3). These results cannot explain the high selectivity of crotyl alcohol ( $\geq$ 90%) at high conversion. To elucidate the discrepancy in the reactivities, a reaction using both crotonaldehyde and crotyl alcohol was carried out (Scheme 2, third row). The conversion of crotyl alcohol was calculated using the difference between the produced amount of 1-butanol (0.07 mmol) and the expected amount of 1-butanol (0.02 mmol) from the result of hydrogenation of crotonaldehyde (Scheme 2, the first row). The details of the calculation method for conversion are described in the Supporting Information. The crotonaldehyde

Scheme 2. Reactivity Comparison of Crotonaldehyde Alone, Crotyl Alcohol Alone, and Both Crotonaldehyde and Crotyl Alcohol $^a$ 

	O Ir-ReO <sub>x</sub> /SiO2	OH+	0+	он
	(3.0 mmol) Conv. 43%	1.23 mmol Selec. 95%	0.04 mmol Selec. 3%	0.02 mmol Selec. 1%
	OH Ir-ReO <sub>x</sub> /SiO <sub>2</sub> (3.0 mmol) Conv.17%	0.50 mmol Selec. 81%		
ОН	+ O Ir-ReO <sub>x</sub> /SiO <sub>2</sub>	OH+	0+	он
3.0 mmol) Conv. 2%)*	(3.0 mmol) Conv. 47%	4.35 mmol	0.01 mmol	0.07 mmol
~~~~0	+ O Ir-ReO <sub>x</sub> /SiO <sub>2</sub>		++ ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Н
3.0 mmol) Conv.45%	(3.0 mmol) Conv. 34%	1.35 mmol Yield 45 % Selec. >99%	0.90 mm Yield 32 Selec. 94	ol % 4%

<sup>*a*</sup>Reaction conditions: substrate,  $H_2O$  3.0 g, Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) 50 mg, 303 K,  $H_2$  0.8 MPa, 1 h. (\*) The detailed calculation method is described in the Supporting Information.

conversion was almost the same as that in the case of crotonaldehyde alone (Scheme 2, first row), but the conversion of crotyl alcohol was only 2%, which was much lower than that in the case of hydrogenation of crotyl alcohol alone (Scheme 2, second row). This result indicates that the hydrogenation of crotonaldehyde preferably took place and that hydrogenation of crotyl alcohol was suppressed, which result is in good accordance with the high selectivity of crotyl alcohol in hydrogenation of crotonaldehyde. In addition, a reaction with both crotonaldehyde and pentanal was also carried out (Scheme 2, fourth row). The crotonaldehyde conversion is slightly lower than that of crotonaldehyde alone, the conversion of pentanal is lower than that expected, and the TOF was calculated to be 130 h<sup>-1</sup>, which is much lower than that in the case of hydrogenation of a saturated aldehyde (about 1/3-fold, Table 4, entry 4). This result indicates that the hydrogenation of crotonaldehyde is more preferable to that of pentanal. From these results, the coexistence of crotonaldehvde drastically suppressed the hydrogenation of crotyl alcohol and butanal to 1-butanol in the hydrogenation of crotonaldehyde, although the reactivity of crotonaldehyde was nearly maintained even in the presence of other compounds, which probably suggests that crotonaldehyde can preferentially access the surface of the catalyst.

The effect of the substrate concentration and  $H_2$  pressure was investigated in the hydrogenation of crotonaldehyde at 303 K using Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) and Ir/SiO<sub>2</sub> catalysts (Figure 2). The reaction orders with respect to the crotonaldehyde

![](_page_5_Figure_3.jpeg)

**Figure 2.** (a) Crotonaldehyde concentration dependence and (b)  $H_2$  pressure dependence in hydrogenation of crotonaldehyde over Ir/SiO<sub>2</sub> and Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1). Reaction conditions: (a) crotonaldehyde 1.0–5.0 mmol, H<sub>2</sub>O 3.0 g, Ir-ReO<sub>x</sub>/SiO<sub>2</sub>(Re/Ir = 1) 50 mg, 303 K, H<sub>2</sub> 0.8 MPa; (b) crotonaldehyde 3 mmol, H<sub>2</sub>O 3.0 g, Ir-ReO<sub>x</sub>/SiO<sub>2</sub>(Re/Ir = 1) 50 mg, 303 K, H<sub>2</sub> 0.8–8 MPa. Detailed results for (a) are shown in Tables S5 and S6 in the Supporting Information, and those for (b) are shown in Tables S7 and S8 in the Supporting Information.

concentration over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) and Ir/SiO<sub>2</sub> catalysts were calculated to be 0.0 and +0.6, respectively (Figure 2a), which indicates that the addition of ReO<sub>x</sub> species decreases the reaction order and that the adsorption of crotonaldehyde is saturated on the surface of Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) under the reaction conditions. With regard to the effect of H<sub>2</sub> pressure (Figure 2b), the reaction orders with respect to H<sub>2</sub> pressure over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) and Ir/SiO<sub>2</sub> catalysts were calculated to be +0.9 and +0.8, respectively, which indicates that a hydrogen species is involved in the rate-determining step. The reaction orders over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) and Ir/SiO<sub>2</sub> are almost the same, which probably suggests that the addition of ReO<sub>x</sub> species has almost no

influence on activation of H<sub>2</sub> under the reaction conditions. In addition, the isotopic effect was studied in the hydrogenation of crotonaldehyde over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) catalyst using H<sub>2</sub> and D<sub>2</sub> (Figure 3). The reaction rate with H<sub>2</sub> was higher

![](_page_5_Figure_8.jpeg)

Figure 3. Isotopic effect of hydrogenation of crotonaldehyde with  $H_2$  and  $D_2$ . Reaction conditions: crotonaldehyde 3.0 mmol,  $H_2O$  3.0 g, Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) 50 mg, 303 K,  $H_2$  or  $D_2$  0.8 MPa.

than that with D<sub>2</sub>, providing the reaction rate ratio  $V_{\rm H2}/V_{\rm D2} \approx$  1.5. This also indicates that a hydrogen species is involved in the rate-determining step, which agrees with the result of the effect of H<sub>2</sub> pressure (Figure 2b). According to previous works on hydrogenolysis of polyols over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1),<sup>12e,18b</sup> the reaction order of about +1 with respect to H<sub>2</sub> pressure means that H<sub>2</sub> is heterolytically dissociated to generate H<sup>+</sup> and H<sup>-</sup> species on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) and the nucleophilic addition of the active H<sup>-</sup> will be the rate-determining step.

**FTIR Studies.** In order to confirm the formation of  $H^-$  and  $H^+$  species from  $H_2$  over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1), adsorption of  $H_2$  and  $D_2$  on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) after reduction was examined by in situ FTIR (Figure 4). The large peaks around

![](_page_5_Figure_12.jpeg)

**Figure 4.** FTIR spectra of (a)  $H_2$  and (b)  $D_2$  adsorption on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) at 7.0 kPa of  $H_2$  or  $D_2$  pressure and 303 K.

3745 cm<sup>-1</sup> are due to the free silanol group of SiO<sub>2</sub>. FTIR spectra of H<sub>2</sub> and D<sub>2</sub> adsorption on the reduced Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) catalyst showed bands at 3676 and 3499 cm<sup>-1</sup> due to the  $\nu$ (OH) species (Figure 4a) and bands at 2717 and 2551 cm<sup>-1</sup> due to the  $\nu$ (OD) species (Figure 4b), respectively. Ir–H and Ir–D species cannot be detected clearly because of the change in the SiO<sub>2</sub> absorption. The position of the observed

bands due to the  $\nu$ (OD) species are in good accordance with the calculated positions (2675 and 2546 cm<sup>-1</sup>) from the 3676 and 3499 cm<sup>-1</sup> bands due to the  $\nu$ (OH) species. Therefore, H<sub>2</sub> will be heterolytically dissociated to produce H<sup>+</sup> and H<sup>-</sup> species on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1), which supports the reaction order with respect to H<sub>2</sub> pressure (about +1, Figure 2b). Taking into consideration that ionic hydrogenation using hydride (H<sup>-</sup>) species is generally effective for hydrogenation of polar double bonds in the organic synthesis,<sup>5</sup> the comparatively high selectivity to crotyl alcohol over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) (95.0%) can be explained mainly by the generation of H<sup>+</sup> and H<sup>-</sup> species on the catalyst surface. The comparatively high selectivity (86.9%) over Ir/SiO<sub>2</sub> can also be explained by the same interpretation, because the reaction order with respect to H<sub>2</sub> pressure over Ir/SiO<sub>2</sub> was almost +1 (Figure 2b).

As discussed in the comparison of reactivities of various substrates (Table 4 and Scheme 2) and the effect of the substrate concentration (Figure 2a), the adsorption state of crotonaldehyde on the catalyst can largely influence the activity and selectivity. The adsorption states of crotonaldehyde on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1), Ir/SiO<sub>2</sub>, ReO<sub>x</sub>/SiO<sub>2</sub>, and SiO<sub>2</sub> were studied at 303 K by in situ FTIR. Since crotonaldehyde can be adsorbed on the SiO<sub>2</sub> support, introduction of a large amount of crotonaldehyde is inappropriate for the assignment of crotonaldehyde adspecies on the catalysts. Thus, a small amount of crotonaldehyde (~0.2  $\mu$ L, ~2.9 × 10<sup>-3</sup> mmol), which is adequately lower than the loaded metal amount of the catalyst disk (~25 mg, amount of Ir (Re) 5.2 × 10<sup>-3</sup> mmol) was adopted in the experiments to precisely estimate the adsorption state of crotonaldehyde. Figure 5 shows the

![](_page_6_Figure_3.jpeg)

**Figure 5.** FTIR spectra of gaseous crotonaldehyde and crotonaldehyde adspecies on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1), ReO<sub>x</sub>/SiO<sub>2</sub>, Ir/SiO<sub>2</sub>, and SiO<sub>2</sub> at 303 K in the region 1550–1800 cm<sup>-1</sup>: (a) gas phase; (b) Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1); (c) ReO<sub>x</sub>/SiO<sub>2</sub>; (d) Ir/SiO<sub>2</sub>; (e) SiO<sub>2</sub>.

crotonaldehyde adspecies on these catalysts in the region 1550–1800 cm<sup>-1</sup>, the fingerprint region of C=O and C=C stretching vibrations of crotonaldehyde. Gaseous crotonaldehyde showed bands at 1711, 1724, and 1647 cm<sup>-1</sup>; the first two bands are due to  $\nu$ (C=O), and the last band is due to  $\nu$ (C=C) (Figure 5a).<sup>21</sup> SiO<sub>2</sub> showed new bands at 1673, 1689, and 1642 cm<sup>-1</sup> (Figure 5e). The first two bands on SiO<sub>2</sub> can be assigned to  $\nu$ (C=O), and the bands were largely shifted to lower wavenumbers in comparison to those of gaseous

crotonaldehyde ( $\sim$ 40 cm<sup>-1</sup>), which indicates that crotonaldehyde was adsorbed on SiO<sub>2</sub>. The last band (1642 cm<sup>-1</sup>) is due to  $\nu(C=C)$ , which was only slightly shifted to a smaller wavenumber ( $\sim 5 \text{ cm}^{-1}$ ) from that of gaseous crotonaldehyde. These results indicate that crotonaldehyde is adsorbed on SiO<sub>2</sub> at the carbonyl group. On the other hand, Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1),  $\text{ReO}_{r}/\text{SiO}_{2}$ , and  $\text{Ir}/\text{SiO}_{2}$  showed similar bands around  $1682 \pm 1$ ,  $1669 \pm 1$ , and  $1642 \pm 1 \text{ cm}^{-1}$  (Figure 5b-d). The first two bands can be assigned to  $\nu$ (C=O) of crotonaldehyde adsorbed on the catalyst, and the last band (1642  $\pm$  1 cm<sup>-1</sup>) can be assigned to  $\nu(C=C)$  of crotonaldehyde. The band shapes of crotonaldehyde adspecies on  $Ir-ReO_r/SiO_2$  (Re/Ir = 1),  $\text{ReO}_r/\text{SiO}_2$ , and  $\text{Ir}/\text{SiO}_2$  are different from those on SiO<sub>2</sub>, indicating that crotonaldehyde can be adsorbed on the Ir metal and  $ReO_x$  species at the aldehyde group, considering that the band shift due to  $\nu$ (C=O) is larger than that due to  $\nu$ (C=C). The similar shapes of the  $\nu$ (C=O) bands on ReO<sub>2</sub>/SiO<sub>2</sub> and Ir/SiO<sub>2</sub> may be attributed to the similar adsorption states of the crotonaldehyde. In addition, in the region of  $2700-3100 \text{ cm}^{-1}$ , the fingerprint region of the C-H stretching vibration, the band positions of the aliphatic and olefinic  $\nu$ (C–H)<sup>22</sup> at 3049, 3007, 2984, 2955, and 2926 cm<sup>-1</sup> were almost the same on all catalysts, and the band positions of the aldehydic  $\nu$ (C–H)<sup>22</sup> at  $2763 \text{ cm}^{-1}$  on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1), ReO<sub>x</sub>/SiO<sub>2</sub>, and Ir/ SiO<sub>2</sub> showed higher wavenumber in comparison to those on SiO<sub>2</sub> (Figure S6 in the Supporting Information), which supports that crotonaldehyde is adsorbed not on SiO<sub>2</sub> but on Ir or  $ReO_x$  species at the aldehyde group.

In order to elucidate which site of Ir metal or  $\text{ReO}_x$  species on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) is the adsorption site for crotonaldehyde, crotonaldehyde adsorbed on all the catalysts was desorbed by increasing the temperature from 303 to 373 K, and the change in the bands was monitored by FTIR. Figure 6a

![](_page_6_Figure_9.jpeg)

**Figure 6.** (a) Change in FTIR spectra of crotonaldehyde adspecies on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) at 303–373 K (a, 303 K; b, 313 K; c, 323 K; d, 333 K; e, 343 K; f, 353 K; g, 363 K; h, 373 K). (b) Band area change of crotonaldehyde adspecies on ( $\bigcirc$ ) Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1), ( $\square$ ) ReO<sub>x</sub>/SiO<sub>2</sub>, ( $\diamondsuit$ ) Ir/SiO<sub>2</sub>, and ( $\triangle$ ) SiO<sub>2</sub>. The band area (%) was normalized by the area at 303 K.

shows the band change of the crotonaldehyde adspecies on the catalyst Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) as a model case. The intensity of the band gradually decreased with an increase in the temperature, maintaining the shape of the band. This result indicates that crotonaldehyde was desorbed by heating without decomposition of crotonaldehyde. The change in the band area in the range 1550–1750 cm<sup>-1</sup> on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1), ReO<sub>x</sub>/SiO<sub>2</sub>, Ir/SiO<sub>2</sub>, and SiO<sub>2</sub> was plotted as a function of temperature versus area percent of the corresponding band at 303 K (Figure 6b). The band area on SiO<sub>2</sub> decreased more easily in comparison to those on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1), ReO<sub>x</sub>/SiO<sub>2</sub>, and Ir/SiO<sub>2</sub>, indicating that the adsorption

strength of crotonaldehyde on SiO<sub>2</sub> is weaker than that on the other catalysts. Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) and ReO<sub>x</sub>/SiO<sub>2</sub> showed similar desorption profiles, and the adsorption strength of the crotonaldehyde adspecies on these catalysts is larger than that on Ir/SiO<sub>2</sub>, which can be related to the slightly lower wavenumbers of  $\nu$ (C=O) on Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) and  $\text{ReO}_{r}/\text{SiO}_{2}$  in comparison to that on  $\text{Ir}/\text{SiO}_{2}$ , as shown in Figure 5b-d. From these results, crotonaldehyde was adsorbed more strongly on  $\text{ReO}_r$  species than on Ir metal, which is supported by the results of the effect of the crotonaldehyde concentration (Figure 2a). Therefore, crotonaldehyde will be adsorbed on  $\text{ReO}_x$  species of Ir- $\text{ReO}_x/\text{SiO}_2$  (Re/Ir = 1) catalyst at the aldehyde group, and the aldehyde group will be more activated on ReO<sub>x</sub> than on Ir metal. As above, ReO<sub>x</sub> species work as the adsorption site of crotonaldehyde and strengthen the adsorption of crotonaldehyde on the catalyst in comparison with Ir/SiO<sub>2</sub>. This strong interaction of crotonaldehyde with ReO<sub>x</sub> species will place the crotonaldehyde close to the active hydride species on the catalyst efficiently, leading to the high activity of Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1). In addition, activation of crotonaldehyde on ReO<sub>x</sub> species will increase the reactivity of the aldehyde group, leading to improvement in selectivity to crotyl alcohol (Ir/SiO<sub>2</sub> 86.9% (Table 1, entry 9) to Ir-ReO<sub>x</sub>/  $SiO_2$  (Re/Ir = 1) 95.0% (Table 1, entry 1)).

**Reaction Mechanism and Active Sites of Ir-MO**<sub>x</sub>/SiO<sub>2</sub> **Catalyst.** From the above results, the plausible reaction mechanism of the hydrogenation of crotonaldehyde to crotyl alcohol over Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1) catalyst is proposed in Scheme 3. The model of the catalyst Ir-ReO<sub>x</sub>/SiO<sub>2</sub> (Re/Ir = 1)

Scheme 3. Proposed Reaction Mechanism of Hydrogenation of Crotonaldehyde to Crotyl Alcohol over  $Ir-ReO_x/SiO_2$ (Re/Ir = 1)

![](_page_7_Figure_4.jpeg)

was proposed in the previous report on hydrogenolysis of glycerol, where  $\text{ReO}_x$  species are three-dimensional clusters, and they are located on the surface of Ir metal species.<sup>18</sup> For simplicity, only metal species (Ir metal and  $\text{ReO}_x$ ) are depicted in Scheme 3. The reaction proceeds in four steps as follows. (i) Crotonaldehyde is adsorbed on  $\text{ReO}_x$  species at the aldehyde group, and the aldehyde group is activated by  $\text{ReO}_x$ . (ii) Hydrogen is dissociated heterolytically to hydride (H<sup>-</sup>) and proton (H<sup>+</sup>) at the interface between Ir metal and  $\text{ReO}_x$  species. (iii) The produced hydride species attack the carbonyl carbon of crotonaldehyde adspecies to form alkoxide adspecies

on  $\text{ReO}_x$ . (iv) The alkoxide adspecies is protonated to provide crotyl alcohol. The rate-determining step is step iii. The high selectivity can be explained by the formation of the hydride species at the interface between Ir metal and  $\text{ReO}_x$  species and activation of the aldehyde group on  $\text{ReO}_x$  species. Hydrogenation by the hydride species refers to ionic hydrogenation. The high activity can be explained by the activation of the aldehyde group and effective proximity of crotonaldehyde to the active hydride species on the catalyst by virtue of the adsorption of crotonaldehyde on  $\text{ReO}_x$  species.

In the reaction mechanism, the active sites of  $Ir-MO_x$ catalysts will be the interface between Ir metal and metal oxide species. Therefore, the catalytic performance will depend on the state or amount of the interface, and considering that the states of Ir species in  $Ir-MO_x$  catalysts are almost the same, the formation of the active interface sites can be changed by the properties of the metal oxides.  $ReO_x$  and  $MoO_x$  are comparatively reducible and tend to form partially reduced metal oxide species, which favors the formation of the interface between Ir metal and metal oxide species probably due to the high mobility of ReO<sub>x</sub> and MoO<sub>x</sub> species. In contrast, other metal oxides will not be reduced at all or will be reduced to the metallic state. On the other hand, in the case of small amounts of  $WO_x$ ,  $FeO_x$  and  $NbO_y$ , high conversion and selectivity were obtained (Table 2) in spite of the low reducibility of these metal oxides. At present, a detailed structure of these catalysts has not been clarified. In the future, we will address the characterization of these catalysts in order to clarify the role of these metal oxides and the structure of the catalysts.

### CONCLUSION

Selective hydrogenation of crotonaldehyde to crotyl alcohol was investigated as a typical reaction by using various metal oxide modified noble metal  $(M+M'O_x)$  catalysts. Ir is the most effective active metal for the selective hydrogenation, and ReO<sub>xt</sub>  $MoO_{xy}$   $WO_{xy}$   $NbO_{xy}$  and  $FeO_x$  are effective metal oxide modifiers for Ir/SiO<sub>2</sub>. These metal oxide modified Ir/SiO<sub>2</sub> (Ir- $M'O_{x}/SiO_{2}$ ) catalysts improved both activity and selectivity to crotyl alcohol, providing high conversion and selectivity (92-95%). Among these catalysts,  $Ir-MoO_x/SiO_2$  (Mo/Ir = 1) catalyst showed the highest activity while maintaining high selectivity (>90%), and the TOF was 227  $h^{-1}$ . In order to clarify the reaction mechanism, various kinetics such as the isotopic effect of the hydrogen source  $(H_2/D_2)$ , dependence of H<sub>2</sub> pressure and crotonaldehyde concentration on the reaction rate, comparison of the reactivities between the aldehyde group and olefin group using various substrates, and FTIR spectroscopic studies such as adsorption of  $H_2/D_2$ , adsorption of crotonaldehyde, and temperature-programmed desorption of crotonaldehyde were performed using  $Ir-ReO_x/SiO_2$  (Re/Ir = 1) as a model catalyst. The reaction proceeds via hydride attack at the carbonyl carbon of crotonaldehyde adsorbed on ReO<sub>x</sub> species as the rate-determining step, and the hydride species is produced from H<sub>2</sub> by heterolytic dissociation on the Ir metal near  $\text{ReO}_x$  species. The formation of the hydride species brings about the high selectivity probably thanks to the ionic hydrogenation, and the strong adsorption of crotonaldehyde on ReO<sub>x</sub> species leads to high activity thanks to the proximity of crotonaldehyde to the active sites and activation of the aldehyde group of crotonaldehyde, which also improves the selectivity.

#### EXPERIMENTAL SECTION

Typical Procedure for Hydrogenation of Crotonaldehyde to Crotyl Alcohol. Activity tests were performed in a 190 mL stainless steel autoclave with an inserted glass vessel. Ir- $\text{ReO}_r/\text{SiO}_2$  (Re/Ir = 1) (50 mg, 0.010 mmol of Ir) and water (3.0 g) were put into an autoclave together with a spinner and heated at 473 K with 8 MPa H<sub>2</sub> for 1 h for the reduction pretreatment. After the pretreatment, the autoclave was cooled and hydrogen was removed; then, 3 mmol of crotonaldehyde (Tokyo Chemical Industry Co., Ltd., >99%) was put into the autoclave. After the reactor was sealed, the air content was quickly purged by flushing three times with 1 MPa hydrogen (99.99%; Nippon Peroxide Co., Ltd.). The autoclave was then heated to 303 K, and the H<sub>2</sub> pressure was increased to 0.8 MPa. After the reaction, the gas phase was collected in a gas bag. The liquid phase in the autoclave was diluted with 10 g of ethanol and transferred to a vial. The catalyst was separated by filtration. Details of the reaction conditions are described in each result. The products were analyzed using GC and GC-MS.

In Situ FTIR Spectroscopy. In situ FTIR spectra were recorded with a Nicolet 6700 spectrometer (Thermo Scientific) equipped with a liquid nitrogen cooled MCT (HgCdTe) detector (resolution 4 cm<sup>-1</sup>), using an in situ IR cell with  $CaF_2$ windows, which was connected to a conventional gas flow system. The sample (about 30 mg of Ir-ReO<sub>x</sub>/SiO<sub>2</sub>, Ir/SiO<sub>2</sub>,  $ReO_x/SiO_2$ , and  $SiO_2$ ) was pressed into a self-supporting wafer (20 mm diameter) and mounted in the IR cell. Adsorption of crotonaldehyde was carried out by the following method. The catalyst was reduced at 473 K under H<sub>2</sub> (30 mL/min) flow for 10 min. Then the catalyst was cooled to 303 K under a He flow (60 mL/min). The baseline spectrum was obtained before injection of crotonaldehyde. Crotonaldehyde (0.2  $\mu$ L) was injected into the gas line heated at 423 K under a He flow, which was fed to the in situ IR cell. Then, IR measurement was carried out at 303 K. Desorption of crotonaldehyde was performed by gradually heating the IR cell from 303 to 373 K. The adspecies of crotonaldehyde at different temperatures was monitored.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b00400.

Detailed experimental methods for the catalyst preparation, reagents, and analyses and Tables S1-S8 and Figures S1-S6 (PDF)

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#### Notes

The authors declare no competing financial interest.

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