[Review Paper]

Recent Developments of Heterogeneous Catalysts for Selective Hydrogenation of Unsaturated Carbonyl Compounds to Unsaturated Alcohols

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Development of heterogeneous catalysts which can achieve both high activity and high selectivity requires establishment of sophisticated and uniform active sites on the surface of solid materials, but formation of uniform active sites is difficult in heterogeneous catalysts because of the nonuniformity of heterogeneous catalysts. Selective hydrogenation of the carbonyl group of unsaturated carbonyl compounds is particularly difficult because hydrogenation of the olefin group is thermodynamically and kinetically preferable to that of the carbonyl groups. Therefore, various heterogeneous catalyst systems have been developed to achieve high selectivity. Recently developed effective heterogeneous catalysts for the selective hydrogenation of unsaturated carbonyl compounds such as unsaturated aldehydes and unsaturated ketones to the corresponding unsaturated alcohols using H₂ as a reducing agent are reviewed. Model reactions include liquid-phase selective hydrogenation of crotonaldehyde and liquid-phase selective hydrogenation of benzylideneacetone using a batch reactor, and gas-phase selective hydrogenation of crotonaldehyde with a fixed-bed reactor. Particularly, this review mainly covers metal oxide- or metal cation-modified noble metal catalysts.

Keywords
Selective hydrogenation, Heterogeneous catalyst, Aldehyde, Ketone, Unsaturated carbonyl compound, Unsaturated alcohol

1. Introduction

Selective hydrogenation of unsaturated carbonyl compounds such as aldehydes and ketones to unsaturated alcohols is very important in organic synthesis because unsaturated alcohols are useful chemicals and important intermediates for perfumes, medicines, and other products. Generally, selective hydrogenation of the carbonyl groups of unsaturated carbonyl compounds is difficult to achieve without hydrogenation of the olefin groups, and involves various routes as shown in Scheme 1. H₂ is the ideal hydrogen source because H₂ is cheap and easily available and no byproduct is formed from H₂. On the other hand, alcohols, typically secondary alcohols, can be also used as a hydrogen source, and such reaction is called transfer hydrogenation, but has some problems such as formation of byproducts derived from the alcohols and reuse of dehydrogenated alcohols.

The ideal reaction is Route 1, but hydrogenation of unsaturated carbonyl compounds to saturated carbonyl compounds can occur (Route 2), leading to selectivity decrease for the target unsaturated alcohols. Generally, hydrogenation of carbonyl groups is thermodynamically and kinetically more unfavorable than that of olefin groups, so that selective reaction is difficult. In addition, over-hydrogenation of the desired unsaturated alcohols can occur to form saturated alcohols (Route 3), which also decreases the selectivity for the unsaturated alcohols. Therefore, effective catalysts are required which can selectively hydrogenate the carbonyl groups. Various homogeneous and heterogeneous catalysts have been reported as effective for selective hydrogenation, achieving high activity and selectivity. Heterogeneous catalysts are preferable to homogeneous catalysts for industrial use based on reusability and durability. However, development of effective heterogeneous catalysts is not easy because of the nonuniformity in the active sites, and selective formation of uniform active sites over heterogeneous catalysts is generally difficult. One typical strategy for the development of effective heterogeneous catalysts is to poison the unfavorable sites of metal catalysts with modifiers such as another metal (metal oxide) or organic modifiers, but such modification often increases the selectivity with the sacrifice of the original activity of the active metal species. Therefore, achievement of high selectivity without loss of original hydrogenation activity of active metal spe-
metal oxide (M O) _x catalysts (M _M'O _x catalysts) have been actively developed and show unique catalytic properties for the hydrogenolysis of polyols and ethers, and hydrogenation of carboxylic acids, amino acids, amides, sulfoxide, and nitroarenes. Particularly, hydrogenolysis of polyols such as glycerol with Ir ReO/SiO _2 catalyst probably involves hydride and proton formation from H _2 by heterolytic dissociation of H _2 at the interface of Ir metals and ReO _x in the catalyst. The rate-determining step of the hydrogenolysis of the C OH bond is attack of the hydride species on the carbon attached to the OH group, and the hydride species formed over M _M'O _x catalysts are very active for hydrogenolysis. Hydride and proton species are effective for the hydrogenation of polar functional groups such as aldehydes and ketones, which is called “ionic hydrogenation”. The M + M'O catalyst system forms hydride and proton species from H _2 at the interface of the noble metals and metal oxides, so will be applicable to the hydrogenation of unsaturated carbonyl compounds to unsaturated alcohols by selective hydrogenation of the carbonyl groups. Our laboratory reported that Ir ReO/SiO _2 and Ir MoO/SiO _2 are effective heterogeneous catalysts for the liquid-phase selective hydrogenation of unsaturated aldehydes, Ir NbO/SiO _2 is effective for the gas-phase selective hydrogenation of unsaturated aldehydes, and Fe cation-modified IrMgO (IrMgO + Fe(NO _3)_3) is effective for the selective hydrogenation of unsaturated ketones.

This review introduces recent progress on the development of heterogeneous catalysts for selective hydrogenation, and particularly focuses on the catalyst systems of heterogeneous metal oxide- or metal cation-modified noble metal catalysts for the selective hydrogenation of unsaturated carbonyl compounds such as unsaturated aldehydes and unsaturated ketones using H _2 as the reducing agent.

2. Selective Hydrogenation of Unsaturated Aldehydes to Unsaturated Alcohols by Using over M + M'O, Catalyst

2.1. Liquid-phase Selective Hydrogenation of Unsaturated Aldehydes to Unsaturated Alcohols

Table 1 shows previous studies on heterogeneous catalysts for the selective hydrogenation of crotonaldehyde to crotyl alcohol as a model reaction achieving high yield (> 60%). Hydrogenation of crotonaldehyde is often used as a model reaction because selectivity for the unsaturated alcohol (crotyl alcohol) is comparatively difficult to obtain due to the absence of directing groups in crotonaldehyde.

Heterogeneous catalysts based on Co, Au, Ag, Ni, Ir, Pt, and Cu achieved high selectivity and yield (Table 1). Miura and co-workers reported that Al _2O _3-supported Co (Co/Al _2O _3) catalyst was effective for the selective hydrogenation of crotonaldehyde, providing crotyl alcohol in moderate yield of 62% at 78% conversion (Table 1). In addition, Fan and co-workers developed effective Fe-modified Co-B (amorphous CoFeB) catalyst (Table 1), based on the finding that Co-B catalyst had moderate selectivity for the reaction (~60%). However, the selectivity for crotyl alcohol of Co-based catalysts was not so high (~60%), and the formation rate (µmol g _noble metal _1 s _1) was also low. Following the discovery by Claus and co-workers that Au and Ag supported catalysts were effective for the selective hydrogenation of acrolein to allyl alcohol, various Ag- and Au-based catalysts were developed, achieving high selectivity and yield (Table 1). Combination catalysts of Au or Ag with In over SBA-15 support and/or modified Au and Ag catalysts were also efficient. However, these catalyst systems generally require high reaction temperature (≥ 333 K), high H _2 pressure (≥ 1.5 MPa) and/or organic solvents, and the product formation rate is not so high. Recently, Au/SiC was reported to be effective for photocatalytic hydrogenation of unsaturated aldehydes to unsaturated alcohol (69% yield using crotonaldehyde). Zeolitic imidazole framework-
supported Cu_Ru bimetallic nanoparticles were reported. Shimazu and co-workers found that TiO_{2} supported Ni/Sn alloy (Ni/Sn) has been far from satisfactory. Recently, reduced graphene oxide-supported SnO-isolated Pt_{3}Sn alloy (Pt_{3}Sn/SnO_{2}/rGO) achieved high selectivity and yield for the reaction at low temperature (303 K) and low H_{2} pressure of 0.8 MPa in water, and the activity was also high in comparison with Ir/SiO_{2}, ReO_{x}/SiO_{2} or MoO_{x}/SiO_{2}. The turnover frequency (TOF) per surface metal (TOF_{\text{surface metal}}) over Ir-ReO_{x}/SiO_{2} and Ir-MoO_{x}/SiO_{2} catalysts reached 210 \times 10^{-3} \text{ s}^{-1} and 850 \times 10^{-3} \text{ s}^{-1}, respectively, despite the high selectivity and yield. In addition, molybdenum carbide supported Ir was also effective for the reaction at high temperature (373 K) and high H_{2} pressure (2.0 MPa), giving high yield of crotyl alcohol (87%).

Here we describe our development of Ir-based catalysts for the phase-selective hydrogenation of unsaturated aldehydes. Based on the development of M + M'O catalyst systems as described in the introduction, we investigated M + M'O, catalysts for the selective hydrogenation of crotonaldehyde to crotyl alcohol as a model reaction. Figure 1 shows the results of ReO_{x}-modified noble metal catalysts (M-ReO_{x} cata-

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Figure 1: Scheme of Ir-ReO_{x}/SiO_{2} catalyst for the selective hydrogenation of crotonaldehyde to crotyl alcohol.}
\end{figure}

Table 1: Comparison of Catalytic Performance of Reported Heterogeneous Catalysts for Liquid-phase Hydrogenation of Crotonaldehyde to Crotyl Alcohol

| Catalyst                  | P_{H_{2}} [MPa] | T [K] | Solvent | Conv. [%] | Sel. [%] | Yield [%] | Formation rate \(\times 10^{3} \text{ [s}^{-1}\) | TOF_{\text{surface metal}} \(\times 10^{3} \text{ [s}^{-1}\) | Year | Ref. |
|---------------------------|-----------------|------|---------|-----------|---------|-----------|----------------------------------------------|---------------------------------------------|------|------|
| Co/Al_{2}O_{3}            | 1.0             | 323  | EtOH    | 79        | 78      | 62        | 8.5                                          | -                                          | 1999 | 79  |
| CoFeB                     | 1.0             | 373  | EtOH    | 95        | 67      | 64        | 4.4                                          | 1.0                                        | 2007 | 80  |
| AuIn/APTMS-SBA-15         | 2.0             | 393  | n-Hexane| 94        | 75      | 71        | 22(1)                                        | -                                          | 2009 | 81  |
| Ag-In/SBA-15              | 2.0             | 413  | n-Hexane| 99        | 87      | 86        | 4.7(1)                                       | -                                          | 2011 | 82  |
| AuFeO_{x}                 | 2.0             | 393  | n-Hexane| >99       | 78      | 77        | 5.0(1)                                       | -                                          | 2011 | 83  |
| Au/meso-CeO_{2}           | 1.0             | 373  | H_{2}O  | >99       | 86      | 86        | 226(1)                                       | -                                          | 2011 | 84  |
| Ni-Sn/CoO_{2}             | 3.0             | 403  | 2-ProOH | 70        | 88      | 62        | 35                                           | -                                          | 2012 | 85  |
| AgNP@CeO_{2}              | 1.5             | 423  | THF     | 96        | 91      | 87        | 12                                           | -                                          | 2013 | 86  |
| AgNP@CeO_{2} + C_{3}O_{4} | 1.5             | 333  | THF     | >99       | 98      | 98        | 5.3                                          | -                                          | 2013 | 87  |
| Ir-ReO_{x}/SiO_{2}        | 0.8             | 303  | H_{2}O  | >99       | 90      | 90        | 170(2)                                       | 210                                        | 2013 | 75  |
| PtSn/SnO_{2}/rGO          | 2.0             | 343  | H_{2}O/ EtOH | >99   | 90      | 90        | 1100                                         | 220                                        | 2015 | 88  |
| Ir-MoO_{x}/SiO_{2}        | 0.8             | 303  | H_{2}O  | >99       | 92      | 92        | 310(2)                                       | 850                                        | 2016 | 76  |
| Ir/MoO_{x}                | 2.0             | 373  | H_{2}O  | >99       | 87      | 87        | 500(1)                                       | -                                          | 2016 | 89  |
| Cu-Ru/MWCNT               | 0.1             | 373  | H_{2}O/EtOH | 86   | 72      | 62        | 16                                           | -                                          | 2016 | 90  |
| Pt/3DHPC                  | 2.0             | 343  | 2-ProOH | >99       | 96      | 96        | 1450                                         | 376                                        | 2018 | 91  |
| PtFe ZNWs                 | 0.1             | 313  | Ethanol | 98        | 77      | 75        | 1.1                                          | -                                          | 2018 | 92  |

a) Literature with high yield (> 60 %) were selected. Abbreviation of the catalysts is as follows: meso-CeO_{2}: mesoporous CeO_{2}, rGO: reduced graphene oxide, 3DHPC: three-dimensionally hierarchical porous carbon, ZNWs: zigzag nanowires.

b) Formation rate was calculated based on the formation of the main active metal (Co, Au, Ag, Ni, Ir, Pt).

c) Formation rate was calculated at low conversion level if the result was available.

d) TOF_{\text{surface metal}} was calculated based on the surface active metal atoms determined by CO adsorption, metal particle size or H_{2} adsorption.
The TOF for C = O and C = C hydrogenation based on total Ir content in Ir–ReO₃/SiO₂ catalyst for each substrate is shown in Fig. 3. The TOFs of C = O and C = C hydrogenation of crotonaldehyde are calculated to be 125 h⁻¹ and 6 h⁻¹, respectively. The TOF for substrates with one functional group, 3-heptene and heptanal, are calculated to be 124 h⁻¹ and 388 h⁻¹. These results indicate that the TOF for hydrogenation of the aldehyde group and olefin groups was decreased by the co-existence of both functional groups. Particularly, the decrease of TOF for hydrogenation of the olefin group (about 1/20) was greater than that for the aldehyde group (1/3), presumably because of the lower electron density in the olefin group of crotonaldehyde induced by conjugation of the olefin and aldehyde groups. The TOF was furthermore decreased to be 41 h⁻¹ for the unsaturated crotyl alcohol, indicating that the presence of the OH group decreased the activity for hydrogenation of the olefin group. One possible explanation is that the olefin group cannot approach the active site due to the adsorption of the OH group at the active site. In addition, hydrogenation of crotonaldehyde with crotyl alcohol was carried out. The TOF of hydrogenation of the olefin group in crotyl alcohol was drastically decreased compared with those of other olefins.
of simple olefin substrates such as 3-heptene and crotyl alcohol, although the TOF of hydrogenation of the aldehyde group in crotonaldehyde in both crotonaldehyde and crotyl alcohol was similar to that of only crotonaldehyde. This result suggests that hydrogenation of crotyl alcohol is suppressed in the presence of crotonaldehyde, due to the difference of adsorption strength of the substrates: crotonaldehyde is adsorbed on the catalyst more strongly than crotyl alcohol, which is supported right in Scheme 3. The main characteristics of the structure are as follows: Ir is in the metallic state, with particle size of about 2-3 nm; Re is in the low valence state (valence of Re: ~ 3), and the structure of ReO x is a three-dimensional cluster, which partially covers the Ir metal (Scheme 3). The catalyst structure is similar to those of Ir-ReO x/SiO2, Pt-ReO x/SiO2, Rh-ReO x/SiO2, and Rh-MoO x/SiO2.

The proposed reaction mechanism is also shown in Scheme 3, which is based on the kinetic studies and Fourier transform infrared spectroscopy (FTIR) analysis. The reaction orders with respect to crotonaldehyde concentration over Ir-ReO x/SiO2 and Ir-ReO x/SiO2 are +0.6 and 0, respectively, suggesting that crotonaldehyde was strongly adsorbed on Ir-ReO x/SiO2. Addition of ReO x species strengthens adsorption of the substrate on the ReO x species at the carbonyl group, which was confirmed by FTIR analysis with various substrates. The reaction orders with respect to H2 pressure over Ir/SiO2 and Ir-ReO x/SiO2 are +0.8 and +0.9, respectively, suggesting that the reaction strongly depends on the H2 pressure, which was also supported by the isotopic effect with H2/D2 (VH2/VD2 = 1.5). Formation of protons was also observed by FTIR analysis with H2 adsorption on Ir-ReO x/SiO2. These results suggest that hydrides and protons were formed by heterolytic dissociation of H2 over Ir-ReO x/SiO2 catalyst. The reaction proceeds in four main steps: (1) adsorption of substrate on ReO x species, (2) heterolytically dissociative adsorption of H2 at the interface between Ir metal and ReO x to produce H+ and H+, (3) H+ attack on the carbonyl carbon to form the alkoxide adspecies on Ir metal, and (4) addition of H+ to the alkoxide adspecies to afford the target product.
The high catalytic activity is derived from two main factors: (i) formation of active H⁻ at the interface between Ir metal and ReOₓ and (ii) adsorption and activation of the carbonyl group on ReOₓ. The high selectivity is also derived from two main factors: (i) adsorption of the substrate at the carbonyl group, which controls the adsorption state of the substrate, and (ii) formation of H⁻ species, which are well-known as active species for hydrogenation of polar functional groups such as aldehydes and ketones. Therefore, the key to improvement of both selectivity and activity is formation of the interface sites of Ir metal and ReOₓ, where the reactive hydride is formed and crotonaldehyde is activated.

2.2. Selective Hydrogenation of Unsaturated Aldehydes to Unsaturated Alcohols with a Fixed Bed Reactor

Generally, use of a fixed bed reactor is preferable to a batch reactor for industrial applications. Table 2 shows previous studies on heterogeneous catalysts for the selective hydrogenation of crotonaldehyde to crotyl alcohol with a fixed bed reactor as a model reaction achieving high selectivity (≥ 70 %). The yield and selectivity for crotyl alcohol of the gas-phase reactions in the fixed bed reactor tend to be lower than those in the liquid-phase reactions (Tables 1 and 2). Pt(101)~(107), Ir(73,108)~(111,115)~(117), Ru(112,113), based, and bimetallic Ag–Au/SBA-15 (114) heterogeneous catalysts showed high selectivity for the hydrogenation of crotonaldehyde with a fixed bed reactor (Table 2). Modified Pt catalysts and supported Pt-catalysts have long been developed, and modifiers such as Sn and Zn species for Pt/SiO₂ are effective for the reaction (101,106). CeO₂, SnO₂, ZnO and Ga₂O₃ supports are also effective (102)~(105,107). Particularly, Touroude and co-workers found that Pt/ZnO catalyst gave high yield of crotyl alcohol (60 %), and reported that the formation of PtZn alloy and Lewis acidity of ZnO after reduction were key for the high selectivity (105). Moreover, Rynkowski, Touroude and co-workers developed highly active Pt/Ga₂O₃ catalyst (formation rate: 140 μmol g⁻¹ noble metal⁻¹ s⁻¹) with high selectivity for crotyl alcohol of about 90 % at low conversion level (10 %), although the selectivity decreased with higher conversion (107). ZnO-supported Ru catalysts such as Ru/ZnO and Ru–Ir/ZnO also had high selectivity for crotyl alcohol (112,113). Luo and co-workers demonstrated that Ru/ZnO achieved high selectivity at high conversion (84 % selectivity at 80 % conversion) in the initial stage, but the catalyst was rapidly deactivated with longer time on stream, although the high selectivity (90 %) was maintained (112). In addition, the same research group found that ZnO-supported Ru–Ir bimetallic catalyst enhanced the selectivity for crotyl alcohol and catalyst stability compared with Ru/ZnO, providing high yield of crotyl alcohol (81 %) (113). The high selectivity will depend on the presence of Ir species because Ir-supported catalysts showed comparatively higher selectivity than other metal-supported catalysts as shown in the previous section. The activity of Ru-based catalysts was not so high compared with Pt and Ir-based catalysts.
As described in the liquid phase reaction, Au or Ag metals are effective for the selective hydrogenation of unsaturated aldehydes in the liquid phase reaction, but the stability of these metals is generally low also in a fixed bed reaction, and lower conversion and selectivity with longer reaction time were observed with Au-based catalysts such as Au/SBA-15 (Ref.114) and Au/CeO$_2$ (Ref.118). SBA-15 supported Au-Ag alloy catalyst had better catalyst stability compared to the Au-supported catalyst, with high selectivity and yield for crotyl alcohol (70 % selectivity at 72 % conversion) even at longer reaction time (Ref.114).

As discussed in the liquid phase reaction, Ir metal is the most effective for the selective hydrogenation of the carbonyl group in unsaturated carbonyl compounds in the liquid phase reaction. Ir-based catalysts are also efficient for attaining high selectivity and yield for crotyl alcohol in the gas-phase reaction (Ref.77),108),111),115),117). Various metal oxides such as Ga$_2$O$_3$, TiO$_2$, ZrO$_2$, SiO$_2$ and ZnO are used as supports for Ir-based catalysts (Ref.108~111), and Ga$_2$O$_3$ is the most effective support because the activity was very high with high selectivity. According to the previous report by Rynkowski, Touroude and co-workers on Ir/Ga$_2$O$_3$, Pt/Ga$_2$O$_3$ and Ru/Ga$_2$O$_3$ catalysts in the gas-phase selective hydrogenation of crotonaldehyde (Ref.108), the reducibility of Ga$_2$O$_3$ in Ir/Ga$_2$O$_3$ and Pt/Ga$_2$O$_3$ leads to decoration of the noble metal species, which will be the key for the high selectivity. The catalyst system will be similar to the M-M’O$_x$ catalyst system.

As for the M-M’O$_x$ catalysts, Luo and co-workers found that FeO$_x$-modified Ir/SiO$_2$, (FeO$_x$-Ir)/SiO$_2$ and FeO$_x$-modified Ir/BN catalysts showed higher selectivity and yield for crotyl alcohol, and the activity was comparatively high (Ref.115), indicating that FeO$_x$ modification is effective for Ir metal species in the selective hydrogenation of the carbonyl groups. Recently, we reported that Ir-NbO$_x$/SiO$_2$ was an effective heterogeneous catalyst for the gas-phase selective hydrogenation of crotonaldehyde, providing high yield of crotyl alcohol (87 %) with comparatively high activity (Ref.77). In this section, the details of the Ir-NbO$_x$/SiO$_2$ catalyst are introduced below.

Gas-phase reaction is commonly conducted at high temperature without solvents, in contrast to the liquid phase reaction. Such differences often affect the reactivity of the substrate, and the activity and stability of the catalysts. The performances of various Ir+M’O$_x$...
catalysts in the gas-phase selective hydrogenation of crotonaldehyde as a model reaction are shown in Fig. 4. ReO₃, MoO₃, FeO₃, NbO₃ and WO₃ were selected as modifiers because these metal oxides showed high selectivity for crotyl alcohol in the liquid phase selective hydrogenation of crotonaldehyde (Fig. 2). The reaction was conducted at 373 K and ambient H₂ pressure (0.1 MPa). Compared with the results of Ir-ReO₃/SiO₂ and Ir-MoO₃/SiO₂ catalysts in the liquid phase reaction (Fig. 2), the selectivity for crotyl alcohol over these catalysts was lower (60-70 %), although the activity was high compared with other catalysts, possibly due to the high temperature and solvent effect. FeO₃, NbO₃, and WO₃-modified Ir/SiO₂ (Ir-FeO₃/SiO₂, Ir-NbO₃/SiO₂ and Ir-WO₃/SiO₂) catalysts showed high selectivity for crotyl alcohol (> 85 %) with moderate conversion (10-25 %), and Ir-NbO₃/SiO₂ showed the highest selectivity of 96 %.

Effect of the Nb/Ir molar ratio in the same reaction is also shown in Fig. 4, as the Nb/Ir molar ratio was changed from 0 to 1.5. Selectivity for crotyl alcohol gradually increased with higher Nb/Ir molar ratio, and the highest selectivity of 96 % was obtained at the Nb/Ir molar ratio of 1. However, the conversion decreased at Nb/Ir molar ratio higher than 0.5, and the highest conversion was obtained at the Nb/Ir molar ratio of 0.5, which is higher than that with Ir-NbO₃/SiO₂ with Nb/Ir molar ratio of 1. Ir-NbO₃/SiO₂ with Nb/Ir molar ratio of 0.5 was preferable for the optimum selectivity and activity.

The contact time dependence of the gas-phase selective hydrogenation of crotonaldehyde over Ir-NbO₃/SiO₂ catalysts is shown in Fig. 5. Ir-NbO₃/SiO₂ maintained high selectivity for crotyl alcohol even at high conversion level (~90 %), but the selectivity rapidly decreased after the conversion reached 100 % (Fig. 5(a)). At the same time, the selectivity for 1-butanol increased, meaning that over-hydrogenation of the produced crotyl alcohol occurred. This result implies that adsorption of the aldehyde group is stronger than that of the olefin group, which is supported by the zero reaction order with respect to crotonaldehyde concentration over Ir-NbO₃/SiO₂. On the other hand, the selectivity to crotyl alcohol was high at low conversion level (~10 %), but decreased even at conversion level below 50 %, and the selectivity to 1-butanol steadily increased over Ir/SiO₂ (Fig. 5(b)). This result indicates that over-hydrogenation of the crotyl alcohol occurred even at low conversion level. The high activity for over-hydrogenation of crotyl alcohol...
Comparison of Catalytic Performance of Heterogeneous Catalysts for the Selective Hydrogenation of Benzylideneacetone to 4-Phenyl-3-buten-2-ol

| Catalyst          | Solvent     | \(P_t\) [MPa] | \(T\) [K] | \(t\) [h] | Conv. [%] | Sel. [%] | Yield \(\mu\text{mol} \text{ g}_{\text{noble metal}}^{-1} \text{s}^{-1}\) | TOF_{surface metal} \(\text{s}^{-1}\) | Ref. |
|-------------------|-------------|---------------|-----------|-----------|-----------|---------|------------------------------------------------|------------------|------|
| Au/Fe\(_2\)O\(_3\) | EtOH        | 0.1          | 333       | 3         | 91        | 68      | 61 0.08(0.14) \(^{(6)}\)                  | -                | 2003 119) |
| Au/Fe\(_2\)O\(_3\) | EtOH        | 0.1          | 333       | 2         | 91        | 59      | 53 1.6(2.6) \(^{(6)}\)                  | -                | 2004 120) |
| Au(PVP)_{nano}-ZnO | EtOH        | 4            | 333       | 40        | 93        | 69      | 64 2.3                                      | -                | 2007 121) |
| Au\(_2\)(SCH\(_2\)CH\(_2\)Ph)\(_{12}\)/Fe\(_2\)O\(_3\) | toluene/ethanol | 0.1          | 273       | 3         | 43        | >99     | 43 4.2                                      | -                | 2010 122) |
| Au/meso-CeO\(_2\) | H\(_2\)O/EtOH (12/3) | 1            | 373       | 4         | 97        | 66      | 64 23(64) \(^{(6)}\)                  | -                | 2011 123) |
| Ir/MgO + Fe(NO\(_3\))\(_3\) | CH\(_3\)OH  | 8            | 303       | 0.17      | >99       | 90      | 90 \(375(1000)^{6}\)                  | \(500(1400)\) \(^{(6)}\) | 2016 78) |
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- no data.
a) Heterogeneous catalysts showing more than 40 % yield were selected.
b) Formation rate was calculated by the following equation: Formation rate = (amount of unsaturated alcohol (\(\mu\text{mol}\)))/(total Au or Ir amount (g))/(time (s)).
c) TOF_{surface metal} was calculated by the following equation: \(\text{TOF}_{\text{surface metal}} \left( \text{s}^{-1} \right) = \text{(amount of unsaturated alcohol (mmol))}/(\text{surface Au or Ir amount (mmol))}/(\text{time (s))}.\)
d) Number in the parenthesis is initial formation rate.

over Ir/SiO\(_2\) decreased the selectivity for the target crotyl alcohol.

Various characterizations such as XRD, TEM, TPR, CO-adsorption, and XAS analyses\(^{77}\) have shown that the catalyst structure of Ir-NbO\(_x\)/SiO\(_2\) is similar to those of Ir-ReO\(_2\)/SiO\(_2\) and Ir-MoO\(_x\)/SiO\(_2\) except that Nb is in a highly oxidized state with valence of about +5\(^{75,76}\), Ir is in the metallic state, and the particle size is about 3 nm. The NbO\(_x\) species are highly dispersed and the Ir metal is partially covered by NbO\(_x\) species. In addition, the kinetic studies with the catalyst characterization suggest a similar reaction mechanism to that over Ir-ReO\(_2\)/SiO\(_2\) and Ir-MoO\(_x\)/SiO\(_2\) (Scheme 3)\(^{77}\).

Clearly, the most effective catalyst is different for each reaction system: Ir-ReO\(_2\)/SiO\(_2\) and Ir-MoO\(_x\)/SiO\(_2\) for the liquid-phase reaction\(^{75,76}\), and Ir-NbO\(_x\)/SiO\(_2\) for the gas-phase reaction\(^{77}\). In fact, Ir-NbO\(_x\)/SiO\(_2\) catalyst was also effective for the liquid-phase hydrogenation of crotonaldehyde, with high selectivity for crotyl alcohol (~85 %, \textbf{Fig. 2}), but the activity of Ir-NbO\(_x\)/SiO\(_2\) catalyst in the liquid-phase reaction was much lower than those of Ir-ReO\(_2\)/SiO\(_2\) and Ir-MoO\(_x\)/SiO\(_2\) catalysts, and also showed the same tendency in the gas-phase reaction. One possible explanation of this tendency is the difference in the Lewis acidity of the metal oxides species. FTIR analyses of crotonaldehyde adsorption on Ir-ReO\(_2\)/SiO\(_2\) and Ir-NbO\(_x\)/SiO\(_2\) catalysts\(^{76,77}\) showed clearly stronger adsorption of crotonaldehyde on Ir-NbO\(_x\)/SiO\(_2\) catalyst than on Ir-ReO\(_2\)/SiO\(_2\) catalyst from the shift value of \(\nu(C=O)\), indicating that the Lewis acidity of NbO\(_x\) species is higher than that of ReO\(_2\) species. This result is comprehensible, considering that the valence of NbO\(_x\) (about +5) was higher than those of ReO\(_2\) (about +3 to 4) and MoO\(_x\) (about +3) in these reaction systems. Control of the adsorption state of the unsaturated aldehyde is important factor for high selectivity in the hydrogenation of unsaturated aldehydes, and the adsorption state is controlled by adsorption of the aldehyde group on the Lewis acid sites of NbO\(_x\), ReO\(_2\), and MoO\(_x\) species. Gas-phase hydrogenation of crotonaldehyde required higher temperature than liquid-phase hydrogenation due to the boiling point of crotonaldehyde (373 K for gas-phase hydrogenation, 303 K for liquid-phase hydrogenation), and so stronger adsorption of the substrate is required in gas-phase hydrogenation to control the adsorption state at higher temperature. Ir-NbO\(_x\)/SiO\(_2\) catalyst has the strong Lewis acid sites of NbO\(_x\) species, which strongly adsorb crotonaldehyde, leading to high selectivity for crotyl alcohol in the gas-phase hydrogenation of crotonaldehyde.

3. Liquid-phase Selective Hydrogenation of Unsaturated Ketones to Unsaturated Alcohols

Generally speaking, selective hydrogenation of unsaturated ketones to unsaturated alcohols over heterogeneous catalysts is more difficult than that of unsaturated aldehydes because the ketone group has lower reactivity than the aldehyde group. \textbf{Table 3} shows the most effective heterogeneous catalysts for the selective hydrogenation of the ketone group in benzylideneacetone as a model reaction\(^{78,120}\)~\(^{123}\). Au- and Ir-supported catalysts were efficient for the reaction. In particular, meso-CeO\(_2\)\(^{123}\), ZnO\(^{121}\), and FeO\(_2\)\(^{119,120,122}\)-supported Au catalysts showed high selectivity of about 60 % for the unsaturated alcohol. Recently, FeO\(_2\) supported Au clusters (Au\(_{25}\)(SCH\(_2\)CH\(_2\)Ph)\(_{10}\)/FeO\(_2\)) were also
Ir/SiO2 with FeOzylideneacetone as a model substrate. Modification of
modifiers (FeOx) activity, and achieved high yield of the unsaturated alcohol
method with MgO and H2IrCl6, and Ir/MgO shown in
Ir/SiO2 in the hydrogenation of benzylideneacetone is
below.
was conducted at 303 K in methanol solvent with ben-

Fig. 6 Effect of Metal Oxide Modifiers of Ir + M’O /SiO2 (Ir: 4 wt%) and Effect of Supports of Ir–FeOx (Ir: 4 wt%) Catalysts in Hydrogenation of Benzylideneacetone over M + M’O, Catalysts

reported to be effective for the reaction, providing high selectivity for the unsaturated alcohol (>99 %) at moderate conversion (43 %). However, the activity of the Au catalysts was not so high, therefore high temperature was often required. Recently, we demonstrated that Fe(NO3)3-modified Ir/MgO (Ir/MgO + Fe(NO3)3) provided high activity for the reaction with high selectivity, and achieved high yield of the unsaturated alcohol (90 %)78). Ir/MgO was prepared by the impregnation method with MgO and H2IrCl6, and Ir/MgO + Fe(NO3)3 was formed in-situ in the reactor, by adding Fe(NO3)3 to the substrates, solvent and Ir/MgO in the reactor. In the catalyst system, Ir/MgO was modified with Fe-
cation species, similar to M + M’O, catalysts, resulting in high activity and selectivity. The detailed performance of the Ir/MgO + Fe(NO3)3 catalyst is introduced below.

The catalytic performance of metal oxide-modified
Ir/SiO2 in the hydrogenation of benzylideneacetone is shown in Fig. 678). The selection of metal oxide mod-
ifiers (FeOx, NbOx, MoOx, WOx, and ReOx) was based on the results of the hydrogenation of unsaturated aldehydes with M + M’O, catalysts (Fig. 2). The reaction was conducted at 303 K in methanol solvent with benzylideneacetone as a model substrate. Modification of Ir/SiO2 with FeOx showed comparatively high selectivity for the unsaturated alcohol ( ~40 %), which was higher that of Ir/SiO2, but the conversion was half that of Ir/ SiO2. The effect of supports in Ir–FeOx catalysts is shown in Fig. 678). MgO and Al2O3 showed almost the same selectivity for the unsaturated alcohol as SiO2, and MgO showed the highest conversion (~40 %) among the metal oxide supports tested. Therefore, FeOx, and MgO were the most effective modifier and support for Ir metal in the reaction.

The effect of metal salt addition to the reaction mix-
ture of the substrate, Ir/MgO and solvent before the reaction is shown in Fig. 778). Addition of Fe(NO3)3 greatly increased the conversion and selectivity for the unsaturated alcohol, and other Fe salts also gave high selectivity (~80 %), but the conversion depended on the salts. The activity of Ir and/or FeOx-supported cata-
lyst of Ir–FeOx/MgO and Ir/MgO were investigated using Ir–FeOx/MgO and Ir/MgO prepared by the (sequential) impregnation method. The activity and selectivity were much higher than Ir–FeOx/SiO2 cata-
lyst, indicating that addition of Fe salt greatly improved the selectivity and activity. Other metal salts such as CoCl2, NiCl2, RuCl3, LaCl3, SnCl4, AlCl3, YCl3 and AgNO3 showed clearly lower selectivity for the unsaturated alcohol than Fe salts. Therefore, Fe salts were the most effective in combination with Ir/MgO for the hydrogenation of unsaturated ketones.

The time-course of the hydrogenation of benzylideneacetone over Fe(NO3)3 added Ir/MgO (Ir/MgO + Fe(NO3)3) is shown in Fig. 8. The selectivity for the unsaturated alcohol was high at the initial stage, and the selectivity was maintained after conversion reached 100 %, which indicates that over-hydrogenation of the target unsaturated alcohol was completely suppressed in this catalyst system. On the other hand, over-
hydrogenation of the saturated ketone proceeded to form the saturated alcohol. These results suggest that hydrogenation of the olefin group was selectively sup-

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pressed over Ir/MgO + Fe(NO₃)₃ catalyst.

The scope of various unsaturated ketones with Ir/MgO + Fe(NO₃)₃ catalyst is shown in Scheme 4⁷⁸). Benzylideneacetone derivatives were converted to the corresponding unsaturated alcohols with high selectivity (84-90 %). A γ-branched unsaturated ketone, 4-methyl-3-penten-2-one also showed high selectivity for the unsaturated alcohol (84 %), although the reactivity was quite low. Linear and γ-branched unsaturated ketones showed moderate selectivity to the corresponding unsaturated alcohol (~50 %), indicating that steric hindrance near the olefin group is necessary for obtaining high selectivity. On the other hand, the catalyst was applicable to unsaturated aldehydes, providing the corresponding unsaturated alcohols quantitatively.

The catalyst structure was proposed based on various characterizations such as XRD, TEM, XPS, XAS, TPR and CO-adsorption as follows⁷⁸): Ir species exist as Ir metals and IrOₓ (Ir₀: ~60 %, Ir⁴⁺ ~40 %); Fe species have valence +2 in the reaction, produced by reduction of Fe³⁺ species over the catalyst; and Fe²⁺O²⁻ cation-anion pair sites are formed by addition of Fe cation species during the reaction.

The proposed reaction mechanism based on the catalyst characterization and kinetic studies is shown in Scheme 5⁷⁸). The reaction orders with respect to benzylideneacetone concentration over Ir/SiO₂, Ir/MgO and Ir/MgO + Fe(NO₃)₃ were 0.7, 0 and 0, respectively, suggesting that the MgO support facilitates the adsorption of substrate. The reaction orders with respect to H₂ pressure over Ir/SiO₂, Ir/MgO and Ir/MgO + Fe(NO₃)₃ were 0.6, 0.6 and 0.9, respectively, suggesting that Fe(NO₃)₃ addition increases the reaction order, and that hydrides and protons are formed on the Ir/MgO + Fe(NO₃)₃ catalyst. The reaction mainly consists of four steps: (1) dissociation of H₂ species over Ir metal near the Fe²⁺O²⁻ cation-anion pair site to give hydride (H⁻) and proton (H₊); (2) adsorption of unsaturated ketone on the Ir⁴⁺ at the carbonyl group; (3) attack of H⁻ on the adsorbed carbonyl group to form the alkoxyl adspecies; (4) addition of H⁺ to the alkoxide adspecies, forming the alcohol. The high selectivity of this catalyst system is derived from formation of the hydride species. The Fe²⁺O²⁻ cation-anion pair site can promote the formation of hydride species near the adsorption site of the carbonyl group in the unsaturated ketones. On the other hand, the high activity is derived from the activation of the carbonyl group by adsorption of the carbonyl group of the substrate on Ir⁴⁺.

Scheme 5 Proposed Reaction Mechanism of Selective Hydrogenation of Unsaturated Ketones over Ir/MgO + Fe(NO₃)₃ Catalyst⁷⁸)
for enhancing the activity. Therefore, the important steps for achieving both activity and selectivity are formation of the $\text{Fe}^{2+}\text{O}^{2-}$ cation-anion pair site and formation of $\text{Ir}^{3+}$, where the reactive hydride species is formed and the substrate is activated at the same time.

4. Conclusion
Recent progress on heterogeneous catalysts, particularly metal oxide- or metal cation-modified noble metal metal catalysts, for the selective hydrogenation of unsaturated carbonyl compounds to the corresponding unsaturated alcohols was reviewed. Modification of noble metal species with cationic species such as metal oxides and metal cations is an effective strategy for achieving both high activity and selectivity. Adequately high selectivity and activity have been obtained in the selective hydrogenation of unsaturated aldehydes, but the selectivity to the unsaturated alcohols remains unsatisfactory, and the scope of substrates is also quite limited. More sophisticated modification of the present catalyst systems or development of new catalyst systems are required in the future to improve the low selectivity in the hydrogenation of unsaturated ketones over heterogeneous catalysts.

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要  旨
不飽和カルボニル化合物の選択的水素化による不飽和アルコール合成用不均一系触媒の最近の進歩

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高活性かつ高選択性を同時に実現できる不均一系触媒の開発には，固体物質表面に簡易に制御されかつ均一な活性サイトの構築が求められる。しかしながら，不均一系触媒は，一般的に活性サイトが不均一であるため，均一な活性点を構築することさえ難しい。様々な有機合成反応において，不飽和カルボニル化合物のカルボニル基の選択的水素化は，熱力学的，速度論的，選択的水素化がカルボニル基の水素化よりも優先されるため，高選択性の一つである。したがって，高選択性を実現できる様々な不均一系触媒の開発が行われてきた。本論文では，水素を過元種として用いた不飽和アルデヒドや不飽和ケトンなどの不飽和カルボニル化合物の選択的水素化による不飽和アルコール合成反応に高選択性を実現できる高効率不均一系触媒の最近の進歩について解説する。モデル反応としては，パッチ，液相でのクロトンアルデヒドおよびペンジデンアセトンの選択的水素化，固定床，気相でのクロトンアルデヒドの選択的水素化を用いた。特に，金属酸化物もしくは金属イオン修飾貴金属触媒の詳細について紹介する。

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