

## [Review Paper]

## Supported Metal Catalysts for Total Hydrogenation of Furfural and 5-Hydroxymethylfurfural

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Total hydrogenation of furfural and 5-hydroxymethylfurfural (HMF), both of which are important platform chemicals from biomass, produces tetrahydrofurfuryl alcohol (THFA) and 2,5-bis(hydroxymethyl)tetrahydrofuran (BHTHF), respectively, and these products can be used as solvent or raw material of resin. Ni catalysts can give good yields in these reactions; however the low activity and stability are problems. Supported monometallic Pd and Ru catalysts have been reported to be also active in hydrogenation, although the selectivity for total hydrogenation tends to be lower. Other monometallic catalysts such as Cu and Pt generally have low activity in furan ring hydrogenation of furfuryl alcohol (FOL) and 2,5-bis(hydroxymethyl)furan intermediates. We explored various multicomponent catalysts and found that Ni-Pd/SiO<sub>2</sub>, Pd-Ir/SiO<sub>2</sub> and Rh-Ir-ReO<sub>x</sub>/SiO<sub>2</sub> give good yield of THFA or BHTHF with much higher activity than the mixture of each component supported on SiO<sub>2</sub>.

**Keywords**

Hydrogenation, Furan ring, Biomass, Alloy catalyst, Supported catalyst

**1. Introduction**

The use of biomass-derived compounds as substitutes of petroleum has received much attention<sup>1)~4)</sup>. Because of the complex nature of biomass, the conversions of biomass to chemicals usually start with the production of small molecules called platform chemicals by thermal, chemical or biological processing<sup>5)</sup>. Among these platform chemicals, furfural<sup>6)</sup> and 5-hydroxymethylfurfural (HMF)<sup>7)</sup> are especially important ones, which are produced from pentoses and hexoses, respectively, by acid-catalyzed dehydration. Production of furfural has been already commercialized.

Various methods of furfural or HMF conversions to useful chemicals have been reported including reduction, oxidation and condensation<sup>8),9)</sup>. Because of the high unsaturation, reduction with hydrogen is one of the most important conversion methods<sup>10)</sup>. However, there are a number of potential products from furfural or HMF reduction: products from furfural include furfuryl alcohol, tetrahydrofurfuryl alcohol, 1,2,5-pentanetriol, pentanediols, pentanols, cyclopentanone, cyclopentanol, 2-methylfuran, and 2-methyltetrahydrofuran (**Fig. 1**). More kinds of products can be formed from HMF which has more complex structure than furfural. In

addition, polymerization of furfural, HMF and furfuryl alcohol to brown solid, which is called humin, is frequently observed, especially in aqueous conditions. High selectivity to one product is sometimes difficult to obtain, while selective hydrogenation of furfural to furfuryl alcohol has been well established<sup>11)</sup>.

Total hydrogenation reaction of furfural and HMF gives tetrahydrofurfuryl alcohol (THFA) and 2,5-bis(hydroxymethyl)tetrahydrofuran (BHTHF), respectively. In addition to the utilization of THFA as solvent, the utilization of THFA and BHTHF as a source of polymer has attracted much attention since a selective hydrogenolysis system of THFA to 1,5-pentanediol was discovered by our group in 2009<sup>12)</sup>. We and other research groups have intensively investigated the hydrogenolysis of THFA and BHTHF to  $\alpha,\omega$ -diol (1,5-pentanediol and 1,6-hexanediol, respectively), which can be used as monomers of polyurethane or polyester resin (**Fig. 2**)<sup>13)~16)</sup>. The hydrogenolysis systems dissociate the C–O bond neighboring –CH<sub>2</sub>OH group. The effective catalysts are the bimetallic ones with the combination of group 9 noble metal (Rh or Ir) and group 5–7 transition metal such as V, Mo, W and Re, and water solvent is particularly effective. The yield of 1,5-pentanediol from THFA can reach 80–90%. Therefore, the importance of total hydrogenation of furfural and HMF is growing. Aqueous phase reaction is preferred to the reactions in other solvents in view of the total process into  $\alpha,\omega$ -diol; however water solvent is disadvantageous to obtain high selectivity in

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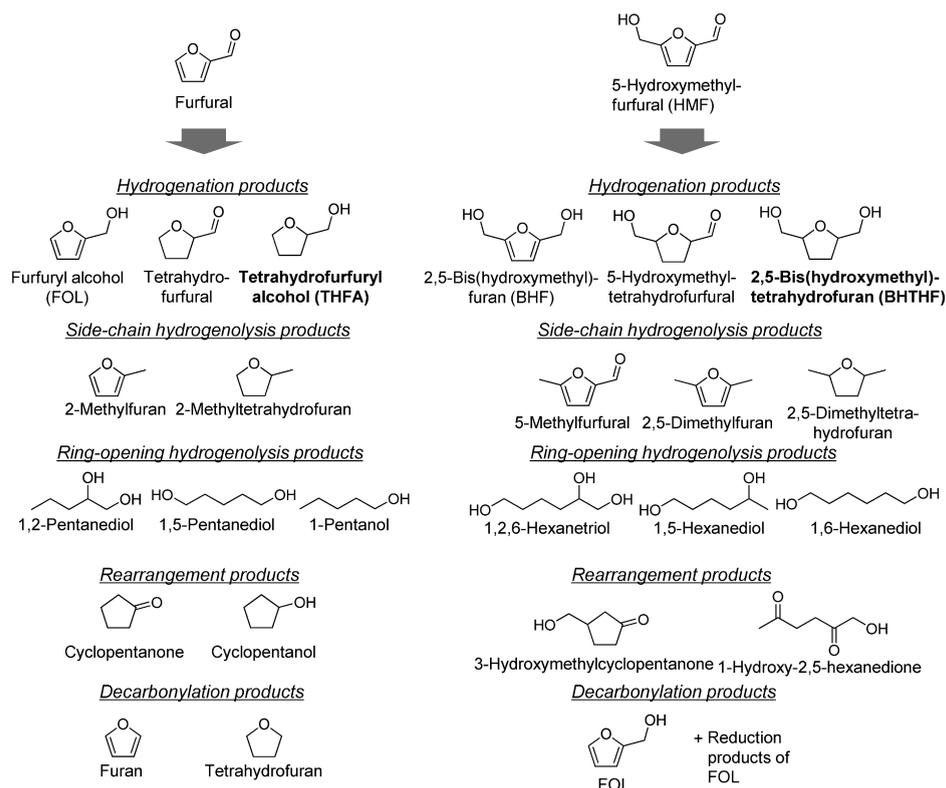


Fig. 1 Products in Reduction of Furfural or 5-Hydroxymethylfurfural (HMF)

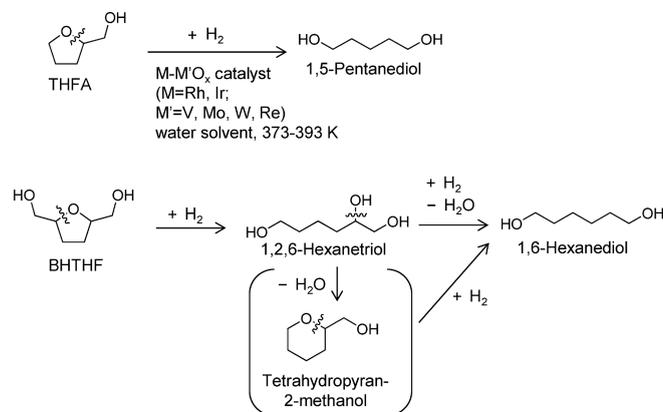


Fig. 2 Production of  $\alpha,\omega$ -Diol from Tetrahydrofurfuryl Alcohol (THFA) and 2,5-Bis(hydroxymethyl)tetrahydrofuran (BHTHF)

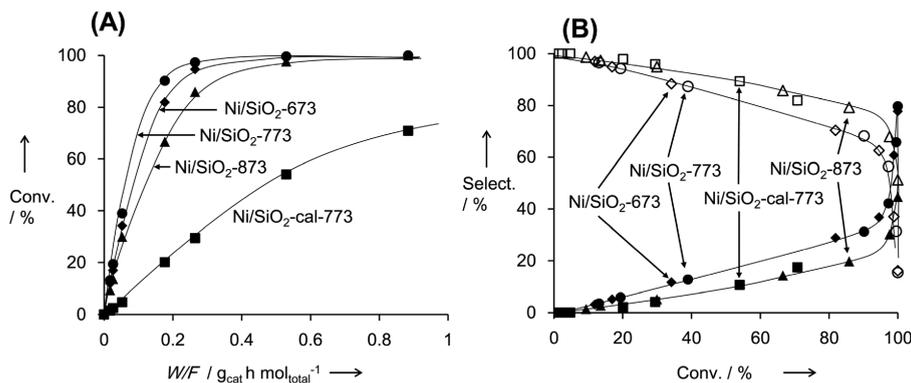
total hydrogenation. In this context, we have searched effective catalysts in total hydrogenation of furfural and HMF in aqueous phase or non-solvent systems, and discovered several good heterogeneous metal catalysts with simple support such as  $SiO_2$ . Here, we summarize our and other groups' recent results for total hydrogenation of furfural and HMF with heterogeneous catalysts. The systems using non-conventional solvents or supports are excluded in practical view.

## 2. Monometallic Catalysts

### 2.1. Ni Catalysts

Total hydrogenation of furfural or HMF requires hydrogenation of all the conjugated  $C=C$  and  $C=O$  bonds. Ni is known to be active in both of these hydrogenation reactions, and total hydrogenation process of crotonaldehyde to 1-butanol over Ni catalyst was well established<sup>17)</sup>.

The vapor pressure of furfural is high enough to apply gas-phase hydrogenation. We conducted the



Furfural/H<sub>2</sub>/N<sub>2</sub> = 1 : 36 : 72, 403 K. Closed and open markers in (B) represent the selectivities to THFA and FOL, respectively.

Fig. 3 Furfural Hydrogenation over Various Ni/SiO<sub>2</sub> Catalysts  
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hydrogenation of furfural over Ni/SiO<sub>2</sub> in gas phase with a fix-bed reactor and the effect of Ni particle size was investigated<sup>18</sup>). Four Ni/SiO<sub>2</sub> catalysts were prepared by impregnation with the same SiO<sub>2</sub> support, Ni precursor (Ni(NO<sub>3</sub>)<sub>2</sub>) and Ni loading amount (10 wt%). Three catalysts were prepared by reduction of SiO<sub>2</sub>-supported Ni(NO<sub>3</sub>)<sub>2</sub> with H<sub>2</sub> at different temperature, and they were denoted as Ni/SiO<sub>2</sub>-673, Ni/SiO<sub>2</sub>-773 and Ni/SiO<sub>2</sub>-873, where the appended number was the reduction temperature in K. The other one catalyst was prepared by calcination of Ni(NO<sub>3</sub>)<sub>2</sub>/SiO<sub>2</sub> at 773 K and subsequent reduction with H<sub>2</sub> at 773 K (denoted as Ni/SiO<sub>2</sub>-cal-773). The reduction was conducted just before catalytic use or characterization. The H<sub>2</sub> adsorption, X-ray diffraction (XRD) and transmission electron microscope (TEM) analysis showed that the Ni particle size was 2.6, 3.2, 4.0 and 12.8 nm in Ni/SiO<sub>2</sub>-673, Ni/SiO<sub>2</sub>-773, Ni/SiO<sub>2</sub>-873 and Ni/SiO<sub>2</sub>-cal-773, respectively. The main products of the hydrogenation were THFA and furfuryl alcohol (FOL), which is the product of C=O hydrogenation. Many types of by-products were detected including 2-methylfuran, 2-methyltetrahydrofuran and furan; however, the amount of by-products was small (total < 6 %) unless the reaction temperature was higher (≥ 423 K). The results of furfural hydrogenation are shown in **Fig. 3**. Selectivity to FOL was high at short contact time, and it decreased and that to THFA increased at longer contact time, indicating that FOL was the intermediate of THFA. The activity per catalyst weight decreased in the following order: Ni/SiO<sub>2</sub>-773 ≥ Ni/SiO<sub>2</sub>-673 > Ni/SiO<sub>2</sub>-873 ≫ Ni/SiO<sub>2</sub>-cal-773. This order agreed with the order of the number of surface Ni atoms. The TOF values of furfural conversion based on the H<sub>2</sub> adsorption amount were similar for Ni/SiO<sub>2</sub>-673, Ni/SiO<sub>2</sub>-773 and Ni/SiO<sub>2</sub>-873 ((1.2 ± 0.1) × 10<sup>2</sup> h<sup>-1</sup>). The activity of Ni/SiO<sub>2</sub>-cal-773 was even lower in view of TOF

(0.63 × 10<sup>2</sup> h<sup>-1</sup>), showing that very large Ni particles are not effective in furfural hydrogenation. The selectivity-conversion curves (**Fig. 3(B)**) show that Ni/SiO<sub>2</sub>-673 and Ni/SiO<sub>2</sub>-773 have higher activity in FOL hydrogenation to THFA than Ni/SiO<sub>2</sub>-873 and Ni/SiO<sub>2</sub>-cal-773. The higher FOL hydrogenation activity was also confirmed by the separated reaction test using FOL as the substrate: The TOF ratio of FOL hydrogenation/furfural hydrogenation was 2.6, 2.6, 1.4 and 1.4 h<sup>-1</sup> for Ni/SiO<sub>2</sub>-673, Ni/SiO<sub>2</sub>-773, Ni/SiO<sub>2</sub>-873 and Ni/SiO<sub>2</sub>-cal-773, respectively. These data indicate that smaller Ni particles have higher FOL hydrogenation activity. It should be noted that the selectivity to THFA rose sharply in furfural hydrogenation when conversion was increased above 90 % for all catalysts, while the TOF value of FOL hydrogenation was higher than that of furfural hydrogenation when the reactions were conducted separately. This behavior can be explained by that furfural was more strongly adsorbed on the active site than FOL. In fact, the reaction order of furfural hydrogenation with respect to substrate partial pressure was almost zero over Ni/SiO<sub>2</sub>-773 while that of FOL hydrogenation was positive. The proposed reaction mechanisms are shown in **Fig. 4**. In the case of furfural hydrogenation to FOL, furfural molecule is strongly adsorbed on the Ni surface with an η<sup>2</sup>(C,O) type configuration. In the case of FOL, the -CH<sub>2</sub>OH group outside the furan ring assists the adsorption, especially on the rough Ni surfaces (*e.g.* edge or corner).

Among the four catalysts, Ni/SiO<sub>2</sub>-773 has the highest activity in furfural hydrogenation to THFA. At longer contact time ( $W/F = 0.884 \text{ g}_{\text{cat}} \text{ h mol}_{\text{total}}^{-1}$ ) at 413 K, 94 % yield of THFA was obtained. The activity gradually decreased with time, and residual FOL started to appear after 120 min. At 510 min, the yield of THFA and FOL was 91.4 % and 4.3 %, respectively.

Because of the very high boiling point of HMF, the

gas-phase hydrogenation is unrealistic for HMF. The liquid phase hydrogenation has been applied to HMF instead. Connolly *et al.* reported the hydrogenation of HMF to BHTHF with Raney Ni catalyst in methanol solvent at 333 K under 0.48 MPa H<sub>2</sub><sup>19</sup>. Quantitative yield was obtained; however, very large amount of catalyst was used: the used Raney Ni (38 g) was comparable to HMF substrate in weight (50 g) and even larger in molar basis (1.5 eq). We also synthesized BHTHF from HMF with Raney Ni catalyst in ethanol solvent at ~333 K under 8 MPa H<sub>2</sub>. The reaction stopped before total conversion of 2,5-bis(hydroxymethyl)furan (BHF) intermediate when the catalyst weight was half of the weight of HMF substrate (1 eq in molar basis). Continuing the reaction after replenishment of fresh Raney Ni catalyst gave good yield of BHTHF.

Anyway, the catalyst life is a severe problem of the Ni catalysts in hydrogenation of furfural and HMF, especially in the liquid-phase hydrogenation. Another problem of Ni-catalyzed liquid phase hydrogenation is leaching. To make matters worse, the catalysts for hydrogenolysis of THFA to 1,5-pentanediol such as Rh-ReO<sub>x</sub>/SiO<sub>2</sub> and Ir-ReO<sub>x</sub>/SiO<sub>2</sub> are strongly deactivated by the Ni species in the media. Preventing the leaching of Ni is important to prolong the catalyst life of both total hydrogenation and subsequent hydrogenolysis

processes.

The solvents for Ni catalysts may be either organic solvents or water. However, reduction of furfural in water solvent at high temperature ( $\geq 353$  K) leads to acid-catalyzed rearrangement of FOL intermediate to C5 ring<sup>20</sup>. Typical products of furfural reduction in hot water are cyclopentanone and cyclopentanol which have been obtained over various metal catalysts<sup>21)~25)</sup> including Ni<sup>26,27)</sup>.

## 2.2. Ru and Pd Catalysts

Noble metal catalysts are generally more active than Ni catalysts, and the leaching of noble metals is less severe. The particle size of supported noble metal is easier to set small than that of supported Ni, leading to higher activity based on catalyst weight as well as higher surface-based TOF. However, noble metal catalysts often show activity in various side reactions such as C-O or C-C hydrogenolysis reactions, and the selectivity in total hydrogenation tends to be low.

There are a limited number of systems for total hydrogenation of furfural or HMF over supported noble metal catalysts. Alamillo *et al.* reported that Ru particles on oxide supports with isoelectric point  $> 7$  such as CeO<sub>2</sub> catalyzed total hydrogenation of HMF to BHTHF in 1-butanol/water biphasic solvent at 403 K (maximum yield 91%; **Table 1**)<sup>28)</sup>. Ru catalysts on carbon or non-basic support gave significant amount of 1,2,5- and 1,2,6-hexanetriols, 1,2,5,6-hexanetetraol and unidentified products in addition to BHTHF. Pure water solvent also increased the formation amounts of these by-products.

While Pd catalysts such as Pd/C are well-known alkene hydrogenation catalysts, they are generally not selective in furfural or HMF hydrogenation. One of typical side reactions over Pd catalysts is decarbonylation (furfural to furan; HMF to FOL) which is dominant at high temperature (*e.g.*  $> 393$  K)<sup>29,30)</sup>. Pd catalysts can be selective in total hydrogenation at low temperature. Bhogeswararao and Srinivas reported excellent selectivity of THFA in furfural hydrogenation over Pd/Al<sub>2</sub>O<sub>3</sub> catalyst in 2-propanol solvent at 298 K<sup>31)</sup>. Water solvent significantly decreased the

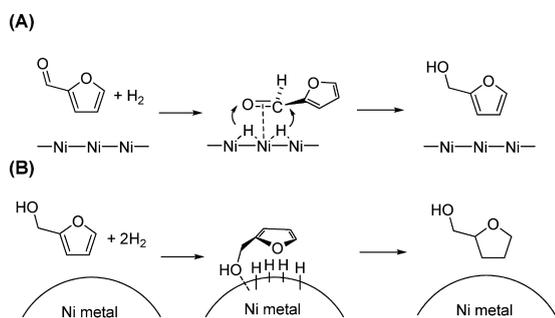


Fig. 4 Proposed Mechanism for Hydrogenation (A) Furfural and (B) FOL over Ni/SiO<sub>2</sub> Catalysts  
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Table 1 Hydrogenation of HMF over Ru Catalysts<sup>28)</sup>

Catalyst	Reaction time [h]	Selectivity [%]				
		BHF	BHTHF	Hexanetriols	1,2,5,6-Hexanetetraol	Undetected/others
Ru/CeO <sub>2</sub>	12	0	91	4	5	0
Ru/MgO-ZrO <sub>2</sub>	20	0	88	2	1	8
Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	12	0	89	5	5	0
Ru/SiO <sub>2</sub>	2	0	53	16	20	11
Ru/C (vulcan XC-72)	1	0	51	11	28	10
Ru black <sup>a)</sup>	2	0	46	26	11	16
Ru black <sup>a),b)</sup>	2	0	22	37	13	28

Conditions: Catalyst (1 wt% Ru, 200 mg), water + 1-butanol (8 g + 16 g), HMF (0.4 g), H<sub>2</sub> (2.8 MPa), 403 K. Conversion was  $> 99$  % for all cases. BHF = 2,5-bis(hydroxymethyl)furan, BHTHF = 2,5-bis(hydroxymethyl)tetrahydrofuran.

a) Ru black catalyst (50 mg). b) Pure water solvent (24 g).

selectivity.

### 2. 3. Other Metal Catalysts

Reductions of furfural or HMF have been also reported with other metal catalysts than Ni, Pd or Ru. However, these catalysts generally have low activity in furan ring hydrogenation. Complete reduction of side chain(s) instead of furan ring hydrogenation proceeds over Cu catalysts at high temperature, giving 2-methylfuran or 2,5-dimethylfuran<sup>32)~34)</sup>. Under milder conditions, selective production of FOL is possible over Cu catalysts<sup>35)~37)</sup>. Selective production of FOL or BHF has been also reported with Pt<sup>38)</sup>, Co<sup>39)</sup> and Ir<sup>40)</sup> catalysts. As introduced in section 2. 1., produced FOL or BHF can react in hot water solvent. High cyclopentanone and 3-hydroxymethylcyclopentanone yields from furfural and HMF, respectively, have been reported with Pt<sup>21),22),41)</sup> or Au<sup>42)</sup> catalysts and water solvent. Reductive ring opening of FOL in basic conditions to 1,2- or 1,5-pentanediols has been also reported with Pt<sup>40),43)</sup> or Cu<sup>44)</sup> catalysts. While good yield of 1,2-pentanediol was reported (>70 %), that of 1,5-pentanediol was not so high (<40 %). All of these reactions (side chain reduction, rearrangement to cyclopentanone, and reductive ring opening) involve FOL or BHF as an intermediate, and they do not proceed from THFA or BHTHF. Therefore, high activity of furan ring hydrogenation (C=C hydrogenation) will suppress these reactions.

### 3. Alloy Catalysts

The addition of secondary metals is a frequently-used approach to improving the performance of metal catalysts. The hydrogenolysis catalysts for THFA conversion to 1,5-pentanediol, which are the combinations of group 9 noble metal (Rh or Ir) and group 5-7 additive, are representative example<sup>12)~16)</sup>. However, for hydrogenation reactions, bimetallic catalysts typically show higher activity in C=O hydrogenation and not higher activity in C=C hydrogenation than monometallic catalysts, especially when the additive is a non-noble-metal oxophilic element<sup>45)</sup>. The reasons may include the adsorption of the oxygen atom of C=O bond on the secondary metal atom and the induction of hydride-like nature on the active hydrogen species by the ligand effect. There are a number of reports on selective hydrogenation of furfural and HMF to FOL and BHF, respectively, using bimetallic catalysts such as M-Re<sup>46)~48)</sup>, M-W<sup>49)</sup>, M-Fe<sup>50),51)</sup> and M-Sn<sup>52)~54)</sup> (M = noble metal, Cu or Ni). On the other hand, we have recently reported several bimetallic and trimetallic catalysts with good performance in total hydrogenation.

#### 3. 1. Ni-Pd Catalysts

As discussed in previous sections, both Ni and Pd are effective in total hydrogenation; however the activity of Ni catalyst and the selectivity of Pd catalyst are low.

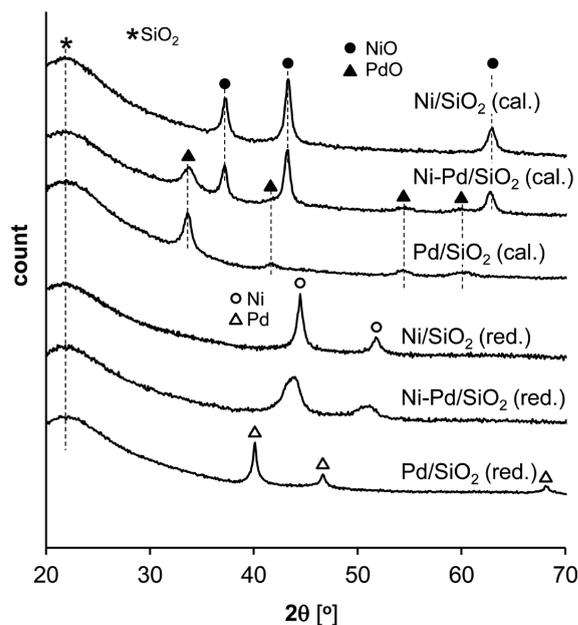


Fig. 5 XRD Patterns of Calcined (cal.) or Reduced (red.) Ni/SiO<sub>2</sub>, Ni-Pd/SiO<sub>2</sub> (Ni/Pd = 7) and Pd/SiO<sub>2</sub> Catalysts<sup>55)</sup>

We have found that alloying Ni with small amount of Pd increases the activity with retaining the high selectivity of Ni<sup>55)</sup>. The Ni-Pd/SiO<sub>2</sub> catalysts were prepared by simple co-impregnation method. While the Ni and Pd species were in separated oxide states (NiO and PdO) after calcination, Ni-Pd alloy was formed by the reduction of calcined NiO-PdO/SiO<sub>2</sub> with H<sub>2</sub> as shown by the XRD peaks located between those of Ni and Pd metals (Fig. 5). However, the homogeneity of Ni-Pd alloy was not confirmed; the segregation of Pd on the outer layers in the Ni-Pd bimetallic particles has been reported in the literature<sup>56)</sup>.

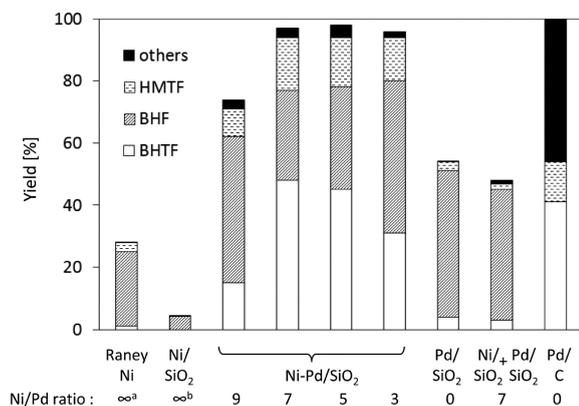
The reaction results of HMF over the Ni-Pd/SiO<sub>2</sub> catalysts are shown in Fig. 6. The catalyst with Ni/Pd = 7 in molar ratio showed the highest activity, and the activity was much higher than those of Raney Ni, Ni/SiO<sub>2</sub>, Pd/SiO<sub>2</sub> and the mixture of Ni/SiO<sub>2</sub> + Pd/SiO<sub>2</sub>. Increasing the reaction time to 2 h with Ni-Pd/SiO<sub>2</sub> (Ni/Pd = 7) catalyst gave 96 % BHTHF yield. Furfural hydrogenation in the same reaction conditions gave 96 % THFA yield at 2 h. The Ni-Pd/SiO<sub>2</sub> catalyst worked well in the presence of small amount of acid. Because the reaction temperature was low (313 K), the role of acid may be the removal of oxidized Ni species on the catalyst surface. Considering the possible surface segregation of Pd, Pd may be the main active site in the Ni-Pd catalyst.

In spite of the high activity of Ni-Pd/SiO<sub>2</sub>, the problems of Ni catalysts in leaching and short life were not solved: the inductive coupled plasma (ICP) analysis showed evident Ni leaching (16 % Ni, while leaching of Pd was negligible), and the reuse experiments showed

activity decrease.

### 3.2. Pd-Ir Catalyst and Other Combinations of Noble Metals

In order to overcome the leaching and life problems, we explored the combination of Pd and another noble metal for the catalytic hydrogenation of furfural<sup>57</sup>. The catalysts were simply prepared by co-impregnation and reduction with H<sub>2</sub> at 573 K. The reaction results are summarized in **Table 2**. Pd-Ir/SiO<sub>2</sub> catalyst showed the highest activity, and the difference in activity between Pd-Ir/SiO<sub>2</sub> and monometallic catalysts was very large. One feature of the Pd-Ir/SiO<sub>2</sub> catalyst was the significant formation of tetrahydrofurfural (~20 % selectivity at short reaction time). The hydrogenation of tetrahydrofurfural was slow over this catalyst. Nevertheless, at longer reaction time and larger catalyst amount (6 h, 150 mg), 94 % yield of THFA was obtained. The reaction temperature should be low in this aqueous phase reaction: the best temperature (275 K)



Conditions: HMF (0.5 M aq., 10 mL), catalyst (100 mg; Pd 0.019 mmol), acetic acid (0.1 mmol), H<sub>2</sub> (8 MPa), 313 K, 0.5 h. HMTF = 5-hydroxymethyltetrahydrofurfural; BHTF = BHTHF. a) Raney Ni (100 mg), b) 10 wt% Ni/SiO<sub>2</sub>.

Fig. 6 Hydrogenation of HMF over Various Catalysts [Reprinted with permission from Ref. (55). Copyright (2010) Elsevier.]

was near the freezing point of water. The reusability test showed that the hydrogenation activity was slightly decreased during the reuses, and the regeneration of the used catalyst by calcination-reduction sequence at 573 K totally restored the activity.

Pd-Ir/SiO<sub>2</sub> catalyst was characterized by XRD, temperature-programmed reduction (TPR), TEM-energy dispersive X-ray fluorescence spectrometer (TEM-EDX), CO adsorption amount and Fourier transform infrared spectroscopy (FT-IR) of adsorbed CO. Although it was not clear whether completely uniform solid solution was formed or not, the formation of bimetallic Pd-Ir alloy was confirmed. The particle size was ~4 nm, and it was similar to that of Pd/SiO<sub>2</sub> and Ir/SiO<sub>2</sub>. It is possible to compare the kinetic behavior of Pd-Ir/SiO<sub>2</sub> with those of monometallic catalysts. The TOF of C=O hydrogenation over Pd-Ir ( $1.1 \times 10^4 \text{ h}^{-1}$ ) was about one order higher than Pd ( $0.2 \times 10^4 \text{ h}^{-1}$ ). The TOF of furan ring hydrogenation, which was determined using FOL as the substrate, over Pd-Ir ( $0.4 \times 10^4 \text{ h}^{-1}$ ) was also higher than Pd ( $0.2 \times 10^4 \text{ h}^{-1}$ ); however the difference was not large. Monometallic Ir has much lower TOF for both C=O hydrogenation ( $0.03 \times 10^4 \text{ h}^{-1}$ ) and furan ring hydrogenation ( $0.005 \times 10^4 \text{ h}^{-1}$ ) than Pd or Pd-Ir. In addition, the furan ring (in FOL) hydrogenation over Ir was totally suppressed in the presence of furfural, while this suppression was not severe for Pd and Pd-Ir catalysts. This behavior can be explained by the strong adsorption of C=O group on Ir site. The schematic picture of furfural adsorption on the Pd, Ir, and Pd-Ir catalysts is shown in **Fig. 7**. The adsorption of C=O on surface Ir atom can cause the much higher activity in C=O hydrogenation over Pd-Ir than Pd.

### 3.3. Trimetallic Rh-Ir-ReO<sub>x</sub> Catalyst

The alloy catalysts in the above sections (3.1. and 3.2.) have Pd as a key component, which agrees with the fact that Pd is a very active metal in alkene hydrogenation. On the other hand, we have recently found that the trimetallic Rh-Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst has good activity in total hydrogenation of furfural<sup>58</sup>. The catalyst

Table 2 Hydrogenation of Furfural over M-M'/SiO<sub>2</sub> Catalysts (M, M': noble metal)<sup>57</sup>

Catalyst	Catalyst amount [mg]	Conv. [%]	Selectivity [%]			
			THFA	FOL	Tetrahydrofurfural	Others
Pd/SiO <sub>2</sub>	50	63	27	33	28	13
Pd-Ir/SiO <sub>2</sub>	10	67	31	47	19	3
Pd-Ru/SiO <sub>2</sub>	10	14	23	49	20	8
Pd-Rh/SiO <sub>2</sub>	10	5.7	13	77	3	7
Pd-Pt/SiO <sub>2</sub>	10	2.5	5	79	< 1	16
Ir/SiO <sub>2</sub>	50	14	< 1	96	< 1	4
Pd/SiO <sub>2</sub> -L <sup>a)</sup>	50	25	19	69	7	5
Pd/SiO <sub>2</sub> -L <sup>a)</sup> + Ir/SiO <sub>2</sub>	25 + 25	26	10	85	1	4

Conditions: Catalyst (2 wt% Pd or 4 wt% Ir, M'/M = 1), water (9 g), furfural (0.5 g), H<sub>2</sub> (8 MPa), 275 K, 1 h. THFA = tetrahydrofurfuryl alcohol, FOL = furfuryl alcohol.

a) Pd-SiO<sub>2</sub>-L: Catalyst with larger Pd particles (7 nm) than the standard Pd/SiO<sub>2</sub> (4 nm).

was prepared by sequential impregnation method in the order of Rh (impregnated first), Ir and Re (last). The catalysts were calcined at 773 K after the last impregnation, and reduced at 473 K in water just before use. The reaction results are summarized in **Table 3**. Rh-Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst showed good THFA yield although the activity was slightly lower than Pd-Ir-ReO<sub>x</sub>/SiO<sub>2</sub>, as shown by the residual FOL amounts. On the other hand, the physical mixtures of Rh/SiO<sub>2</sub> + Ir-ReO<sub>x</sub>/SiO<sub>2</sub> and Rh-ReO<sub>x</sub>/SiO<sub>2</sub> + Ir-ReO<sub>x</sub>/SiO<sub>2</sub> showed very low THFA yield, and the main product was FOL. The mixture of Rh-Ir/SiO<sub>2</sub> and Ir-ReO<sub>x</sub>/SiO<sub>2</sub> had some activity in THFA formation; however, considering the mobile nature of Re species (Re<sub>2</sub>O<sub>7</sub> is soluble in water), the activity can be due to the *in-situ* formed Rh-Ir-ReO<sub>x</sub>/SiO<sub>2</sub>. The inherent activity of the mixture of Re-free Rh-Ir/SiO<sub>2</sub> and Ir-ReO<sub>x</sub>/SiO<sub>2</sub> should be also very low in THFA formation. Therefore, the synergistic interaction among all the three components enhanced the hydrogenation activity of furan ring.

Characterization of TPR, XRD, X-ray absorption fine structure (XAFS), TEM-EDX and FT-IR of adsorbed CO suggested that the Rh-Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst had the structure of Ir-Rh alloy particles with 2-3 nm size which were partially covered with ReO<sub>x</sub> species. A strong evidence of alloy formation is the extended X-ray absorption fine structure (EXAFS) result: the ratios of coordination number of M-Ir to M-Rh (M = Rh, Ir) were similar (M = Rh, 3.5; M = Ir, 3.9) to the total mole fraction ratio of Ir to Rh (3.3). These agreements mean the well mixing of Rh and Ir in the particles.

The mechanism of the induction of hydrogenation activity has not been explained yet. There may be

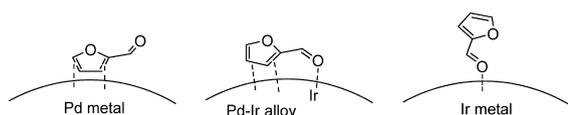


Fig. 7 Proposed Adsorption Structure of Furfural on Pd, Pd-Ir and Ir Particle Surface

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other catalytically active combinations of three or more components which are not active when used alone.

The Rh-Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst was originally developed as the catalyst with both hydrogenation activity of furfural to THFA and hydrogenolysis activity of THFA to 1,5-pentanediol in order to establish the one-pot conversion process of furfural to 1,5-pentanediol. As discussed earlier, typical catalysts for hydrogenolysis of THFA such as Ir-ReO<sub>x</sub>/SiO<sub>2</sub> have almost no activity in hydrogenation of furan ring in furfural. With Rh-Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst and two-step temperature conditions (313 K, 8 h and 373 K, 32 h), furfural in water solvent can be converted to 1,5-pentanediol in 78 % yield. The yield value is comparable to that of the combination of two separated processes (~95 % × 80-90 %). Constant-temperature reaction such as 373 K hardly produced 1,5-pentanediol because of the formation of humin before completion of total hydrogenation. The Pd-Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst can be also used in this one-pot conversion process with two temperature steps<sup>59</sup>. Although Pd-Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst has higher activity in total hydrogenation than Rh-Ir-ReO<sub>x</sub>/SiO<sub>2</sub>, it was much less active in hydrogenolysis which took long reaction time. The maximum 1,5-pentanediol yield (71 %) was lower and the total reaction time (8 + 72 h) was longer than the case of Rh-Ir-ReO<sub>x</sub>/SiO<sub>2</sub> catalyst (78 %, 8 + 32 h).

#### 4. Conclusions

Various catalysts have been reported for hydrogenation of furfural and 5-hydroxymethylfurfural (HMF). Ni is the most selective active metal to the total hydrogenation product (tetrahydrofurfuryl alcohol (THFA) and 2,5-bis(hydroxymethyl)tetrahydrofuran (BHTHF)). However, Ni catalysts are not very active and stable: in the case of traditional Raney Ni catalyst, even more than 1 equivalent of Ni has been used. The leaching of Ni to the reaction solution is also a severe problem. Ni-Pd alloy catalyst can overcome the low activity; however the leaching problem remained. Noble metal catalysts are resistant to leaching. Pd and Ru catalysts are active in the total hydrogenation; however, the

Table 3 Hydrogenation of Furfural over Rh, Ir, and ReO<sub>x</sub> Catalysts<sup>58)</sup>

Catalyst	Conv. [%]	Selectivity [%]					
		THFA	FOL	Pentanediols	Pentanol	1,2,5-Pentanetriol	Undetected/others
Rh-Ir-ReO <sub>x</sub> /SiO <sub>2</sub>	> 99.9	58.2	14.4	1.0	0.2	4.8	21.2
Ir-ReO <sub>x</sub> /SiO <sub>2</sub>	> 99.9	0.5	96.9	0.3	0.2	0.0	2.1
Rh/SiO <sub>2</sub> + Ir-ReO <sub>x</sub> /SiO <sub>2</sub>	> 99.9	6.6	86.6	0.8	0.2	0.0	6.0
Rh-Ir/SiO <sub>2</sub> + Ir-ReO <sub>x</sub> /SiO <sub>2</sub>	> 99.9	21.5	55.7	1.5	0.4	0.0	21.0
Rh-ReO <sub>x</sub> /SiO <sub>2</sub> + Ir-ReO <sub>x</sub> /SiO <sub>2</sub>	> 99.9	1.9	81.7	0.0	0.0	0.0	16.5
Pd-Ir-ReO <sub>x</sub> /SiO <sub>2</sub>	> 99.9	66.8	0.0	1.9	0.1	6.5	24.6

Conditions: Catalyst (0.66 wt% Rh or Pd, 4 wt% Ir, 7.6 wt% Re, 300 mg each), water (3 g), furfural (3 g), H<sub>2</sub> (6 MPa), 313 K, 8 h. THFA = tetrahydrofurfuryl alcohol, FOL = furfuryl alcohol.

selectivity is lower than Ni, especially when the reaction is conducted in water solvent and acidic conditions. Pd-Ir/SiO<sub>2</sub> alloy catalyst is highly active and selective in cold water solvent. One cause of high activity of Pd-Ir alloy is the synergy of hydrogen activation on Pd and adsorption of C=O group on Ir. Interestingly, although the activity is lower than Pd-based catalyst, trimetallic Rh-Ir-ReO<sub>x</sub> catalyst has activity in total hydrogenation only when these three components are located on the same support. There may be other active catalysts with combinations of three or more components.

### References

- 1) Corma, A., Iborra, S., Velty, A., *Chem. Rev.*, **107**, (6), 2411 (2007).
- 2) Chheda, J. N., Huber, G. W., Dumesic, J. A., *Angew. Chem., Int. Ed.*, **46**, (38), 7164 (2007).
- 3) Marshall, A.-L., Alaimo, P. J., *Chem. Eur. J.*, **16**, (17), 4970 (2010).
- 4) Besson, M., Gallezot, P., Pinel, C., *Chem. Rev.*, **114**, (3), 1827 (2014).
- 5) Bozell, J. J., Petersen, G. R., *Green Chem.*, **12**, (4), 539 (2010).
- 6) Lange, J.-P., van der Heide, E., van Buijtenen, J., Price, R., *ChemSusChem*, **5**, (1), 150 (2012).
- 7) van Putten, R.-J., van der Waal, J. C., de Jong, E., Rasrendra, C. B., Heeres, H. J., de Vries, J. G., *Chem. Rev.*, **113**, (3), 1499 (2013).
- 8) Karinen, R., Vilonen, K., Niemelä, M., *ChemSusChem*, **4**, (8), 1002 (2011).
- 9) Nakagawa, Y., Liu, S., Tamura, M., Tomishige, K., *ChemSusChem*, **8**, (7), 1114 (2015).
- 10) Nakagawa, Y., Tamura, M., Tomishige, K., *ACS Catal.*, **3**, (12), 2655 (2013).
- 11) Hoydonckx, H. E., Van Rhijn, W. M., Rhijn, W., De Vos, D. E., Jacobs, P. A., "Furfural and Derivatives" in "Ullman's Encyclopedia of Industrial Chemistry," Wiley-VCH, (2007) (DOI: doi.org/10.1002/14356007.a12-119.pub2).
- 12) Koso, S., Furikado, I., Shima, A., Miyazawa, T., Kunimori, K., Tomishige, K., *Chem. Commun.*, (15), 2035 (2009).
- 13) Buntara, T., Noel, S., Phua, P. H., Melián-Cabrera, I., de Vries, J. G., Heeres, H. J., *Angew. Chem., Int. Ed.*, **50**, (31), 7083 (2011).
- 14) Nakagawa, Y., Tomishige, K., *Catal. Today*, **195**, (1), 136 (2012).
- 15) Tomishige, K., Tamura, M., Nakagawa, Y., *Chem. Rec.*, **14**, (6), 1041 (2014).
- 16) Nakagawa, Y., Tamura, M., Tomishige, K., *Catal. Surv. Asia*, **19**, (4), 249 (2015).
- 17) Fernandez, J. E., Solomons, T. W. G., *Chem. Rev.*, **62**, (5), 485 (1962).
- 18) Nakagawa, Y., Nakazawa, H., Watanabe, H., Tomishige, K., *ChemCatChem*, **4**, (11), 1791 (2012).
- 19) Connolly, T. J., Considine, J. L., Ding, Z., Forsatz, B., Jennings, M. N., MacEwan, M. F., McCoy, K. M., Place, D. W., Sharma, A., Sutherland, K., *Org. Proc. Res. Dev.*, **14**, (2), 459 (2010).
- 20) Li, G., Li, N., Zheng, M., Li, S., Wang, A., Cong, Y., Wang, X., Zhang, T., *Green Chem.*, **18**, (12), 3607 (2016).
- 21) Hronec, M., Fulajtarová, K., *Catal. Commun.*, **24**, 100 (2012).
- 22) Hronec, M., Fulajtarová, K., Liptaj, T., *Appl. Catal. A: General*, **437-438**, 104 (2012).
- 23) Hronec, M., Fulajtarová, K., Vávra, I., Soták, T., Dobročka, E., Mičušík, M., *Appl. Catal. B: Environmental*, **181**, 210 (2016).
- 24) Wang, Y., Zhou, M., Wang, T., Xiao, G., *Catal. Lett.*, **145**, (8), 1557 (2015).
- 25) Fang, R., Liu, H., Luque, R., Li, Y., *Green Chem.*, **17**, (8), 4183 (2015).
- 26) Yang, Y., Du, Z., Huang, Y., Lu, F., Wang, F., Gao, J., Xi, J., *Green Chem.*, **15**, (7), 1932 (2013).
- 27) Zhou, M., Zhu, H., Niu, L., Xiao, G., Xiao, R., *Catal. Lett.*, **144**, (2), 235 (2014).
- 28) Alamillo, R., Tucker, M., Chia, M., Pagán-Torres, Y., Dumesic, J., *Green Chem.*, **14**, (5), 1413 (2012).
- 29) Wang, C., Wang, L., Zhang, J., Wang, H., Lewis, J. P., Xiao, F.-S., *J. Am. Chem. Soc.*, **138**, (25), 7880 (2016).
- 30) Mitra, J., Zhou, X., Rauchfuss, T., *Green Chem.*, **17**, (1), 307 (2015).
- 31) Bhogswararao, S., Srinivas, D., *J. Catal.*, **327**, 65 (2015).
- 32) Sitthitha, S., Sooknoi, T., Ma, Y., Balbuena, P. B., Resasco, D. E., *J. Catal.*, **277**, (1), 1 (2011).
- 33) Dong, F., Ding, G., Zheng, H., Xiang, X., Chen, L., Zhu, Y., Li, Y., *Catal. Sci. Technol.*, **6**, (3), 767 (2016).
- 34) Kumalaputri, A. J., Bottari, G., Erne, P. M., Heeres, H. J., Barta, K., *ChemSusChem*, **7**, (8), 2266 (2014).
- 35) Sitthitha, S., Resasco, D. E., *Catal. Lett.*, **141**, (6), 784 (2011).
- 36) Nagaraja, B. M., Padmasri, A. H., Raju, D., Rao, K. S. R., *J. Mol. Catal. A: Chemical*, **265**, 90 (2007).
- 37) Jiménez-Gómez, C. P., Cecilia, J. A., Durán-Martín, D., Moreno-Tost, R., Santamaría-González, J., Mérida-Robles, J., Mariscal, R., Maireles-Torres, P., *J. Catal.*, **336**, 107 (2016).
- 38) Chatterjee, M., Ishizaka, T., Kawanami, H., *Green Chem.*, **16**, (11), 4734 (2014).
- 39) Audemar, M., Ciotonea, C., Vigier, K. D. O., Royer, S., Ungureanu, A., Dragoi, B., Dumitriu, E., Jérôme, F., *ChemSusChem*, **8**, (11), 1885 (2015).
- 40) Mizugaki, T., Yamakawa, T., Nagatsu, Y., Maeno, Z., Mitsudome, T., Jitsukawa, K., Kaneda, K., *ACS Sustainable Chem. Eng.*, **2**, (10), 2243 (2014).
- 41) Ohyama, J., Kanao, R., Ohira, Y., Satsuma, A., *Green Chem.*, **18**, (3), 676 (2016).
- 42) Ohyama, J., Kanao, R., Esaki, A., Satsuma, A., *Chem. Commun.*, **50**, (42), 5633 (2014).
- 43) Xu, W., Wang, H., Liu, X., Ren, J., Wang, Y., Lu, G., *Chem. Commun.*, **47**, (13), 3924 (2011).
- 44) Liu, H., Huang, Z., Zhao, F., Cui, F., Li, X., Xia, C., Chen, J., *Catal. Sci. Technol.*, **6**, (3), 668 (2016).
- 45) Mäki-Arvela, P., Hájek, J., Salmi, T., Murzin, D. Y., *Appl. Catal. A: General*, **292**, 1 (2005).
- 46) Tamura, M., Tokonami, K., Nakagawa, Y., Tomishige, K., *Chem. Commun.*, **49**, (63), 7034 (2013).
- 47) Tamura, M., Tokonami, K., Nakagawa, Y., Tomishige, K., *ACS Catal.*, **6**, 3600 (2016).
- 48) Chen, B., Li, F., Huang, Z., Yuan, G., *Appl. Catal. A: General*, **500**, 23 (2015).
- 49) Baijun, L., Lianhai, L., Bingchun, W., Tianxi, C., Iwatani, K., *Appl. Catal. A: General*, **171**, (1), 117 (1998).
- 50) Li, H., Luo, H., Zhuang, L., Dai, W., Qiao, M., *J. Mol. Catal. A: Chemical*, **203**, (1), 267 (2003).
- 51) Halilu, A., Ali, T. H., Atta, A. Y., Sudarsanam, P., Bhargava, S. K., Hamid, S. B. A., *Energy & Fuels*, **30**, (3), 2216 (2016).
- 52) Merlo, A. B., Vetere, V., Ruggera, J. F., Casella, M. L., *Catal. Commun.*, **10**, (13), 1665 (2009).
- 53) Rodiansono, Khairi, S., Hara, T., Ichikuni, N., Shimazu, S., *Catal. Sci. Technol.*, **2**, (10), 2139 (2012).
- 54) Malifal-Ganesh, R. V., Xiao, X., Goh, T. W., Wang, L.-L., Gustafson, J., Pei, Y., Qi, Z., Johnson, D. D., Zhang, S., Tao, F., Huang, W., *ACS Catal.*, **6**, (3), 1754 (2016).
- 55) Nakagawa, Y., Tomishige, K., *Catal. Commun.*, **12**, (3), 154 (2010).

- 56) Valcarcel, A., Morfin, F., Piccolo, L., *J. Catal.*, **263**, 315 (2009).  
 57) Nakagawa, Y., Takada, K., Tamura, M., Tomishige, K., *ACS Catal.*, **4**, (8), 2718 (2014).  
 58) Liu, S., Amada, Y., Tamura, M., Nakagawa, Y., Tomishige, K.,  
*Catal. Sci. Technol.*, **4**, (8), 2535 (2014).  
 59) Liu, S., Amada, Y., Tamura, M., Nakagawa, Y., Tomishige, K.,  
*Green Chem.*, **16**, (2), 617 (2014).

要 旨

フルフラールおよび5-ヒドロキシメチルフルフラール完全水素化用担持金属触媒

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フルフラールと5-ヒドロキシメチルフルフラールはバイオマスから誘導される基幹化学品であり, これらの完全水素化により溶剤や樹脂原料に利用可能なテトラヒドロフルフリルアルコール (THFA) と2,5-ビス(ヒドロキシメチル)テトラヒドロフラン (BHTHF) がそれぞれ合成される。Ni 触媒ではこれらの反応に高収率が得られるが, 低い活性と安定性が問題である。Pd と Ru の単金属担持触媒も水素化活性を示すが完全水素化への選択率は低くなりやすいことが報告されている。Cu や

Pt など他の単金属触媒は中間体であるフルフリルアルコールや2,5-ビス(ヒドロキシメチル)フランのフラン環水素化に対する活性が一般に低い。我々は複数の金属を含む触媒を検討し, Ni-Pd/SiO<sub>2</sub>, Pd-Ir/SiO<sub>2</sub>, Rh-Ir-ReO<sub>3</sub>/SiO<sub>2</sub>で高いTHFAまたはBHTHF 収率が得られ, その活性はそれぞれの構成金属を別々にSiO<sub>2</sub>に担持したものを混合した場合に比べはるかに高いことを見出した。