The Effect of Ru Precursor and Support on the Hydrogenation of Aromatic Aldehydes/Ketones to Alcohols

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Supported Ru catalysts were prepared by using different Ru precursors and examined for the hydrogenation of benzaldehyde to CHM. The catalyst prepared from Ru(III) precursor and examined for the hydrogenation of benzaldehyde, hydrogenation of cyclohexanecarboxaldehyde or benzyl alcohol are generally produced via catalytic hydrogenation of benzaldehyde. Ru(OH)HT support exhibited high yield of CHM. Moderate acidic and basic nature of HT was favourable to control the selectivity for CHM. The physicochemical properties analysis revealed that highly dispersed Ru nanoparticles were effective for the hydrogenation of benzaldehyde. Ru(OH)HT catalyst was tolerant to different functional groups and was stable until 7th cycle of recycle study.

Introduction

Cyclohexanemethanol (CHM) is an important intermediate for the synthesis of pharmaceutical drugs and biodegradable detergents. Traditionally, CHM is produced by catalytic hydrogenation of cyclohexanecarboxaldehyde or benzyl alcohol, hydroformylation of cyclohexene, and hydroboration of cyclohexanecarboxaldehyde. Among these methods, catalytic hydrogenation is a simple and atom-efficient route for the synthesis of CHM. However, cyclohexanecarboxaldehyde and benzyl alcohol are generally produced via hydrogenation benzaldehyde. Therefore, one-step CHM synthesis from benzaldehyde is highly desirable. Nevertheless, this transformation is still a challenging task due to the instability of C–O bond which undergoes hydrolysis reaction and generates toluene or methylcyclohexane as byproduct.

In 2012, supported Ru catalyst have been reported for the hydrogenation of benzaldehyde by using high pressure of H2 (6 MPa) and compressed (CO2 + H2O) system. High yield of CHM was achieved using mild acidic additive (CO2). Later, colloidal Ru and Ir nanoparticles catalysts have been developed. Interestingly, in these catalytic methods, the selectivity for benzyl alcohol and CHM was modified using BMIMBF3 and H2O as reaction solvent respectively. Not only solvent but the crystallographic phase of Ru was also a crucial factor hydrogenation of benzaldehyde. Ru catalyst with hcp phase demonstrated higher activity than fcc phase for the hydrogenation of aromatic ring. Furthermore, hcp phase was useful to suppress hydrolysis reaction in the hydrogenation of benzaldehyde, but aromatic hydrogenation of benzyl alcohol was also affected. Recently, succinyl-β-cyclodextrin modified Ru catalyst showed high efficiency under mild reaction conditions (30 °C and 0.1 MPa H2). This catalytic system suffers from limited scope and long reaction time (17 h) and limited scope. Even though the green solvent (water) is used in all catalytic methods, solvent-free conditions are more favorable for the industrial applications to reduce cost and energy consumption (Scheme 1).

Generally, supported Ru catalysts are prepared using RuCl3 or Ru(NO)(NO3)3 precursors. Nevertheless, the counter ion (Cl–) could not remove completely from the surface of catalyst and consequently, it affects the catalytic
activity of Ru. Furthermore, these two precursors are unable to produce highly dispersed Ru nanoparticles on the support. On the other hand, Ru\textsubscript{3}(CO)\textsubscript{12} precursor provides highly dispersed Ru nanoparticles without any counter ion effect\textsuperscript{[27–29]} \textsuperscript{[30,31]} Recently, our group demonstrated that the choice of Ru precursor can modify not only dispersion but Ru morphology also\textsuperscript{[30,31]} For instance, Ru\textsubscript{3}(CO)\textsubscript{12} precursor was dispersed on Pr\textsubscript{2}O\textsubscript{3} support in the form of low-crystalline Ru nanolayers. Whereas, Ru nanoparticles were obtained from Ru(acac)\textsubscript{3} precursor and Pr\textsubscript{2}O\textsubscript{3} support. Interestingly, this Ru nanolayers catalyst showed higher activity than Ru nanoparticles catalyst for the synthesis of 2-substituted quinolines.\textsuperscript{[31]} For the hydrogenation of benzaldehyde, Ru was the most studied metal, but Ru precursor effect has never been explored systematically\textsuperscript{[17,18,20–22]}

Hydrotalcites (HT) or layered double hydroxides are a class of two-dimension (2D) layered nanostructured inorganic materials, which is often used as catalyst or support.\textsuperscript{[25–27,32–34]} HT exhibits several properties such as high specific surface area, high adsorption capacity, tunable acidic-basic properties and good thermal stability. With such desirable properties of HT and Ru metal, a new catalyst can be developed to control the selectivity of the desired product (CHM). Herein, we report HT-supported Ru catalyzed hydrogenation of benzaldehyde to CHM under solvent-free conditions.

Results and Discussion

HT-supported Ru catalysts were prepared using different Ru precursor by impregnation method. The designation “CO”, “AC”, “NO” and “CL” indicates that the catalyst was prepared by using Ru\textsubscript{3}(CO)\textsubscript{12}, Ru(acac)\textsubscript{3}, Ru(NO)(NO\textsubscript{3})\textsubscript{3} and RuCl\textsubscript{3} precursor respectively. Initially, we examined these catalysts for hydrogenation of benzaldehyde as a model reaction under solvent-free conditions. As shown in Table 1, Ru\textsubscript{3}(CO)\textsubscript{12}/HT was found to be the most active catalyst for selective hydrogenation of benzaldehyde to CHM (entry 1). The catalyst prepared from Ru(acac)\textsubscript{3} precursor showed moderate (82\%) yield of CHM with methylvyclohexane (5\%). Surprisingly, Ru\textsubscript{3}(CO)\textsubscript{12}/HT catalyst was unable for aromatic hydrogenation of benzyl alcohol and benzyl alcohol was obtained (entry 2). Ru\textsubscript{3}(CO)\textsubscript{12}/HT catalyst was ineffective for the hydrogenation of carbonyl group as well as aromatic ring. Next, we examined the effect of support on the activity of Ru catalysts. MgO and Al\textsubscript{2}O\textsubscript{3} gave 82\% and 48\% yield of CHM respectively. The difference in selectivity of HT, MgO and Al\textsubscript{2}O\textsubscript{3} support can be explained by the nature of the support. In previous reports, it is suggested that the adsorption of substrate can exist in co-planar or non-planar form according to the nature of support and affects the selectivity of desired product.\textsuperscript{[35,36]} For instance, acidic support (Al\textsubscript{2}O\textsubscript{3}) showed co-planar and basic nature of support (MgO) showed non-planar adsorption form. Al\textsubscript{2}O\textsubscript{3} supported Ru catalyst showed high yield (37\%) of methylvyclohexane which indicated that co-planar adsorption might be responsible for the formation of methylcyclohexane (Table 1, entry 6). Basic support (MgO) gave low yield (2\%) of methylcyclohexane (entry 5). However, Ru/MgO catalyst was unable to produce CHM selectively. Probably, acidic-basic sites of hydrotalcite in the vicinity of Ru were useful to produce CHM. Moreover, neutral silica gave also methylcyclohexane as major product. Ru\textsubscript{3}(CO)\textsubscript{12} and HT were unable hydrogenate benzaldehyde (entries 8 and 9).

To understand high activity of Ru\textsubscript{3}(CO)/HT catalyst, we characterized all catalysts by BET analysis, H\textsubscript{2} chemisorption and TEM analysis (Table 2). The specific surface area of all catalyst was not changed significantly. Furthermore, the Ru loading amount and particle size were nearly same. Nevertheless, the aggregated Ru nanoparticles were also observed in TEM images of Ru\textsubscript{3}(CO)/HT and Ru\textsubscript{3}(CO)/HT catalysts. Ru particle size of Ru\textsubscript{3}(CO)/HT and Ru\textsubscript{3}(CO)/HT was calculated by omitting the aggregated particles. Ru dispersion was remarkably changed in all catalysts. Ru\textsubscript{3}(CO)/HT catalyst showed higher Ru dispersion than that of other catalysts. Probably, high activity of Ru\textsubscript{3}(CO)/HT was attributed to high Ru dispersion on HT. In previous reports, it is suggested that hydroxyl groups on the supports

### Table 1. Hydrogenation of benzaldehyde to CHM over various catalysts.\textsuperscript{[34]}

| Entry | Catalyst          | Conv. [%]\textsuperscript{[30]} | Yield [%]\textsuperscript{[30]} | Yield [%]\textsuperscript{[30]} | Yield [%]\textsuperscript{[30]} | Yield [%]\textsuperscript{[30]} |
|-------|-------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 1     | Ru\textsubscript{3}(CO)/HT | 99                            | 91                            | 2                             | 0                             | 7                             |
| 2     | Ru\textsubscript{3}(CO)/HT | 99                            | 82                            | 0                             | 0                             | 5                             |
| 3     | Ru\textsubscript{3}(CO)/HT | 99                            | 0                             | 99                            | 0                             | 99                            |
| 4     | Ru\textsubscript{3}(CO)/HT | 20                            | 0                             | 20                            | 0                             | 0                             |
| 5     | Ru\textsubscript{3}(CO)/MgO | 99                            | 82                            | 5                             | 0                             | 2                             |
| 6     | Ru\textsubscript{3}(CO)/Al\textsubscript{2}O\textsubscript{3} | 99                            | 48                            | 0                             | 0                             | 37                            |
| 7     | Ru\textsubscript{3}(CO)/SiO\textsubscript{2} | 99                            | 0                             | 18                            | 0                             | 42                            |
| 8     | Ru\textsubscript{3}(CO)/HT | 10                            | 4                             | 0                             | 0                             | 0                             |
| 9     | HT                | 0                             | 0                             | 0                             | 0                             | 0                             |

[a] Reaction conditions: 1 (1 mmol), catalyst (1 mol%) of Ru, 100°C, 9 h, H\textsubscript{2} (3.5 MPa), (b) GC.
plays a crucial role for highly dispersed Ru nanoparticles from Ru₃(CO)₁₂ precursor. The reaction between Ru₃(CO)₁₂ precursor and hydroxyl groups on the support produces ruthenium-hydride species which reacts with some fractions of CO in Ru surface species and finally, it gives highly dispersed Ru nanoparticles. Furthermore, Li et al. described high metal dispersion using HT support. During reduction process, metal redispersed on the surface of HT via interacting with Al³⁺ or the surface defects related to Al³⁺ which leads to formation of abundant low-coordinated Pd sites (terrace, edge, and defect). The catalysts prepared from other Ru precursors showed low dispersion and gave low yield of CHM. With physicochemical properties and Table 1, we concluded that high dispersion of Ru metal over support was a crucial factor for the high selectivity of RuCO/HT catalyst.

Next, we investigated the general applicability of RuCO/HT catalyst for the hydrogenation of different benzaldehyde (Table 3). The reactivity of ortho, meta and para methyl-substituted benzaldehyde was investigated (entries 2–4). p-Methyl-benzaldehyde showed the higher yield than o-methyl-benzaldehyde due to the steric effect of substituent. Furthermore, high yield (94%) of 4-tert-cyclohexanemethanol was achieved when 4-tert-benzaldehyde was used as a reactant (entry 5). Hydrogenation of 4-chlorobenzaldehyde underwent dehalogenation reaction and CHM was observed as product (entry 6). In addition, heterocyclic aldehydes were successfully transformed to the corresponding products (entries 7 and 8).

We further expanded the general applicability of RuCO/HT for the hydrogenation of aromatic ketones (Table 4). Acetophenone bearing with electron-donating or electron-withdrawing group afforded high yield of corresponding product (entries 1–3). 3-acetopyridine was smoothly converted to 1-(piperidin-3-yl)ethanol.

The reusability of RuCO/HT was examined for the hydrogenation of benzaldehyde under optimized reaction conditions (1 mol% RuCO/HT, 3.5 MPa H₂, 100 °C, and 9 h). After each cycle, the catalyst separated from reaction mixture by centrifugation and washed with acetone three times. Then, the catalyst was dried at 40 °C for 12 h, reduced and used for the next cycle. RuCO/HT showed good stability and was recycled for 6 cycles (Figure 1).

In 7th cycle, the reaction rate for aromatic hydrogenation of benzalcohol was decreased and 75% yield of CHM was observed with 25% yield of benzyl alcohol. To study the loss in catalytic activity, we examined the fresh and recovered catalysts after 7th cycle by scanning transmission electron.

| Table 2. Physicochemical properties supported Ru catalysts. |
|-----------------------------------------------|
| Catalyst | BET surface area [m² g⁻¹] | Ru loading [%] | Ru dispersion [%] | Ru size [nm] |
| RuCO/HT | 194 | 7.8 | 66 | 1.2 ± 0.7 |
| RuCO/HT | 214 | 7.2 | 22 | 1.5 ± 0.7 |
| RuCO/HT | 168 | 7.8 | 0.1 | – |
| RuCO/Al₂O₃ | 48 | 6 | 34 | 1.3 ± 0.8 |
| RuCO/SiO₂ | 157 | 7.1 | 23 | 0.6 ± 0.2 |
| RuCO/SiO₂ | 325 | 5.8 | 11.15 | 1.4 ± 0.7 |

[a] XRF analysis; [b] Estimated using H₂ chemisorption; [c] TEM analysis.

| Table 3. Hydrogenation of substituted aromatic aldehydes by RuCO/HT. |
|-----------------|-----------------|-----------|-----------|
| Entry | Aldehyde | Time [h] | Conv [%] | Yield [%] |
| 1 | | | | |
| 2 | | | | |
| 3 | | | | |
| 4 | | | | |
| 5 | | | | |
| 6 | | | | |
| 7 | | | | |
| 8 | | | | |

[a] Reaction conditions: aldehyde (1 mmol), catalyst (1 mol% of Ru), 100 °C, 9 h, H₂ (3.5 MPa). [b] GC.

Figure 1. Recycling study of RuCO/HT for the hydrogenation of benzaldehyde; CHM (black) and benzyl alcohol (grey).
microscopy (STEM). The recovered catalyst showed partially aggregated Ru nanoparticles (Figure S3). To understand Ru aggregation in every cycle, we carried out the reaction under modified reaction conditions for two cycles (1 mol% Ru<sub>CO</sub>_<sub>12</sub>/HT, 3.5 MPa H<sub>2</sub>, 100 °C, and 2 h). STEM analysis showed the catalyst was slightly aggregated after 2<sup>nd</sup> cycle (Figure S4). However, the degree of Ru aggregation was small, and it did not affect the CHM yield until 7<sup>th</sup> cycle.

Moreover, we analyzed the electronic state of fresh and recovered catalyst after 7<sup>th</sup> cycle by X-ray photoelectron microscopy (XPS). In previous reports, different electronic states of Ru were reported.[39–43] The metallic Ru 3P<sub>3/2</sub> state was observed at 461.1 eV ± 0.3 eV and Ru valence between +1 to +3. The metallic Ru 3P<sub>3/2</sub> was observed at 461.1 eV ± 0.3 eV and Ru valence between +1 to +3 appeared at 462.3 eV ± 0.3 eV. Higher oxidation states (+3) and (+4) of Ru was observed at 463.5 eV ± 0.3 and 466.7 eV ± 0.5, respectively. The XPS spectrum of fresh catalyst showed two bands on 461.5 eV and 483.6 eV which were assigned to metallic Ru (Figure 2). On the hand, the recovered catalyst showed higher binding energies than fresh catalyst and consistent with Ru valence between +1 to +3. Therefore, we concluded that Ru metal nanoparticles was aggregated after 7th cycle which led to the loss of catalytic activity of Ru/HT. Although Ru metal was aggregated, the formation of toluene and methylcyclohexane were not observed in 7<sup>th</sup> cycle and resultant in the loss of activity was observed.

Table 4. Hydrogenation of substituted aromatic ketones by Ru<sub>CO</sub>/HT.<sup>24</sup>

| Entry | Ketones | Time [h] | Conv.<sup>[b]</sup> [%] | Yield<sup>[b]</sup> [%] |
|-------|---------|----------|-------------------|-------------------|
| 1     |         | 24       | 99                | 89                |
| 2     |         | 24       | 99                | 95                |
| 3     |         | 24       | 99                | 95                |
| 5     |         | 24       | 99                | 94                |

[a] Reaction conditions: ketone (1 mmol), catalyst (1 mol% of Ru), 100 °C, 24 h, H<sub>2</sub> (3.5 MPa). [b] GC.

Figure 3 shows the reaction profile for the hydrogenation of benzaldehyde under optimized reaction conditions (1 mol% Ru<sub>CO</sub>/HT, 3.5 MPa H<sub>2</sub>, 100 °C, and 9 h). This reaction profile demonstrated a consecutive reaction which was included transformation of benzaldehyde to benzyl alcohol and benzyl alcohol to CHM. Full conversion of alcohol and 28% yield of CHM. Finally, high yield (91%) of CHM was obtained in short time (9 h).

Conclusion

In summary, we have developed an efficient catalytic method for aromatic hydrogenation of aldehydes and ketones under solvent-free conditions. HT-supported Ru catalyst prepared from Ru<sub>3</sub>CO<sub>12</sub> precursor showed higher activity than that of Ru(acac)<sub>3</sub>, Ru(NO)(NO<sub>3</sub>) and RuCl<sub>3</sub> precursors. High dispersion and small Ru particle size in Ru<sub>CO</sub>/HT catalyst were attributed to high catalytic activity of Ru<sub>CO</sub>/HT catalyst. This catalyst was tolerant of different functional groups. N- or O-containing heterocyclic aldehydes/ketones were transformed to saturated cyclic alcohols. Ru<sub>CO</sub>/HT catalyst was stable until 7th cycle of recycle study. HAADF-STEM and XPS analysis showed that Ru metal was partially aggregated after 7th cycle and resultant in the loss of activity was observed.
Experimental Section

Catalyst preparation

Hydrotalcite (Wako Pure Chemical, Japan), MgO (Ube Material Industries, Ltd., Japan), Al₂O₃ (Sumitomo Chemical Co. Ltd, Japan) and SiO₂ (Nippon Aerosil Co., Japan) were used as support. The composition of hydrotalcite was Mg₅Al₇(OH)₁₆CO₃·4H₂O. Ru₃(OH)₉CO₃, Ru(acac)₃, Ru(NO)(NO₃)₃ and RuCl₃ were purchased from Furuya Metal Co., Ltd. and Wako Pure Chemical, Japan. All chemicals were used without further purification. Supported Ru catalysts (5 wt%) were prepared by impregnation method. Tetrahydrofuran was used as solvent to dissolve Ru₃(OH)₉CO₃ or Ru(acac)₃ precursor and water was used as solvent in case of Ru(NO)(NO₃)₃ or RuCl₃ precursor. The solvent was removed using rotavapor from mixture of Ru precursor and support, dried at 60°C for 12 h followed by calcination at 500°C in Ar or O₂. All catalysts were pre-reduced in H₂ flow (30 mL/min) at 500°C for 0.5 h.

Typical procedure for hydrogenation reaction

All organic chemicals were purchased Tokyo Chemical Industry, Japan and used without further purification. Hydrogenation reactions were carried out 10 mL autoclave with a glass tube. 1 mmol of substrate and catalyst (1 mol%) were added to the reactor. Then, the reactor was purged by hydrogen multiple time, pressurized to 3.5 MPa H₂, and heated to 100 °C. The reactor was cooled down and depressurized after the completion of the reaction. Then, the reaction crude washed with acetone and filtered by using micro filters (Sartorius RC 0.2 μm). The conversion and yield were calculated by gas chromatography using dodecane as internal standard.

Catalyst characterization

The specific surface area of all catalysts was calculated by the Brunauer-Emmett-Teller (BET) method and BEL-mini instrument (BEL Japan Inc., Japan). X-ray fluorescence (XRF) analyses were carried out using an EDXL 300 (Rigaku, Japan). X-ray photoelectron spectroscopy (XPS) analysis was carried out using an ULVAC-PHI, Japan. X-ray diffraction (XRD) measurements were using a BEL-CAT II apparatus (Microtrac BEL, Japan). X-ray fluorescence (XRF) analyses were carried out by temperature-programmed reduction (TPR) measurements were using a TCD detector using a water trap.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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