Development of Titania-supported Iridium Catalysts for the Acceptor-less Dehydrogenative Synthesis of Benzoxazoles

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Iridium catalysts supported on anatase with high surface area showed excellent activities for the acceptor-less dehydrogenation synthesis of benzoxazoles from 2-aminophenol and primary alcohols. The catalytic activity greatly depended on the titania supports, iridium precursors, and loading of iridium species. Catalysts supported on anatase JRC (Japan Reference Catalyst)-TIO-10 showed the highest activity for the dehydrogenative reaction. Preparation of catalysts using [Ir(cod)Cl]2 (cod = 1,5-cyclooctadiene) as an iridium precursor resulted in higher activity than using Ir(acac)3 (acac = acetylacetonate). Various primary alcohols were reacted to give corresponding benzoxazoles in high to moderate yields. The catalyst could be recycled without significant loss of activity, and no leaching of iridium species occurred into the solution. The hot filtration test strongly suggested that the catalysis occurs on the catalyst surface. Highly dispersed iridium species of less than 2 nm in diameter, which could be reduced at low temperature, were responsible for the excellent activity.

Keywords
Supported catalyst, Iridium, Titania support, Benzoxazole, Dehydrogenation

1. Introduction

Benzoxazoles, aromatic heterocyclic nitrogen-containing compounds, commonly occur in natural products and have various biological activities, so are important intermediates in pharmaceutical, agrochemical, and chemical industries1,2. The most common routes for the synthesis of benzoxazoles3,4 include condensation of 2-aminophenols with carboxylic acid derivatives5, oxidation with aldehydes6,7 or oxidative coupling with amines8. The transition metal complex-catalyzed conversion of alcohols to benzoxazoles via the dehydrogenative pathway9,10 is supposed to provide a more environmentally benign alternative to classical synthetic reactions11. For example, several ruthenium or iridium complex-catalyzed syntheses of 2-substituted benzoxazoles with or without hydrogen acceptors have been reported9,10,12. In addition, reactions are known via aerobic oxidation of alcohols13a–13c, electrochemical oxidation of alcohol14, and transition metal-catalyzed 2-arylbenzoxazole formation from o-nitrophenols and benzylic alcohols using hydrogen transfer15,16.

Heterogeneous catalysis has advantages from both practical and environmental viewpoints, such as easy recovery and reuse of the catalysts, prevention of contamination of the products by heavy metallic species, and other factors17,18. The present authors previously developed heterogeneous supported ruthenium17a,17b and rhodium19 catalysts which enable various highly atom-efficient organic transformations. In particular, titania-supported iridium catalysts are effective for the synthesis of benzimidazoles via acceptor-less dehydrogenative or hydrogen transfer routes20–23, which are dependent on the high activity of iridium in hydrogen activation24 and coordinatively unsaturated titanium sites on the TiO2 surface as adsorption and/or activation sites of alcohols25. Pt/Al2O3 catalysts have also been developed for the acceptor-less dehydrogenative synthesis of benzothiazoles and benzimidazoles26. Titania-supported gold catalysts achieved benzoxazole formation from 2-nitrophenols and primary alcohols...
2. Preparation of Supported Iridium Catalyst
sphere in Schlenk tubes.

2.1. General Information

2.2. Experiment Section

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The present recyclable catalysts are advanta-

2-substituted benzoxazoles in moderate to excellent
alcohols could be reacted to give the corresponding
azoles. The titania supports had important effects on
the activity of the iridium catalysts, and various primary
alysts not requiring additives for this reaction would be
very valuable.

Our present study extended the application of the
simple, recyclable titania-supported iridium catalysts to
the acceptor-less dehydrogenative synthesis of benzox-
azes. The titania supports had important effects on the
activity of the iridium catalysts, and various primary
alcohols could be reacted to give the corresponding
2-substituted benzoxazoles in moderate to excellent
yields. The present recyclable catalysts are advantage-
ous from both environmental and practical perspec-
tives.

2. Experiment Section

2.1. General Information

Tris(acetylacetonate)iridium(III) (Ir(acac), C₁₅H₂₁O₆Ir),
di-μ-chlorobis[(η-cycloocta-1,5-diene)iridium(І)]
([Ir(cod)Cl]₂), C₁₅H₂₁Cl₂Ir₂), mesitylene, biphenyl and
benzyl alcohol were obtained from Wako Pure Chem.
Ind., Ltd. Methanol, 1-octanol, tetrahydrofuran (THF),
and phosphoric acid were obtained from Nacalai
Tesque, Inc. 2-Aminophenol, 4-methylbenzyl alcohol,
4-methoxybenzyl alcohol, 4-chlorobenzyl alcohol, and
4-fluorobenzyl alcohol were obtained from Takachiho
Chemical Industrial Co., Ltd. JRC (Japan Reference
Catalyst) titania powders (here designated as TIO-4, 6,
7, 8, 9, 10 and 11) were obtained from the Catalysis So-
ciety of Japan. All reagents were used as received,
and reactions were carried out under an argon atmo-
sphere in Schlenk tubes.

2.2. Preparation of Supported Iridium Catalyst

The supported catalysts were prepared by an impreg-
nation method as shown in Scheme 1. Iridium pre-
cursor was dissolved in 10 mL of methanol for Ir(acac)₃
or THF for [Ir(cod)Cl]₂; under stirring, then 1.0 g of tita-
nia was added in air at 80 °C. Subsequently, the ob-
tained sample was dried overnight in air at 80 °C. The
resulting powder was reduced in an H₂ (2 vol%)/Ar
flow (40 cm³ min⁻¹) at 500 °C (ramping rate of 10 °C
min⁻¹) for 30 min in a conventional flow reactor to give
the Ir/TiO₂ catalysts. After N₂ purging, the catalysts
were passivated in an O₂ (2 vol%)/N₂ flow (40 cm³
min⁻¹) at 50 °C for 5 min for safety reasons.

2.3. General Procedure for Catalytic Runs

Catalytic reactions were performed in a glass Schlenk
tube reactor (20 cm³) equipped with a hot stirrer and
cooling block to reflux the reaction solution. A typical
reaction procedure for the synthesis of the desired prod-
uct is as follows: the substrates and solvent were added
into the Schlenk tube containing the Ir/TiO₂ catalyst.
The reaction mixture was stirred at the desired tempera-
ture for 18 h under an argon atmosphere. Then the
solid catalyst was removed by passing the mixture
through a polytetrafluoroethylene (PTFE) filter (Milli-
pore Millex LH, 0.45 μm), and the yield of products
was quantified by gas-liquid chromatography using bi-
phenyl as an internal standard.

2.4. Physical and Analytical Measurements

The organic products of catalytic runs were analyzed by
GC-MS (Shimadzu GC-MS Parvum 2; Zebron ZB-1
capillary column, i.d. 0.25 mm, length 30 m, at 50-
250 °C) and gas-liquid chromatography (Shimadzu GC-
14A; Zebron ZB-1 capillary column, i.d. 0.25 mm,
length 30 m, at 50-250 °C). The amount of hydrogen
gas formed during the reaction was monitored with a
Shimadzu SAIT gas chromatograph (Molecular Sieves
5A column, i.d. 3 mm, length 2 m, at 50 °C) with a
thermal conductivity detector (TCD).

Powder X-ray diffraction (XRD) patterns were recorded
using Cu Kα radiation (40 kV, 40 mA) and a

carbon monochromator (Shimadzu XRD-6100). Scan-
ing electron microscopy (SEM) (JEOL Ltd., JSM-
5500S) was performed to measure the size and mor-
phology of the crystalline samples. Transmission
electron microscopy (TEM) was performed on a JEOL
Model JEM-3010 system at 300 kV, and the powder
sample was supported on a Cu microgrid. Tempera-
ture-programmed reduction (TPR) was performed with
a gas flow system, using hydrogen (2 vol% in Ar; atmo-
spheric pressure of 40 cm² min⁻¹) fed into a quartz tube
containing the catalyst. The tube was heated in an
electric furnace at a heating rate of 10 °C min⁻¹ and the
amount of H₂ consumed was monitored with a TCD.
X-ray photoelectron spectroscopy (XPS) spectra of the
catalysts were recorded using a ULVAC-PHI 5500MT
system equipped with a hemispherical energy analyzer.
Reduced catalysts without passivation were mounted on
iridium foil in a glovebox (Korea Kiyon, O₂ < 0.5 ppm)
and then transferred to an XPS analysis chamber without any contact with air. The spectra were measured at room temperature using Mg Kα radiation (1254 eV) generated by an X-ray tube operating at 15 kV, 400 W. The electron take-off angle was set at 45°. The residual gas pressure during data acquisition was less than \(1 \times 10^{-8}\) Torr (1 Torr; 133.3 N m\(^{-2}\)). Binding energies were referenced to the C 1s level of residual graphitic carbon\(^{28}\). Inductively coupled plasma atomic emission spectroscopy (ICP/AES) used a Hitachi High-Tech Science PS7800 (sequential type ICP optical emission spectrometer).

3. Results and Discussion

3.1. Effects of Titania Support on the Dehydrogenative Synthesis of 2-Phenyl Benzoxazole

The activities of various titania-supported iridium catalysts for the reaction of 2-aminophenol (1 mmol) with benzyl alcohol (0.41 mL) were examined at 80 to 170 °C for 18 h in the presence of mesitylene (2 cm\(^3\)) as a solvent (Eq. (1) in Table 1). Table 1 shows the results of the reactions in the presence of 1.0 mol% Ir titania-supported iridium catalysts prepared using Ir(acac)\(_3\) as the iridium source. All catalysts were used after calcination at 400 °C in air followed by reduction at 500 °C in a hydrogen stream. Anatase and rutile are denoted as (A) and (R) in Table 1, respectively. XRD revealed that the titania supports in the catalysts had both anatase and rutile structures (Fig. S1)\(^{29}\). The diffraction peak of the iridium phase was not observed in the XRD patterns due to the low loading weight. Field emission scanning electron microscope (FE-SEM) images of the catalysts (Fig. S2) showed that Ir/TIO-7, 9, and 10 consisted of small aggregated particles of the supported catalysts, whereas Ir/TIO-6, 8, and 11 formed

![Chemical structure](image)

**Table 1  Effects of Various Titania Supports on the Activity of the Iridium Catalysts Prepared from Ir(acac)\(_3\).**

| Reaction | Support | Crystal structure\(^a\) | \(S_{BET}\) of support \([\text{m}^2 \text{g}^{-1}]\) | Temperature \([\text{°C}]\) | Yield of 3aa \([\%]\) |
|----------|---------|------------------------|---------------------------|-----------------|-----------------|
| 1        | TIO-4   | A/R                   | 50                        | 170             | 9               |
| 2        | TIO-6   | R                     | 100                       | 170             | 48              |
| 3        | TIO-7   | A                     | 270                       | 80              | 5               |
| 4        |         |                       |                           | 100             | 5               |
| 5        |         |                       |                           | 120             | 13              |
| 6        |         |                       |                           | 130             | 15              |
| 7        |         |                       |                           | 150             | 35              |
| 8        |         |                       |                           | 170             | 58              |
| 9        | P\(_{0.02}\)-TIO-7\(^{30}\) | A | / | 130 | 16 |
| 10       |         |                       |                           | 150             | 22              |
| 11       |         |                       |                           | 170             | 29              |
| 12       | TIO-8   | A                     | 338                       | 130             | 13              |
| 13       |         |                       |                           | 150             | 20              |
| 14       |         |                       |                           | 170             | 68              |
| 15       | TIO-9   | A                     | 300                       | 130             | 11              |
| 16       |         |                       |                           | 150             | 25              |
| 17       |         |                       |                           | 170             | 58              |
| 18       | TIO-10  | A                     | 100                       | 130             | 16              |
| 19       |         |                       |                           | 150             | 36              |
| 20       |         |                       |                           | 170             | 74              |
| 21       | TIO-11  | A/R                   | 97                        | 130             | 6               |
| 22       |         |                       |                           | 150             | 6               |
| 23       |         |                       |                           | 170             | 7               |
| 24       | PA-135-3.5\(^{30}\) | A | 66 | 130 | 17 |
| 25       |         |                       |                           | 150             | 6               |
| 26       |         |                       |                           | 170             | 8               |
| 27       | SiO\(_2\) |                       | 130                       | 170             | trace           |
| 28       | Al\(_2\)\(_2\)O\(_3\) |                       | 180                       | 170             | trace           |
| 29       | CeO\(_2\) |                       | 92                        | 170             | trace           |

\(a\) A: anatase, R: rutile, A/R and R/A: mixtures, predominantly anatase and predominantly rutile, respectively.

\(b\) P\(_{0.02}\)-TIO-7 is phosphorus-modified TIO-7 with phosphoric acid (P/Ti molar ratio of 0.02)\(^{30}\).

\(c\) PA-135-3.5 is \{010\}/\{101\}-faceted anatase developed by our group\(^{30}\).
The synthesis of benzimidazole 21) shown effective catalyst support for the synthesis of benzimidazole 20). However, the hydrogen transfer reaction of 2-(benzylideneamino)phenol was detected by GC-MS. No benzaldehyde was detected with these three catalysts.

To investigate the catalytic efficiency of iridium species for the dehydrogenative reactions, the activities of TIO-10-supported catalysts with different iridium loadings were compared at 130, 150 and 170 °C, respectively. Here, the weight of the catalysts was fixed at 100 mg, so the substrate to catalyst (S/C) ratio decreased with higher loading. Figure 1 shows the yield of the desired product, 3aa, linearly increased with higher loading at 130 °C and 150 °C. The yield markedly increased up to 1.0 wt% (0.50 mol% as Ir) at 170 °C, but increased less significantly over 1.0 wt%, indicating that the activity per unit amount of iridium species was highest at around 1.0 wt% or lower.

3.2. Effect of [Ir(cod)Cl]2 as an Ir Precursor on the Catalytic Activity

To further optimize the activity of the catalyst, [Ir(cod)Cl]2 was used as the iridium source in the catalyst preparation (Eq. (2) in Table 2). Table 2 shows the activities of these Ir/TIO-10 catalysts with different iridium loadings for the dehydrogenative synthesis of 2-phenylbenzoxazole. The weight of the catalysts was fixed at 100 mg. The yield of 3aa monotonically increased with higher iridium loading at 170 °C, and the highest yield of 3aa, 81%, was achieved with Ir (2.0 wt%)/TIO-10 catalyst (1.0 mol% as Ir). However, 1.0 wt%-loaded catalysts showed higher activity than 2.0 wt%-loaded catalysts at the same amount of Ir species (0.50 mol% Ir) as shown in reactions 9 and 10 of Table 2.

To examine the material balance, double scale reaction of 1a (2.0 mmol) and 2a (2.2 mmol) was performed for 18 h at 170 °C in the presence of the Ir/TIO-10 catalysts prepared using [Ir(cod)Cl]2. As shown in Eq. (3), the conversions of 1a and 2a were 100% and 97%, respectively, whereas the yield of 3aa was 72%, indicating the selectivity for 3aa was 72%. Benzaldehyde and its derivatives could not be detected in the reaction mixture. GC-MS detected formation of small amounts of byproducts of m/z 197, 289, and 287, which could be 2-(benzylideneamino)phenol, N,N-dibenzyl-2-phenylazophenol, and an isomer of tribenzylamine, respectively. GC analysis detected evolution of 2.8 mmol of hydrogen gas, which is consistent with the acceptor-less dehydrogenation pathway.

Table 3 shows the activities of the Ir/TIO-10 catalyst for reactions with representative benzylic alcohols and simple aliphatic alcohol. Both primary benzylic alcohols bearing electron-donating and electron-withdrawing substituents could be used as the substrates and the corresponding benzoxazoles were selectively formed in

\[ \text{Conversion of benzyl alcohol 2a was negligible for the Ir/SiO}_2 \text{ and Ir/CeO}_2 \text{-catalyzed reactions, while only 15% with Ir/Al}_2\text{O}_3 \text{ and the formation of a small amount of 2-(benzylideneamino)phenol was detected by GC-MS. No benzaldehyde was detected with these three catalysts.} \]

\[ \text{The catalysts prepared using [Ir(cod)Cl]}_2 \text{ showed excellent activity of rutile-supported catalysts for the dehydrogenative reaction.} \]

\[ \text{The results of reactions 3 to 8 indicate that reaction of 2-aminophenol requires a relatively high temperature of 170 °C, markedly different to the dehydrogenative synthesis of benzimidazoles which smoothly proceeds at 100 to 120 °C.} \]

\[ \text{Catalysts supported on JRC anatase (TIO-7, 8, 9, 10) showed higher activities than those on TIO-4 (P-25 equivalent) and TIO-11 which contained mixtures of anatase and rutile. Ir/TIO-10 catalyst achieved almost 100% conversion of 2-aminophenol (1a) at 170 °C.} \]

\[ \text{Our previous study of the dehydrogenative synthesis of benzimidazole} \]

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Table 2  Activities of the Ir/TIO-10 Catalysts Prepared Using [Ir(cod)Cl]₂ for the Synthesis of 2-Phenylbenzoxazole

![Chemical structure of 2-Phenylbenzoxazole](image)

| Reaction | Ir loading [wt%, mol% as Ir in the parenthesis] | Temperature [°C] | Yield of 3aa [%] |
|----------|-----------------------------------------------|------------------|-----------------|
| 1        | 0.10 (0.050)                                  | 150              | 7               |
| 2        | 0.20 (0.10)                                   | 160              | 8               |
| 3        | 1.0 (0.50)                                    | 170              | 6               |
| 4        | 0.4 (0.20)                                    | 160              | 10              |
| 5        | 1.0 (0.50)                                    | 170              | 17              |
| 6        | 2.0 (0.50)[^a]                                | 170              | 26              |
| 7        | 2.0 (0.50)[^b]                                | 170              | 42              |
| 8        | 2.0 (1.0)                                     | 170              | 81              |

[^a]: catalyst 50 mg.  
[^b]: 2a 1.5 mmol.

Table 3  Activities of Ir/TIO-10 for the Synthesis of 2-Substituted Benzoxazole

| Reaction | Substrate | Product | Yield [%] |
|----------|-----------|---------|-----------|
| 1        | ![2b](image) | ![3ab](image) | 68        |
| 2        | ![2c](image) | ![3ac](image) | 99        |
| 3        | ![2d](image) | ![3ad](image) | 90        |
| 4        | ![2e](image) | ![3ae](image) | 99        |
| 5        | ![2f](image) | ![3af](image) | 40        |

Reaction conditions: 2-aminophenol (1a, 1.0 mmol), alcohols (1.5 mmol), mesitylene (1 cm³), Ir/TIO-10 (prepared using [Ir(cod)Cl]₂ as an iridium source, 2.0 wt%, Ir: 1.0 mol%, 100 mg), 20 h, at 170 °C, in Ar.
high yields using 2.0 wt% catalyst. Simple aliphatic alcohol, octan-1-ol, was also applicable and the desired product was formed in moderate yield. Unfortunately, reaction of 1a with methanol at 100 °C (bath temp.) did not produce any benzoxazole.

Figure 2 shows the effect of hot filtration on the yield of 3aa over Ir/TIO-10.

To investigate the reusability of the catalyst, the used Ir/TIO-10 catalyst (prepared using [Ir(cod)Cl]2, 2.0 wt%, 1.0 mol% as Ir) was simply separated from the reaction solution by centrifugation and washed with THF after reaction at 170 °C for 18 h (3aa yield; 81%). The resulting powder was reduced in a stream of 2% H2/Ar gas at 500 °C for 30 min and passivated at 50 °C for 5 min as usual. The treated catalyst gave 3aa in 69% yield, indicating the catalyst is basically recyclable (Scheme 2). Further optimization of the recovery procedure is ongoing.

Figure 3 shows TEM images of TIO-10-supported iridium catalysts prepared from Ir(acac)3 and [Ir(cod)Cl]2, respectively, after reduction at 500 °C for 30 min. Most TIO-10 secondary particles were in the range of 300-400 nm diameter as shown in Fig. 3(a), and consisted of many smaller particles with 10-20 nm diameter. Figures 3(b) and 3(c) and the iridium particle distribution histograms indicate the formation of iridium nanoparticles of less than 2 nm diameter on the surfaces of both Ir/TIO-10 catalysts, which may explain the high activity of the Ir/TIO-10 catalyst. Note that much smaller iridium nanoparticles were formed on the surface of TIO-7 than on TIO-10 (see Fig. S3), as previously reported[22]. The size effect of metal nanoparticles is well known in catalysis[31]. The activity of the catalyst is significantly promoted by decreasing the size of metal nanoparticles, probably because the smaller nanoparticles have higher surface area, more exposed surface atoms, and more surface defects, or affect the surface atomic structure, electronic structure, and quantum size effect[32]. However, iridium nanoparticles show different contradictory effects in specific catalytic reactions[33], as this catalyst does not comply with the expected association of smaller size and greater activity, because the iridium sub-nano cluster has stronger CO
adsorption than iridium single atoms, thus favoring the oxidation of CO with higher TOF\textsuperscript{21}).

The reduction characteristics of the catalysts were studied by temperature-programmed reduction by hydrogen (H\textsubscript{2}-TPR). Figure 4 shows the H\textsubscript{2}-TPR profiles of the present Ir/TiO\textsubscript{2} catalysts. The TPR profile of 2 wt\% Ir/TiO\textsubscript{2} catalyst prepared using [Ir(cod)Cl\textsubscript{2}] showed a clear-defined peak at 123 °C, which was identified as reduction of the iridium species, and a broad peak around 250 to 500 °C which was associated with reduction of the surface Ti\textsuperscript{4+} species to Ti\textsuperscript{3+}. Significant shift of the peak towards high temperature (ca. 140 °C) for the Ir/TiO\textsubscript{2} catalyst suggested stronger interaction between the iridium species and TiO\textsubscript{2} surface. The lower reducibility of iridium species on TiO\textsubscript{2} is consistent with the lower CO adsorption, as discussed above\textsuperscript{21}). Two reduction peaks appeared at around 200 °C for Ir/TiO\textsubscript{2} prepared using Ir(acac\textsubscript{3}), but no peaks in this region for the catalyst prepared from [Ir(cod)Cl\textsubscript{2}]. Formation of such less reducible iridium species on the surface may account for the lower activities of Ir/TiO\textsubscript{2} catalysts prepared from Ir(acac\textsubscript{3}) as well as the Ir/TiO\textsubscript{2} catalyst (see Tables 1 and 2).

The Ir 4f XP spectrum of the fully reduced Ir/TiO\textsubscript{2} catalyst (prepared from [Ir(cod)Cl\textsubscript{2}], 1.0 wt\%) is shown in Fig. 5. Considering the severe overlapping of the Ti 3s band, the Ir 4f spectrum consists of bands at 60.3 eV and 61.8 eV, which were assigned to metallic Ir\textsuperscript{0} (60.3 eV) and intermediate oxidation state Ir\textsuperscript{3+} (61.8 eV), respectively, indicating iridium on titania is partially reduced. The ratio of Ir\textsuperscript{0} to Ir\textsuperscript{3+} was ca. 0.7 to 0.3, which compares well to the reduced Ir/TiO\textsubscript{2} catalysts in which partially oxidized iridium species are more predominant\textsuperscript{21}). This result suggests the reduced iridium species Ir\textsuperscript{0} is responsible for the catalytic activity.

Previous investigations of acceptor-less dehydrogenative synthesis of benzimidazoles revealed that fully-reduced, well-dispersed small iridium nanoparticles are responsible for the excellent catalytic activity\textsuperscript{20,21,23}). The iridium nanoparticles were smaller and better dispersed on titania than on other oxides such as silica or alumina\textsuperscript{20}). In addition, the crystalline structure of titania affected both the size and reducibility of surface iridium species\textsuperscript{21}). The present study showed suitable interaction between iridium species and the TiO\textsubscript{2} surface would enable the formation of very small, well-dispersed, highly-reduced iridium nanoparticles, so further detailed study is intended.

Scheme 3 shows a possible reaction mechanism for the dehydrogenative synthesis of benzoxazole, as previously proposed\textsuperscript{12}). The reaction is initiated by the abstraction of hydrogen from alcohol to form a corresponding aldehyde, and successive reaction of this aldehyde with 2-aminophenol proceeds to give an imine intermediate, followed by dehydrogenative cyclization to form benzoxazole. Our GC measurement showed that two equivalents of molecular hydrogen were formed after the reaction finished. Dehydrogenative synthesis of benzimidazoles proceeds via a similar mechanism at a significantly lower temperature around 100 °C\textsuperscript{21}). The previous computational study on the iridium complex-catalyzed \textit{N}-alkylation of amines by alcohols revealed that dissociation of the product from
the metal, required to regenerate the catalyst, is difficult, so this step may account for the high temperature required\(^{40}\). Similarly, dissociation of the products from the catalytically active sites may be responsible for the high temperature required in the present system. Further detailed kinetic study on the reaction mechanism is ongoing.

4. Conclusion

The present study developed titania-supported iridium catalysts with excellent activity for the dehydrogenative synthesis of benzoxazoles from 2-aminophenol and primary alcohols. The titania supports had significant effects on the activity of iridium catalysts, with the catalysts supported on TIO-10 showing the highest activity. The use of \([\text{Ir}(\text{cod})\text{Cl}]_2\) as an iridium precursor instead of \([\text{Ir}(\text{acac})_3]\) further promoted catalytic activity.

Supporting information

Supplementary data associated with this article can be found in the online version, at https://jstage.jst.go.jp/browse/jpi-char/en (DOI: doi.org/10.1627/jpi.64.271).

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要　旨

アクセプターレス脱水素型ペンゾキサゾール合成用酸化チタン担持イリジウム触媒の開発

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2-アミノフェノールと第一級アルコールからのアクセプターレス脱水素型ペンゾキサゾール合成に有用な酸化チタン担持触媒を開発した。触媒活性は、チタニア担体、イリジウム前駆体およびイリジウム担持量に依存し、特に [Ir(cod)Cl]2 (cod=1,5-cyclooctadiene) をイリジウム前駆体とするIRC（触媒学会参照触媒）-TIO-10担持触媒が最も高活性を示した。本触媒は多様な第一級アルコールに適用可能で、それぞれ対応するペンゾキサゾールが良好な収率で得られた。また、本触媒は容易に回収・再利用可能であり、反応加熱時の過試験等の結果から不均一系触媒として機能していることが示された。有効な触媒の表面には直径2 nm 未満の高度に分散し容易に還元可能なイリジウム種が形成されており、優れた触媒活性の要因であると推察される。