Effect of Titania Supports on 
Ir-Catalyzed Synthesis of 
Benzimidazoles via Dehydrogenation 
or Hydrogen Transfer

Kenji Wada\textsuperscript{1}, Tatsuhiro Fukutake\textsuperscript{2}, Qi Feng\textsuperscript{1}

\textsuperscript{1}Faculty of Medicine, Kagawa University, Miki-Cho, Kita-Gun, Kagawa, Japan
\textsuperscript{2}Faculty of Engineering, Kagawa University, Takamatsu, Kagawa, Japan

\textsuperscript{*}E-mail: wadaken@med.kagawa-u.ac.jp

The development of solid catalysts which enable highly efficient organic synthesis has attracted much attention, since these solid catalysts can overcome practical and inherent environmental disadvantages of homogeneous catalysis. On the other hand, benzimidazoles are important pharmaceutical and agrochemical law materials, and the development of effective synthetic methods is highly desired. In this context, we have developed heterogeneous Ir/TiO\textsubscript{2} catalyst that realizes the synthesis of benzimidazoles from phenylenediamines and primary alcohols under relatively mild conditions, namely at 120 °C.\textsuperscript{1}

In the present study, we report remarkable effects of the crystalline structures of the titania supports on the activity of iridium catalysts for the synthesis of benzimidazoles via dehydrogenation or hydrogen transfer routes.

For the synthesis of benzimidazoles from \textit{o}-phenylenediamines and primary alcohols (eq.1), iridium catalysts supported on rutile titania, such as JRC-TiO\textsubscript{2} supplied from Catalysis Society of Japan, showed higher activities than anatase-supported catalysts (Table 1): The desired product \textbf{3aa} was obtained in high yields even at 100 °C. On the other hand, the catalysts supported on atanase titanias with high surface areas, namely JRC-TiO\textsubscript{2}-7, did not show significant activity. According to the CO pulse experiments and XPS study, the predominant formation of well-reduced, small iridium nanoparticles (less than 2 nm in diameter) on rutile would be one reason of the excellent activity for the dehydrogenative reactions.

On the other hand, for the synthesis of benzimidazoles from 2-nitroanilines and primary alcohols via hydrogen transfer (eq. 2),\textsuperscript{1} the iridium catalysts supported on anatase with high surface areas such as JRC-TiO\textsubscript{2}-7 showed excellent activity at 80 °C. Note that there are strong positive correlation between BET surface areas and the activities of iridium catalysts. Remarkably, an iridium catalyst supported on a \{010\}-facetted anatase\textsuperscript{4} showed significant activity in spite of its moderate surface area (53 m\textsuperscript{2}g\textsuperscript{-1}), suggesting the selective formation of iridium species suitable for the present reaction. All these solid catalysts could be recycled without loss of the activities, and the leaching of iridium species into the products was negligible.

As discussed above, rutile- and \{010\}-facetted anatase-supported iridium catalysts showed excellent activities for the synthesis of benzimidazoles via dehydrogenation and hydrogen transfer, respectively. The development of supported iridium catalysts for a much wider range of organic syntheses, as well as further study on the nature of surface iridium species on these titanias, are now in progress.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Entry & TiO\textsubscript{2} support & BET S.A. & Yield of \textbf{3aa} from & Yield of \textbf{3aa} from \\
& & (m\textsuperscript{2}g\textsuperscript{-1})\textsuperscript{b} & 1a and 2a at 100 °C & 4a and 2a at 80 °C \\
& & & (%) & (%) \\
\hline
1 & TIO-6(R) & 53 & 59 (90)\textsuperscript{c} & 61 \\
2 & TIO-7(A) & 133 & 17 & 86 (99)\textsuperscript{c} \\
3 & PA-3.5 & 53 & 14 & 96\textsuperscript{c} \\
\hline
\end{tabular}
\caption{Effects of titania supports on the synthesis of 2-phenylbenzimidazole via dehydrogenation or hydrogen transfer\textsuperscript{a}}
\end{table}

\textsuperscript{a}Catalysts were calcined at 400 °C for 30 min followed by the reduction in a H\textsubscript{2} flow at 500 °C for 30 min.

\textsuperscript{b}Surface areas of the supported catalysts.

\textsuperscript{c}Using catalyst prepared without calcination.

REFERENCES