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

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Abstract: 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 are discussed. For example, rutile-supported catalysts enable the synthesis of 2-phenylbenzimidazoles from *o*-phenylenediamines and primary alcohols at 100 °C, while the use of anatase resulted in poor activities. The predominant formation of small, well-reduced iridium nanoparticles on rutiles would be responsible for the excellent activities of rutile-supported catalysts. On the other hand, {010}-facetted anatase-supported iridium catalysts showed excellent activities for the reaction from 2-nitroanilines and primary alcohols via hydrogen transfer.

Keywords: iridium, titania, heterogeneous catalysis

1. Introduction

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_2 catalyst that realizes the synthesis of benzimidazoles from phenylenediamines and primary alcohols under relatively mild conditions, namely at 120 °C.[1]

In the present study, remarkable effects of the crystalline structures of the titania supports on the activity of iridium catalysts for the synthesis of benzimidazoles[2] via dehydrogenation or hydrogen transfer routes are discussed.

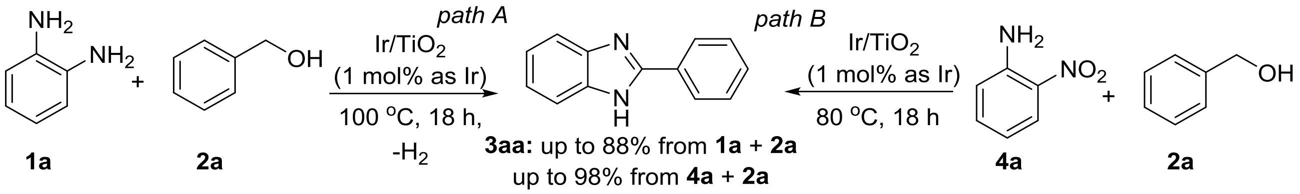
2. Experimental

Supported iridium catalysts were prepared by an impregnation method using a methanol solution of $Ir(acac)_3$. The catalysts were usually reduced in a H_2 (2vol.%)/Ar flow (40 cm^3 min^{-1}) at 500 °C (ramp rate; 10 °C min^{-1}) for 30 min. The reactions were performed using hot stirrers equipped with cooling blocks to reflux the solution. A prescribed amount of substrates and mesitylene (1.0 cm^3) were added to the Schlenk tube containing the reduced catalyst, and the reaction mixture was stirred at 80 °C or 100 °C for 18 h under an argon atmosphere. The products were analyzed by GC and GC-MS.

3. Results and discussion

For the synthesis of benzimidazoles from *o*-phenylenediamines and primary alcohols (*path A*), The synthesis of 2-phenylbenzimidazole (**3**) from *o*-phenylenediamine (**1**) and benzyl alcohol (**2**) at 100 °C in the presence of rutile-supported catalysts proceeded smoothly to give **3** in high yields of up to 88%, while the use of high surface area anatase such as JRC-TIO-7 resulted in poor activities. Similar results were observed for the dehydrogenative conversion of 2-(2-aminophenyl)-ethanol to indole. The reaction at 100 °C for 18 h in the presence of 1.0 mol% iridium on rutile gave indole in a yield of 73%, while the use of anatase-supported catalysts resulted in significantly lower yields. TEM analysis indicated the formation of small, homogeneously-dispersed iridium nanoparticles on rutiles (less than 2 nm in diameter), while the inhomogeneous loading of iridium species was observed on anatase supports. Note that there is a strong correlation between CO uptake by iridium nanoparticles and the activities at 100 °C (Figure 1), suggesting that the predominant formation of well-reduced iridium nanoparticles is one major reason for the excellent activities of rutile-supported catalysts.

On the other hand, for the synthesis of benzimidazoles from 2-nitroanilines (**4a**) and primary alcohols via hydrogen transfer (*path B*),[3] the iridium catalysts supported on anatase with high surface areas such as JRC-TIO-7 showed excellent activities at 80 °C. In good contrast to the dehydrogenative reactions, there are strong positive correlation between BET surface areas and the activities of iridium catalysts, while no correlation between CO uptake and the catalytic activities. Remarkably, an iridium catalyst supported on a {010}-facetted anatase[4] showed significant activity in spite of its moderate surface area (53 m^2g^{-1}). TEM analysis revealed the formation of small iridium nanoparticles (mean diameter; 1.0 nm) on {010}-facetted anatase (Figure 2), which would be responsible for the excellent catalytic activity.



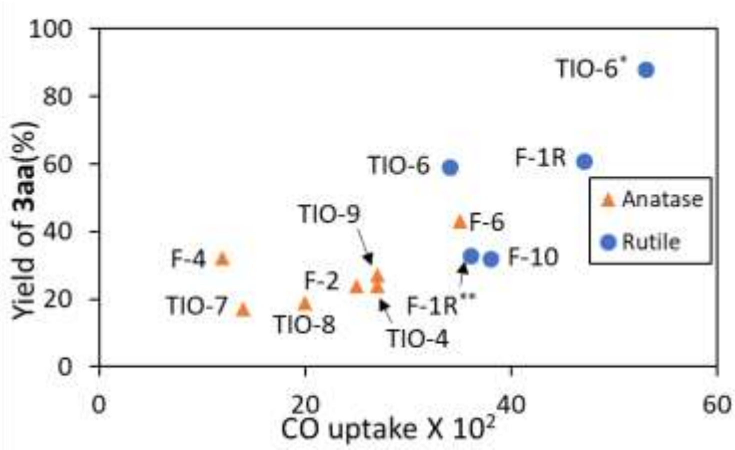


Figure 1. Relationship between CO uptake (mol/mol Ir) by the iridium catalyst and the yields of **3aa** from **1a** and **2a**. *Prepared without calcination. ** Prepared using $[(COD)IrCl]_2$ as an iridium source.

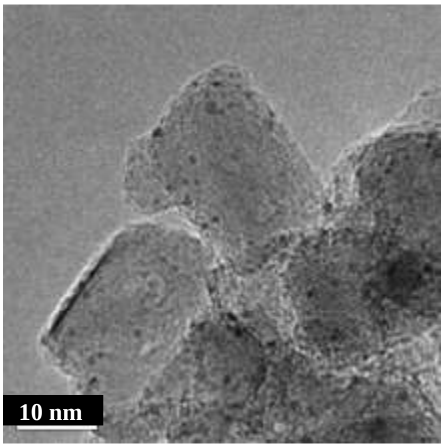


Figure 2. TEM image of Ir (2.0 wt%) supported on {010}-facetted anatase .

4. Conclusions

As discussed above, rutile-supported iridium catalysts showed excellent activities for the synthesis of *N*-containing chemicals via dehydrogenation, and well-reduced iridium species are considered to be responsible for the excellent catalytic activities. On the other hand, {010}-facetted anatase-supported iridium catalysts showed excellent activities for the synthesis of benzimidazoles via hydrogen transfer: For the reactions via hydrogen transfer, the formation of small iridium nanoparticles on the surface would be crucial. Further application of these catalysts for are now in progress.

References

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