

Supporting Information

Dehydrogenative Synthesis of Benzimidazoles under Mild Conditions with Supported Iridium Catalysts

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1. Characterization of the catalysts

Nitrogen gas adsorption of supported iridium catalysts

The BET surface areas of supported iridium catalysts just after calcination at 300 °C for 30 min were calculated from nitrogen gas adsorption isotherms. The results are summarized in Table S1. There was no distinct correlation between the surface area and catalytic activity: For example, silica-supported catalyst has a higher surface area than titania-supported catalysts, but was not effective for the present reaction.

Table S1. BET surface areas of supported iridium catalysts

Entry	Ir catalyst ^a	Surface area (m ² g ⁻¹)
1	Ir(2.0 wt%)/TiO ₂	44
2	Ir(2.0 wt%)/ZrO ₂	96
3	Ir(2.0 wt%)/Al ₂ O ₃	150
4	Ir(2.0 wt%)/CeO ₂	79
5	Ir(2.0 wt%)/MgO	156
6	Ir(2.0 wt%)/SiO ₂	157

^a Calcined at 300 °C for 30 min in air.

XRD study of supported iridium catalysts

Fig. S1 shows XRD patterns of the Ir/TiO₂ and Ir/CeO₂ catalysts before and after the reduction at 500 °C. The Ir/TiO₂ catalysts showed diffraction peaks due to rutile and anatase forms, and the Ir/CeO₂ catalysts showed patterns that can be assigned to cubic ceria. The reductive treatment at 500 °C for 30 min did not affect XRD patterns of all these catalysts. Remarkably, No other diffraction peaks were observed: The absence of peaks due to crystalline IrO₂ indicates that iridium species on these supports are highly dispersed.

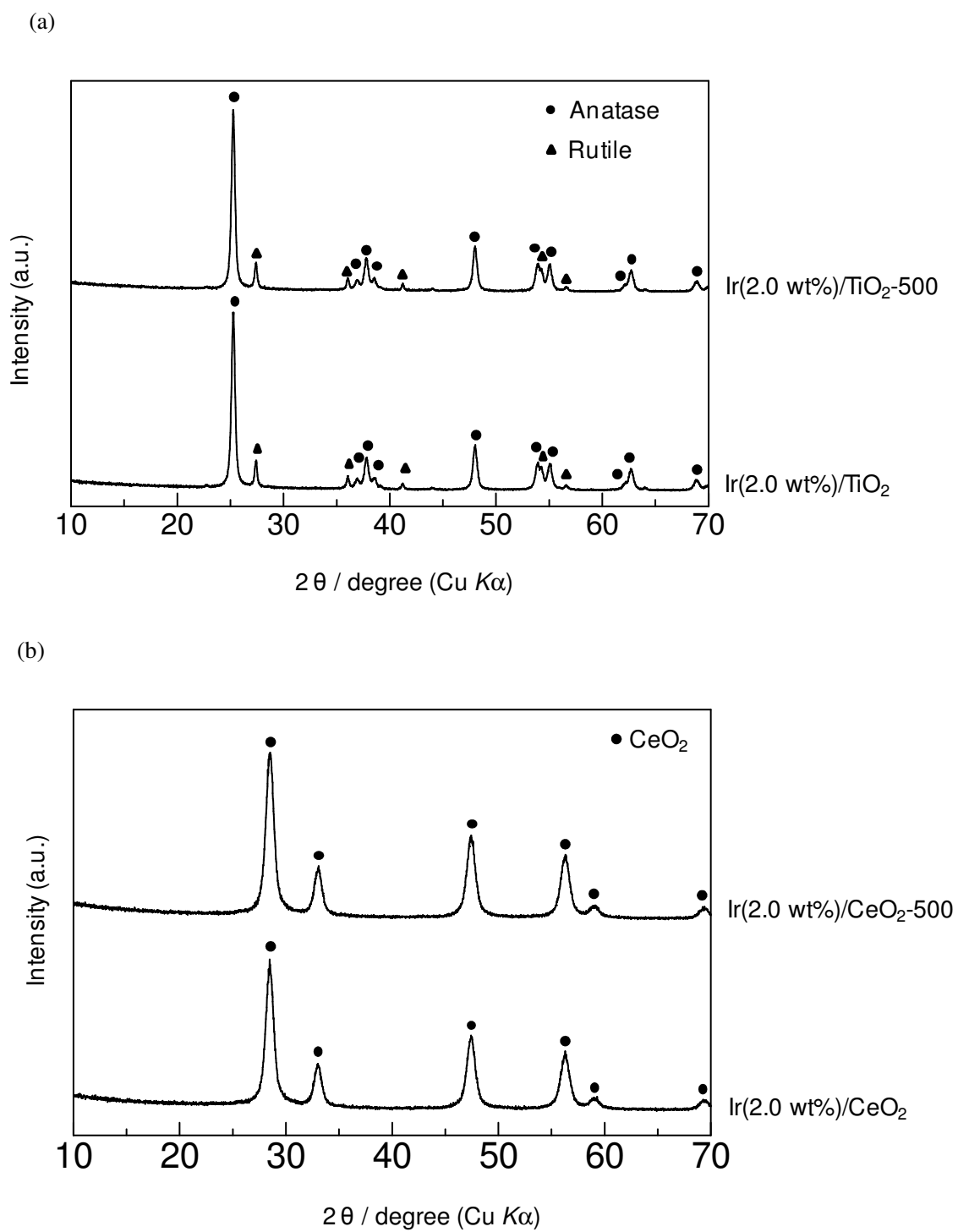


Fig. S1. XRD patterns of (a) Ir(2.0 wt%)/TiO₂ and (b) Ir(2.0 wt%)/CeO₂ catalysts before and after the treatment in a H₂ (2.0 vol%)/Ar flow (180 cm³ min⁻¹) at 500 °C for 30 min.

XP spectra of supported iridium catalysts.

The Ir 4f XP spectra of supported iridium catalysts reduced at 500 °C are shown in Fig. S2. The surface ratios of Ir(0) species (Ir 4f_{7/2} 60.7 eV) and high-valent Ir species (Ir 4f_{7/2} 62.0 eV)^[1] depended on the metal oxide supports.

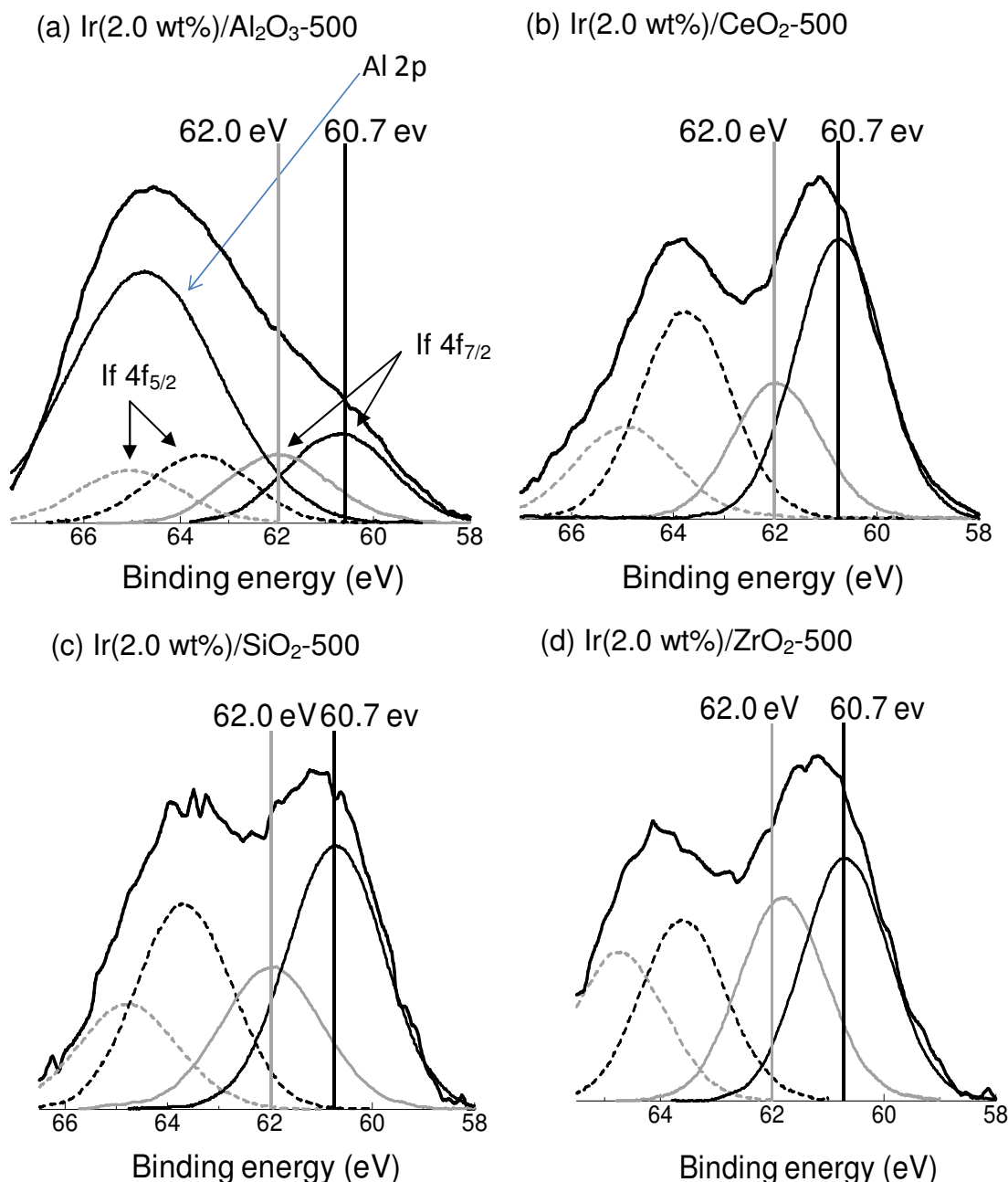


Fig. S2. Ir 4f XP spectra of the catalysts after the treatment a H₂ (2.0 vol%)/Ar flow (180 cm³ min⁻¹) at 500 °C for 30 min. An Al 2p_{3/2} satellite peak was seen at 64.7 eV in the spectrum of Ir(2.0 wt%)/Al₂O₃-500.

Temperature-programmed reduction (TPR) profiles of supported iridium catalysts.

The H₂-TPR profiles of supported iridium catalysts and that of the ceria support are shown in Fig. S3. For all of the catalysts except for Ir/MgO, reduction peaks of oxidized iridium appeared at below 250 °C, whereas the reduction of oxidized Ir/MgO occurred at a higher temperature. Bulk IrO₂ was reduced at around 100 °C. A broad peak observed for Ir/CeO₂ above 600 °C has been reported to be responsible for the reduction of bulk CeO₂.^[2,3] The reduction peak of Ir/CeO₂ at around 100 °C was much larger than those observed for other supported iridium catalysts, and the reduction peak of the CeO₂ surface at 250–450 °C disappeared: Iridium species would accelerate the reduction of surface Ce^{IV}, probably through the migration of surface oxygen species from CeO₂ to iridium species.^[2–5]

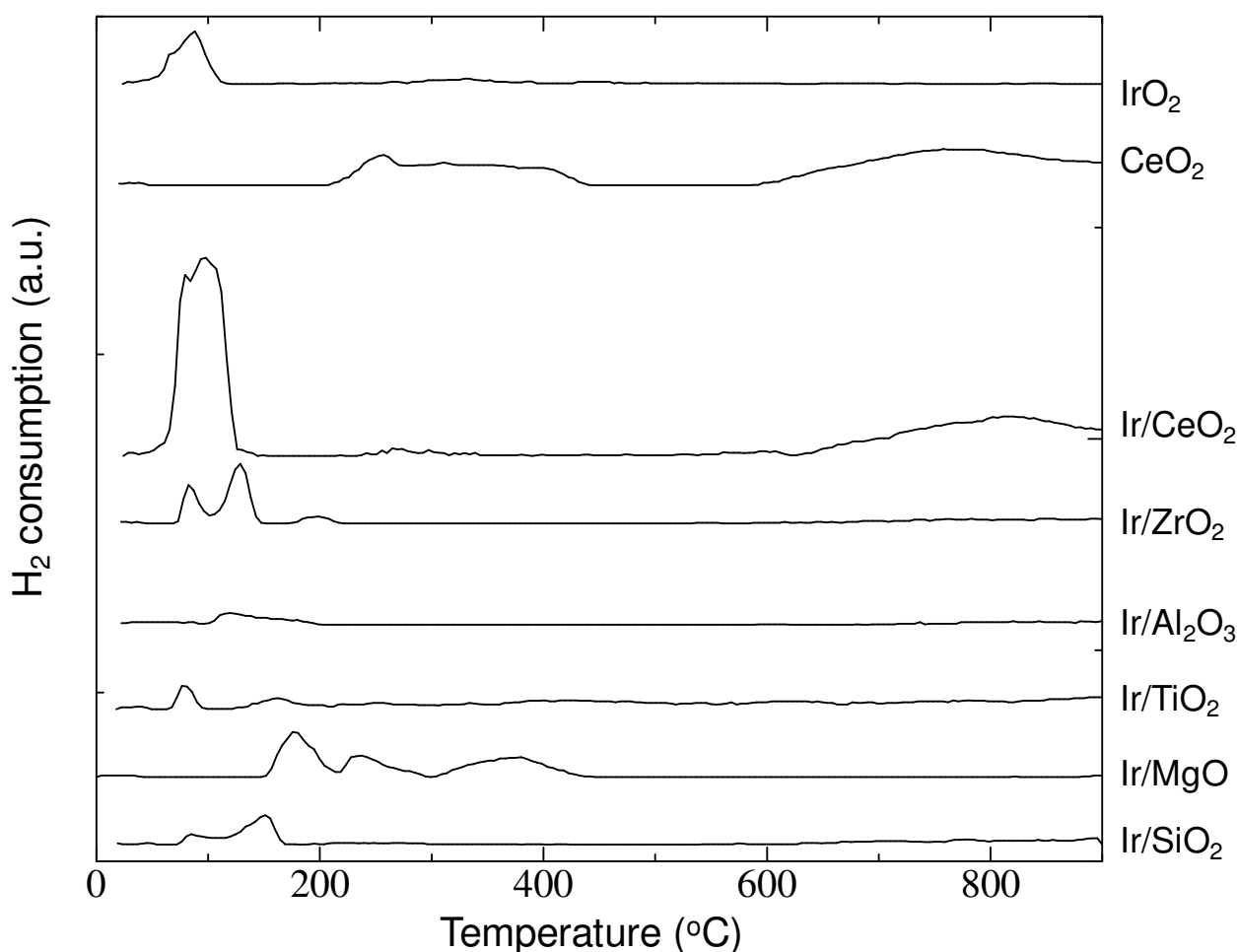


Fig. S3. TPR profiles of supported iridium catalysts

2. Dehydrogenation of benzyl alcohol by the Ir/TiO₂ catalyst

The time-course of the reaction of benzyl alcohol (**2a**) (2.0 mmol) in mesitylene (1.0 cm³) under an argon atmosphere at 120 °C in the presence of Ir(2.0 wt%)/TiO₂-500 (0.010 mmol as Ir) is shown in Fig. S4. The major product is benzaldehyde (**4a**) together with a trace amount of benzyl benzoate. At the initial stage the reaction from **2a** to **4a** and H₂ proceeded at a similar rate with the conversion of **1a** by the dehydrogenative synthesis of 2-phenylbenzimidazole, **3aa**. On the other hand, the yield of **4a** from **2a** gradually slowed down after 3 h.

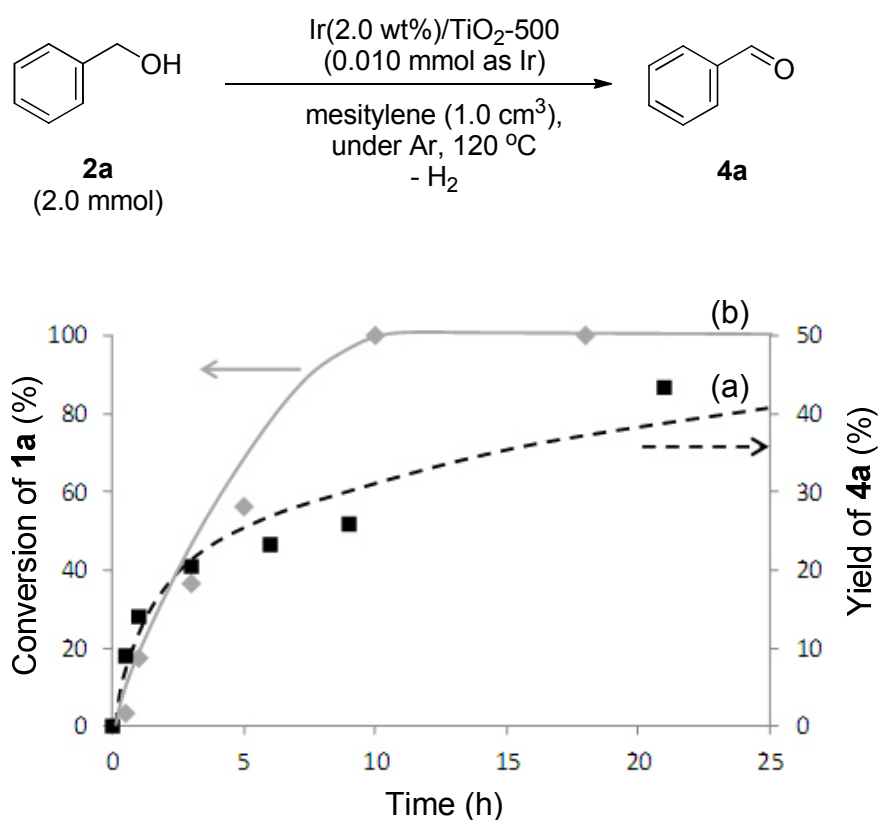


Fig. S4. (a) Time-course of the dehydrogenation of **2a** to **4a**. Solid gray line (b) shows the conversion of **1a** in the dehydrogenative reaction of **1a** with **2a** under the identical conditions for comparison.

Fig. S5 shows the time-course of the reaction of benzyl alcohol (**2a**) (1.0 mmol) in mesitylene (1.0 cm³) under an argon atmosphere at 120 °C catalyzed by Ir(2.0 wt%)/TiO₂-500 (0.010 mmol as Ir) in the presence of benzaldehyde (**4a**) (1.0 mmol). The amount of **4a** was not changed even after the prolonged run and the significant formation of other products was not observed, which clearly indicates that the dehydrogenation of **2a** to **4a** was strongly inhibited by benzaldehyde.

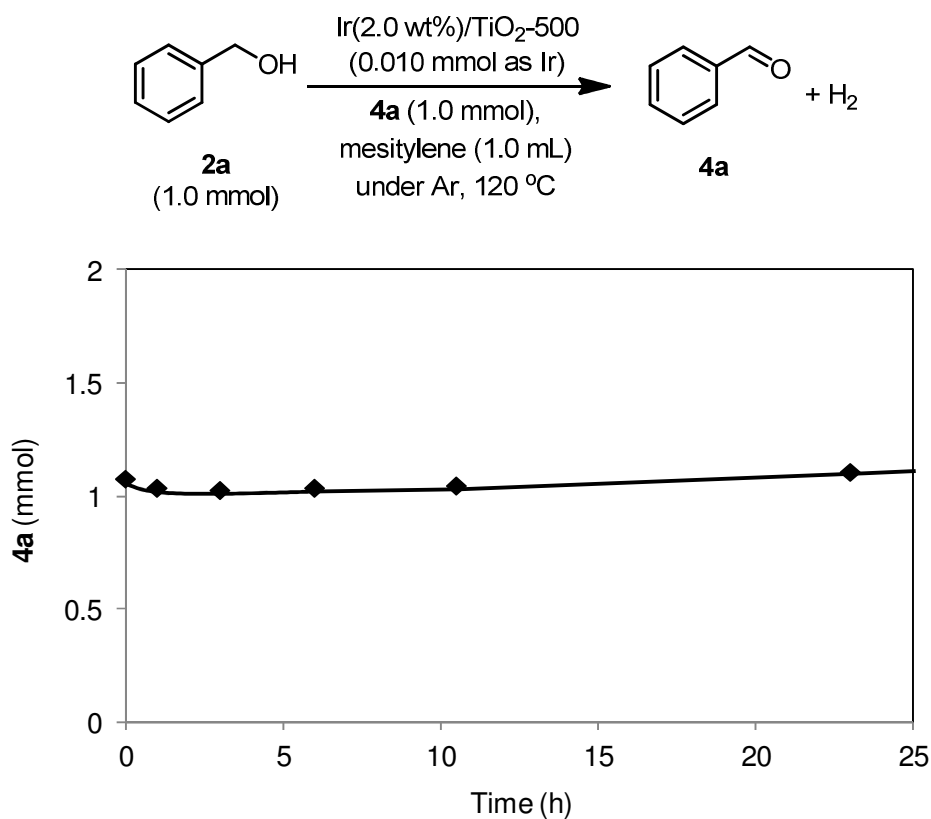


Fig. S5. Time-course of the dehydrogenation of **2a** to **4a** in the presence of **4a** (1.0 mmol).

References

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