

Influence of Calcination Temperatures on Iridium Dispersion and Hydrogenation Activity in Silica-Supported Iridium Catalysts

Ryoji Shibuya, Masa-aki Ohshima,
Hideki Kurokawa, and Hiroshi Miura*

Graduate School of Science and Engineering, Saitama
University, 255 Shimo-okubo, Sakura-ku, Saitama 338-8570

Received February 15, 2010

E-mail: hmiura@mail.saitama-u.ac.jp

The influence of calcination temperatures on the dispersion of Ir/SiO₂ catalysts has been studied. At low calcination temperatures, the chloride precursor was dispersed on the silica surface and formed highly dispersed Ir/SiO₂ catalysts upon reduction. At high calcination temperatures, the formation of IrO₂ was confirmed, which resulted in low dispersion after reduction.

Supported noble metal catalysts are widely used for a variety of catalytic reactions. For example, supported Ru, Rh, and Pd catalysts have shown excellent activity for the hydrogenation of aromatic hydrocarbons, while Pd and Pt catalysts have demonstrated excellent activity for the hydrogenation of unsaturated bonds like C=C and C≡C.¹ In the platinum metal group, Ir is known to be active for NO reduction,^{2–4} partial methane oxidation,⁵ hydrazine decomposition,^{6–8} and selective hydrogenation of α,β -unsaturated aldehydes.^{1,9–13} However, no detailed research has been reported on hydrogenation reactions over Ir catalysts compared to other noble metals. Especially, the effects of catalyst preparation variables are still unknown. Because NO reduction and hydrazine decomposition are high temperature reactions, the catalysts are prepared using procedures involving high temperature calcination. Very low Ir dispersions have been found in some cases,^{2,3} suggesting that the effects of calcination temperatures may be important. In this paper, we report the effect of calcination temperatures on Ir dispersion and activity of Ir/SiO₂ catalysts in hydrogenation reactions. We found a drastic change in Ir dispersion by changing the calcination temperature in a narrow range. Because varieties of Ir catalysts with different Ir dispersions could be prepared by controlling the calcination temperature alone, dispersion effects on the catalytic activity during hydrogenation were readily identified using catalysts prepared through the same procedure, eliminating the effects of preparation variables. We studied crotonaldehyde hydrogenation, which contains C=C and C=O double bonds. Selective hydrogenation of the C=O bond yields unsaturated crotyl alcohol, a useful raw material in pharmaceuticals and fragrances.^{9,10} Ir is reported to be a selective catalyst for this reaction.¹⁰

Experimental

Catalyst Preparation. The Ir/SiO₂ ($w = 2\%$) catalyst was prepared by impregnating a SiO₂ support with a surface area of 346 m² g^{−1} (Silbead, Mizusawa Industrial Chem.) with an aqueous solution of H₂[IrCl₆]· n H₂O (Aldrich). The slurry was stirred for 1 h, vaporized under vacuum, and dried at 403 K in an oven overnight. The residue was heated in an oven at a rate of 4.5 K min^{−1} and calcined at 403–773 K for 3 h. The resulting powder was then placed in a reduction tube and reduced under flowing hydrogen at 673 K for 5 h. The catalysts were sieved and powders of less than 100 mesh (<149 μ m) were used for the liquid phase hydrogenation reaction.

Characterization. Ir dispersion, defined as the ratio of Ir_{surface} over Ir_{total}, was estimated by CO adsorption at 300 K using a dynamic pulse adsorption apparatus (Ohkura Riken, BP-1). The catalyst was pre-reduced at 673 K for 1 h and purged with He for 0.5 h. Oxygen adsorption was also used in a similar manner to confirm the reliability of the dispersion measurements. X-ray diffraction (XRD) patterns were obtained before and after reduction using RINT-Ultima III diffractometer (RIGAKU) with a Cu K α radiation under a voltage of 40 kV, current of 40 mA, and scan speed of 4.0° min^{−1}. X-ray fluorescence (XRF) measurements were performed under vacuum using a Philips PW2400 apparatus.

Crotonaldehyde Hydrogenation. The reaction rate of crotonaldehyde hydrogenation was evaluated in a stainless steel autoclave (100 mL) equipped with a mechanical stirrer, a thermowell, and a pressure gauge. Catalysts were pre-reduced at 673 K for 1 h. Crotonaldehyde (36.5 mmol) in ethanol (50 mL) was used as a reactant. The reaction rate was estimated at 323 K using the catalyst (0.3 g) under an initial H₂ pressure of 1.0 MPa at a 1000 rpm agitation. The products were analyzed by gas chromatography using the Shimadzu GC-18A apparatus equipped with a DB-WAX capillary column (30 m) at 343 K. The turnover frequency (*TOF*) was calculated from the reaction rate and the amount of CO adsorption.

Results and Discussion

Dispersion of Iridium. The dispersion of iridium in Ir/SiO₂ catalysts prepared by calcination at 403–773 K and reduction at 673 K was measured by CO and O₂ adsorption experiments. The dispersion was calculated by assuming that the adsorption stoichiometries corresponded to CO/Ir = 1 and O/Ir = 1.¹⁴

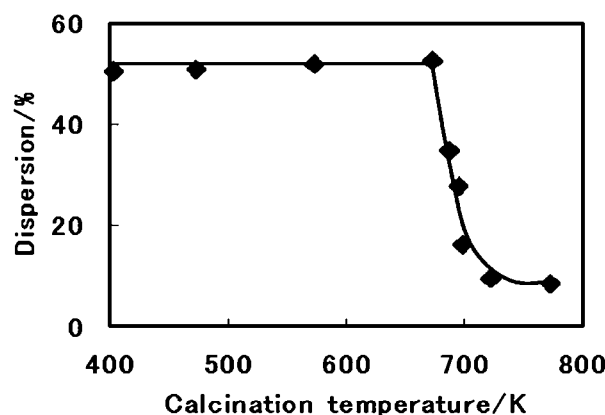
Dispersion values determined by CO adsorption agreed very well with values determined by O₂ adsorption (Table 1). Figure 1 clearly shows that the dispersion was independent of the calcination temperature between 403 and 673 K but decreased drastically between 673 and 723 K. A difference of only 50 K in the calcination temperature caused the dispersion to decrease from above 50 to below 10%.

The influence of reduction temperatures was also studied. A series of catalysts were calcined at 403 K and then reduced at temperatures ranging between 473 and 873 K. Another series of catalysts were calcined at 773 K and then reduced at the same temperature range. Both series of catalysts displayed an almost constant dispersion upon reduction at 473–673 K but dispersion decreased gradually because of sintering when the reduction

Table 1. Amount of Chlorine and Dispersion of Ir/SiO₂ Prepared with Different Calcination Temperatures

Calcination temperature/K	Cl/Ir ratio ^{a)} (after calcination)	Cl/Ir ratio ^{a)} (after reduction)	Dispersion/%	
			CO/Ir ^{b)}	O/Ir ^{c)}
403	5.6	<0.03	50.4	56.3
473	5.2	<0.03	51.2	
573	5.2	<0.03	51.8	59.2
673	2.8	<0.03	52.7	
688	1.5	<0.03	34.6	34.9
695	0.7	<0.03	27.7	31.6
698	0.3	<0.03	16.0	14.9
723	0.3	<0.03	9.4	
773	0.2	<0.03	8.4	10.9

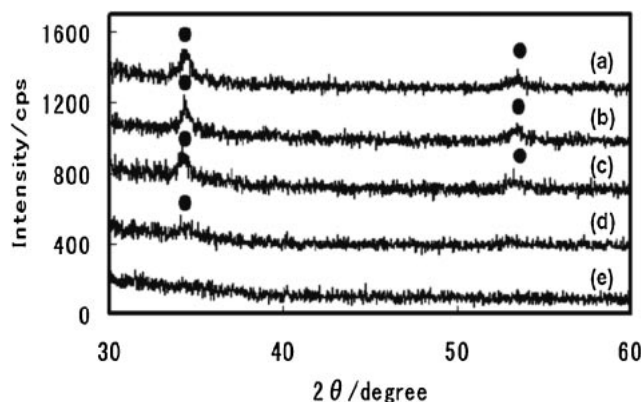
a) Determined by XRF measurement. b) Estimated by CO chemisorption. c) Estimated by oxygen chemisorption.

**Figure 1.** Dependence of Ir dispersion on the calcination temperature of Ir/SiO₂. Dispersion was estimated from CO adsorption measurements.

temperature increased beyond 673 K. However, drastic changes in dispersion were not observed with changing reduction temperature. We concluded that calcination temperatures affected dispersion more drastically than reduction temperatures. Ir precursor condition, after calcination treatment, clearly controlled the Ir dispersion.

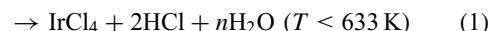
XRD and XRF of Ir/SiO₂. XRD patterns of catalysts calcined at 573 and 773 K and reduced at 673 K were obtained. The catalyst calcined at 573 K exhibited a flat XRD pattern, indicating that Ir was highly dispersed. In contrast, the catalyst calcined at 773 K showed XRD peaks at 2θ values of 41 and 47°, which are ascribed to Ir(111) and Ir(200), respectively, suggesting crystalline iridium growth. The particle size of Ir estimated by XRD (18.5 nm) was in agreement with that estimated by CO adsorption (17.3 nm). Therefore XRD results are in good agreement with the chemisorption-based dispersion measurements.

The Cl content of the catalysts before and after reduction was measured by XRF and the results are shown in Table 1. After hydrogen reduction, Cl contents of all catalysts were below detection level. However, residual Cl was found before reduction. The Cl content was almost constant for catalysts calcined at 573 K and lower temperatures. For calcinations at 673 K and at higher temperatures, the amount of Cl decreased with increasing calcination temperature.

**Figure 2.** XRD patterns of catalyst precursors calcined at (a) 723, (b) 698, (c) 695, (d) 688, and (e) 673 K. ●: IrO₂.

XRD patterns of the catalysts after calcination are shown in Figure 2. Catalysts calcined at 673 K and lower temperatures did not display any diffraction peaks. Catalysts calcined at 688 K and higher temperatures showed XRD peaks at 2θ values of 35 and 54°, which are attributed to IrO₂. This clearly suggests that crystalline IrO₂ was formed as the residual Cl decreased. Using thermal analysis, Hu et al. reported¹⁵ that H₂[IrCl₆]·nH₂O decomposed in air according to the following two stages:

Stage 1: H₂[IrCl₆]·nH₂O



Stage 2: IrCl₄ + O₂ → IrO₂ + 2Cl₂ (T > 633 K) (2)

Stage 1 did not proceed extensively for calcinations at 573 K and lower temperatures because Cl/Ir > 5. Stages 1 and 2 began to proceed at 673 K because Cl/Ir < 3. However, the IrO₂ crystal did not grow significantly as revealed by XRD. Stages 1 and 2 proceeded extensively for calcinations at 688 K and higher temperatures and IrO₂ formed crystalline particles as shown by XRF and XRD.

Table 1 and Figure 2 clearly show that the reduction of the H₂[IrCl₆] and IrCl₄ chloride precursors clearly resulted in highly dispersed Ir catalysts because the precursors were highly dispersed on the support surfaces. On the other hand, the reduction of IrO₂ resulted in poorly dispersed Ir catalysts because IrO₂ formed large particles.

Crotonaldehyde Hydrogenation. Crotyl alcohol and butyraldehyde are the respective products resulting from the hydrogenation of C=O and C=C double bonds in crotonaldehyde. The TOF of C=C and C=O hydrogenations are shown in Figure 3 as a function of Ir dispersion. The TOF of the C=C hydrogenation remained almost constant, independent of Ir dispersion, suggesting that the C=C hydrogenation is structure insensitive. In contrast, the TOF of the C=O hydrogenation increased with decreasing Ir dispersion, indicating the reaction is structure sensitive. As a result, the selectivity of crotyl alcohol formation was found to increase remarkably with decreasing Ir dispersion and increasing Ir particle size.

According to literature,^{9,16} the selectivity of crotyl alcohol formation depends on metal dispersion and increases over larger particles. These reports suggested that the C=C bond has higher affinity for the surface of small metal particles because

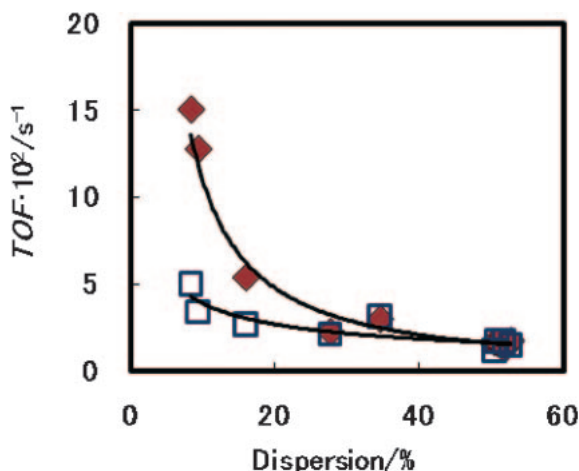


Figure 3. Turnover frequency (TOF) of the hydrogenation of crotonaldehyde over Ir/SiO₂ catalysts with different dispersions. $\blacklozenge$: C=O hydrogenation, $\square$: C=C hydrogenation.

steric effects hinder the approach of the C=C bond positioned at the center of the crotonaldehyde molecule, toward the flat surface of large particles. Consequently, the hydrogenation of the C=C bond decreases over large particles. However, our experimental results contradict this previous explanation. The rate of C=C bond hydrogenation was almost independent of metal particle size. On the other hand, the rate of C=O bond hydrogenation increased with increasing particle size, resulting in higher selectivity toward crotyl alcohol formation.

This increase in C=O bond hydrogenation rates is related to the electron density of the surface Ir atoms. The electron density increases with decreasing dispersion because the degree of coordinative unsaturation decreases on flat surfaces. Gallezot and Richard reported¹⁰ that Fe and Sn additions increased the electron density of Pt. This was advantageous for the formation of adsorbed hydride (H⁻) species, and hydrides easily react with the C=O bond carbon atom.

Conclusion

The effect of calcination temperatures was evaluated on the dispersion and hydrogenation activity of Ir/SiO₂ catalysts. The Ir dispersion did not depend on calcination temperatures between 403 and 673 K but decreased drastically between 673 and 723 K. A difference of only 50 K in calcination temperatures caused the dispersion to decrease from more than 50% to

less than 10%. At lower calcination temperatures, the Ir precursor appeared to be dispersed on the support surface because it displayed no XRD peak. Therefore, highly dispersed Ir/SiO₂ catalysts were obtained after H₂ reduction. At higher calcination temperatures, the Ir precursor formed crystalline IrO₂ as shown by XRD. Reduction of the crystalline IrO₂ resulted in the formation of large Ir particles. The effect of dispersion on hydrogenation rates was tested. The TOF was almost constant over the wide range of dispersion values examined for the hydrogenation of crotonaldehyde C=C bond but increased with decreasing Ir dispersion for the C=O bond. As a result, the selectivity of the crotyl alcohol formation increased significantly with decreasing Ir dispersion.

References

- 1 S. Nishimura, *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, John-Wiley & Sons, New York, **2001**, pp. 29–42.
- 2 E. Iojoiu, P. Gelin, H. Praliaud, M. Primet, *Appl. Catal., A* **2004**, *263*, 39.
- 3 M. Haneda, Pusparatu, Y. Kintaichi, I. Nakamura, M. Sasaki, T. Fujitani, H. Hamada, *J. Catal.* **2005**, *229*, 197.
- 4 H. Inomata, M. Shimokawabe, A. Kuwana, M. Arai, *Appl. Catal., B* **2008**, *84*, 783.
- 5 K. Nakagawa, N. Ikenaga, T. Suzuki, T. Kobayashi, M. Haruta, *Appl. Catal., A* **1998**, *169*, 281.
- 6 W. E. Armstrong, L. B. Ryland, H. H. Voge, U.S. Patent 4124538, **1978**.
- 7 J. L. Falconer, H. Wise, *J. Catal.* **1976**, *43*, 220.
- 8 R. Vieira, D. Bastos-Netto, M. J. Ledoux, C. Pham-Huu, *Appl. Catal., A* **2005**, *279*, 35.
- 9 P. Mäki-Arvela, J. Hájek, T. Salmi, D. Y. Murzin, *Appl. Catal., A* **2005**, *292*, 1.
- 10 P. Gallezot, D. Richard, *Catal. Rev., Sci. Eng.* **1998**, *40*, 81.
- 11 E. N. Bakhanova, A. S. Astakhova, K. A. Brikshtein, V. G. Dorokhov, V. I. Savchenko, M. L. Khidekel, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, *9*, 1993.
- 12 J. P. Breen, R. Burch, J. Gomez-Lopez, K. Griffin, M. Hayes, *Appl. Catal., A* **2004**, *268*, 267.
- 13 P. Reyes, M. C. Aguirre, I. Melián-Cabrera, M. L. Granados, J. L. G. Fierro, *J. Catal.* **2002**, *208*, 229.
- 14 A. Bourane, M. Nawdali, D. Bianchi, *J. Phys. Chem. B* **2002**, *106*, 2665.
- 15 J.-M. Hu, J.-Q. Zhang, C.-N. Cao, *Thermochim. Acta* **2003**, *403*, 257.
- 16 M. Englisch, A. Jentys, J. A. Lercher, *J. Catal.* **1997**, *166*, 25.