

Supporting Information

Air-Stable and Reusable Cobalt Ion-doped Titanium Oxide Catalyst for Alkene Hydrosilylation

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1. General experimental details

All organic reagents were purified before use. $\text{Co}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, HAP (monoclinic), and CoO were purchased from Wako Pure Chemical Industries. Al_2O_3 (AKP-G015) was obtained from Sumitomo Chemical Company. SiO_2 (Q-6) was purchased from Fuji Silysia Chemicals. TiO_2 (JRC TIO-4(2)) and CeO_2 (JRC CEO-2) were provided by the Catalysis Society of Japan as reference catalysts. MgO was purchased from Ube Industries. ^1H nuclear magnetic resonance (NMR) spectra were recorded using a JEM-ARM200F spectrometer. TEM was performed at 200 kV. Co K-edge X-ray absorption spectra were recorded at room temperature using a Si (311) or Si (111) monochromator at the BL01B1 and BL14B2 lines, SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), Harima, Japan. UV–Vis spectra were recorded using a JASCO V-660 spectrometer. XRD was performed using a Philips X'Pert-MPD diffractometer with $\text{Cu-K}\alpha$ radiation.

2. Catalyst preparation

Co/ TiO_2 was prepared as follows. TiO_2 (0.5 g) was soaked in an aqueous solution of $\text{Co}(\text{NO}_3)_2$ (50 mL, 2.5 mM). After stirring for 2 min, the mixture was adjusted to pH 10.0 with aqueous NaOH solution (100 mM) and stirred at room temperature for 6 h in air. The resulting slurry was filtered, and the recovered solid was washed with deionized water and dried at room temperature in vacuo. The obtained powder was calcined at 500 °C for 5 h. Co-containing TiO_2 was then treated under H_2 at atmospheric pressure and 250 °C for 2 h, affording Co/ TiO_2 as a pale green powder. The same procedure was used to prepare other TiO_2 -supported catalysts, namely, Fe/ TiO_2 , Cu/ TiO_2 , and Ni/ TiO_2 , from $\text{Fe}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, and $\text{Ni}(\text{NO}_3)_2$, respectively, and other Co/support catalysts, namely, Co/ Al_2O_3 , Co/ CeO_2 , Co/hydroxyapatite, Co/MgO, and Co/ SiO_2 .

3. Typical reaction procedure

A typical reaction procedure for the hydrosilylation of **1** with **2** using Co/ TiO_2 was as follows. Co/ TiO_2 powder (0.12 g) was placed in a reaction vessel, and **1** (3.0 mmol) and **2** (3.6 mmol) were added. The reaction mixture was stirred vigorously at 100 °C under an Ar atmosphere for

30 min. After the reaction, Co/TiO₂ was removed by filtration and the reaction solution was analyzed by NMR spectroscopy. The hydrosilylation of **1** with **2** using [Co₂(CO)₈] (0.015 mmol) was conducted under the same reaction conditions, except with the reaction time extended to 14 h and the temperature decreased to 40 °C.

4. Recycling experiments

After the catalytic reaction, Co/TiO₂ was removed by filtration and the yield was determined by NMR spectroscopy. The catalyst was washed with a mixture of hexane/acetone (1:1) and calcined at 500 °C for 5 h, followed by treatment with H₂ at atmospheric pressure and 250 °C for 2 h before reuse. A TEM image of the used Co/TiO₂ catalyst (Fig. S3) contained no recognizable Co aggregates.

5. Hot filtration experiment

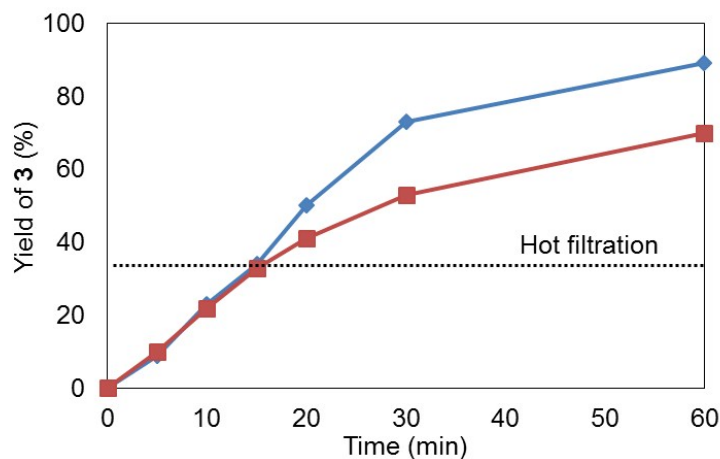


Fig. S1 Hot filtration experiment of Co/TiO₂ without H₂ treatment in hydrosilylation of **1** with **2**.

6. Characterization of Co/TiO₂

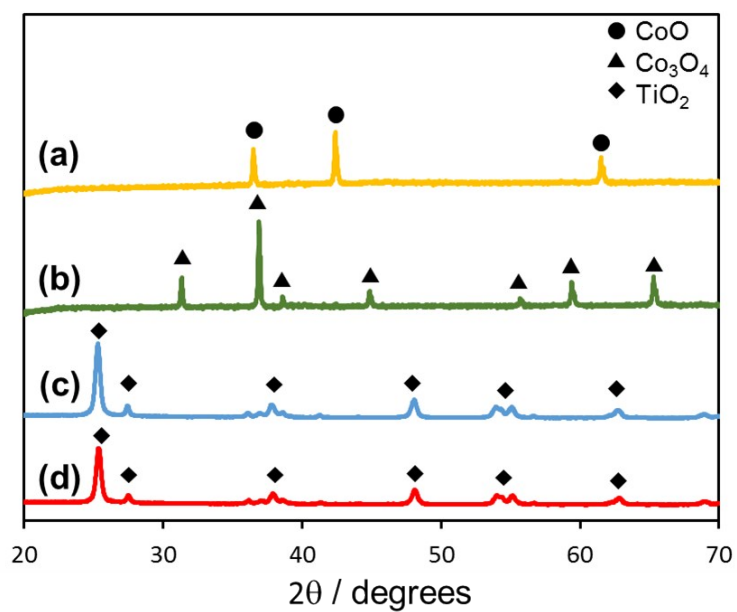


Fig. S2 XRD patterns of (a) CoO, (b) Co₃O₄, (c) TiO₂, and (d) Co/TiO₂.

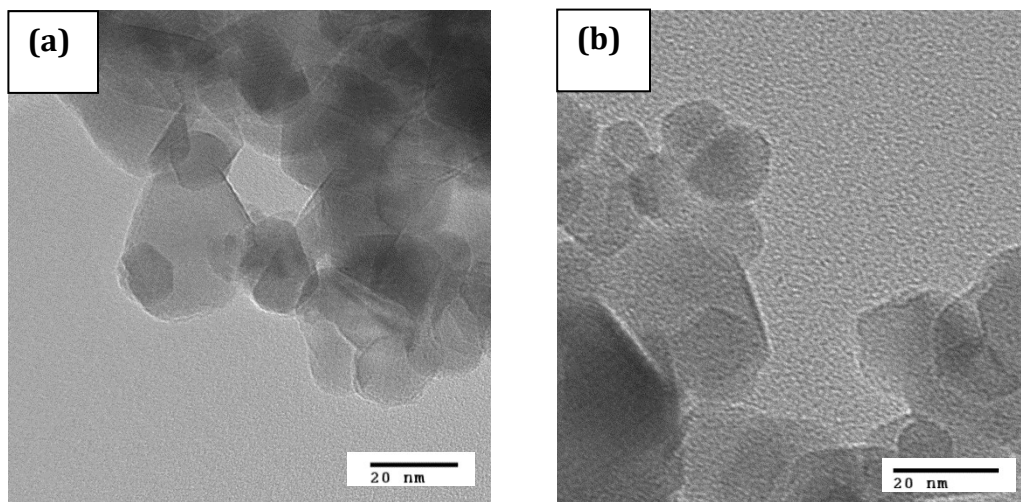


Fig. S3 TEM images of (a) fresh and (b) used Co/TiO₂.

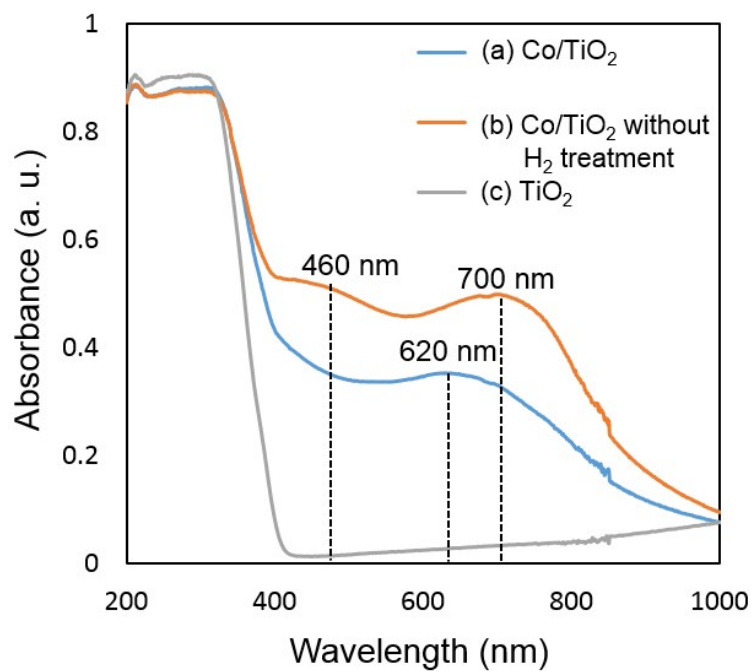


Fig. S4 UV–Vis absorption spectra of (a) Co/TiO₂, (b) Co/TiO₂ without H₂ treatment, and (c) TiO₂.

Table S1 Crystal structure data of TiO₂

Form	CN	Ti-O bond length (Å)	Ref.
Anatase	6	1.943	S1
	4	1.968	S2
	2	2.050	S2
Rutile	4	1.952	S3
	2	1.983	S3

7. Product identification

The substrates and products were characterized using NMR spectroscopy. ¹H-NMR chemical shifts of the substrates and products were in agreement with previously reported values (Table 2, entries 1, 4, 5 and 8-12) (Ref. S4–S8).

Table 2, entry 1

Dimethyl(1-octyl)phenylsilane (S4)

CAS registry No. [64545-08-6]. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.53–7.47 (m, 2H), 7.37–7.31 (m, 3H), 1.35–1.20 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.74 (t, *J* = 7.8 Hz, 2H), 0.25 (s, 6H).

Table 2, entry 2

Dimethyl(1-hexadecyl)phenylsilane

CAS registry No. [1356606-18-2]. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.54–7.48 (m, 2H), 7.38–7.32 (m, 3H), 1.36–1.20 (m, 30H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.74 (t, *J* = 7.8 Hz, 2H), 0.25 (s, 6H).

Table 2, entry 3

Dimethyl(4-methylpentyl)phenylsilane

CAS registry No. [1356955-42-4]. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.55–7.46 (m, 2H), 7.37–7.30 (m, 3H), 1.53 (sept, *J* = 7.7 Hz, 1H), 1.37–1.27 (m, 2H), 1.23–1.14 (m, 2H), 0.83 (d, *J* = 6.4 Hz, 6H), 0.75–0.69 (m, 2H), 0.25 (s, 6H).

Table 2, entry 4

(2-(Cyclohex-3-en-1-yl)ethyl)dimethyl(phenyl)silane (S4)

CAS registry No. [61518-54-5]. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.53–7.48 (m, 2H), 7.38–7.32 (m, 3H), 5.66–5.62 (m, 2H), 2.18–1.93 (m, 3H), 1.80–1.69 (m, 1H), 1.66–1.54 (m, 1H), 1.48–1.38 (m, 1H), 1.33–1.23 (m, 2H), 1.22–1.10 (m, 1H), 0.83–0.71 (m, 2H), 0.25 (s, 6H).

Table 2, entry 5

Dimethylphenyl(3-phenylpropyl)silane (S5)

CAS registry No. [79294-25-0]. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.51–7.54 (m, 2H), 7.38–7.31 (m, 3H), 7.29–7.23 (m, 2H), 7.21–7.10 (m, 3H), 2.65–2.58 (m, 2H), 1.70–1.59 (m, 2H), 0.83–0.75 (m, 2H), 0.25 (s, 6H).

Table 2, entry 6

4-[Dimethyl(phenyl)silyl]pentan-1-ol

CAS registry No. [18410-33-8]. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.55–7.47 (m, 2H), 7.39–7.31 (m, 3H), 3.64–3.57 (m, 2H), 1.59–1.50 (m, 2H), 1.41–1.32 (m, 4H), 1.17 (t, *J* = 5.5 Hz, 2H), 0.80–0.73 (m, 2H), 0.26 (s, 6H).

Table 2, entry 7

Methyl ester 11-[dimethyl(phenyl)silyl]undecanoic acid

¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.53–7.47 (m, 2H), 7.36–7.31 (m, 3H), 3.66 (s, 3H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.37–1.15 (m, 16H), 0.74 (t, *J* = 7.6 Hz, 2H), 0.25 (s, 6H).

Table 2, entry 8

1-[2-(dimethylphenylsilyl)ethyl]-2-pyrrolidinone (S5)

CAS registry No. [2168585-68-8]. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.66–7.63 (m, 2H), 7.47–7.44 (m, 3H), 3.44–3.40 (m, 2H), 3.30–3.08 (m, 2H), 2.34–2.21 (m, 2H), 1.94–1.88 (m, 2H), 1.11–1.03 (m, 2H), 0.25 (s, 6H).

Table 2, entry 9

Dimethyl(phenyl)[2-(trimethylsilyl)ethyl]silane (S6)

CAS registry No. [17123-83-0]. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.56–7.47 (m, 2H), 7.34–7.30 (m, 3H), 0.68–0.60 (m, 2H), 0.45–0.37 (m, 2H), 0.25 (s, 6H), –0.04 (m, 9H).

Table 2, entry 10

[2-(Dimethylphenylsilyl)ethyl]triethoxysilane (S5)

CAS registry No. [61210-59-1]. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.54–7.44 (m, 2H), 7.37–7.29 (m, 3H), 3.83–3.72 (m, 6H), 1.25–1.12 (m, 9H), 0.81–0.73 (m, 2H), 0.58–0.50 (m, 2H), 0.25 (s, 6H).

Table 2, entry 11

Octylphenylsilane (S7)

CAS registry No. [18415-18-4]. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.61–7.57 (m, 2H), 7.40–7.35 (m, 3H), 4.32 (t, *J* = 3.8 Hz, 2H), 1.53–1.43 (m, 2H), 1.42–1.23 (m, 10H), 1.00–0.95 (m, 3H), 0.93–0.88 (m, 2H).

Table 2, entry 12

Octyldiphenylsilane (S8)

CAS registry No. [136795-58-9]. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.57–7.53 (m, 4H), 7.38–7.33 (m, 6H), 4.85 (t, *J* = 3.8 Hz, 2H), 1.48–1.42 (m, 2H), 1.38–1.20 (m, 8H), 1.17–1.11 (m, 2H), 0.87 (t, *J* = 6.6 Hz, 3H).

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