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

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Alkene hydrosilylation is important for the synthesis of organosilicon compounds, for which precious metal complexes have been used as industrial catalysts. Considering environmental and economic concerns, the development of earth-abundant metal catalysts with high stability, easy separability, and high reusability is strongly desired. Herein, we report that a new cobalt ion-doped titanium dioxide (Co/TiO₂) catalyst was synthesized by hydrogen treatment method. The Co/TiO₂ catalyst acts as a highly efficient heterogeneous catalyst for the anti-Markovnikov hydrosilylation of alkenes under solvent-free conditions. Various alkenes were selectively converted to the corresponding alkylsilanes. This catalyst showed high stability in air and high reusability with maintained activity. The investigation of the relationship between the active site structure and catalytic performance of Co/TiO₂ disclosed that the high stability and durability of Co/TiO₂ are originated from the strong interaction between Co and TiO₂ through the formation of CoTiO₃ solid solution species.

Introduction

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Alkene hydrosilylation is important for the synthesis of organosilicon compounds that are widely used in the commercial manufacture of silicon rubbers, silicon-based surfactants, molding products, release coatings, and pressuresensitive adhesives.¹ Precious metal catalysts,^{2,3} typically Pt or Rh, have been developed for alkene hydrosilylation. Pt complexes, such as those developed by Speier et al.^{2e} and Karstedt,^{2f} are of particular note, having served as industrial alkene hydrosilylation catalysts. Although these catalysts are highly active for alkene hydrosilylation, the constituent metals are expensive and rare. Furthermore, these homogeneous catalysts easily become incorporated into the organosilicon products and are difficult to recover, resulting in considerable precious metal loss. In fact, the annual Pt loss in hydrosilylation processes is 5.6 tons.⁴ Considering the above environmental and economic concerns, the development of recoverable and reusable earth-abundant metal catalysts⁵

should be an ultimate goal of present-day alkene hydrosilylation.

Heterogeneous catalysts have numerous advantages over homogeneous catalysts, including their durability, facile separation from the reaction mixture and subsequent reusability, and applicability in packed column reactors and multi-step flow reactors. Accordingly, some heterogeneous base metal catalysts for alkene hydrosilylation have been reported.^{6–8} However, these catalysts still suffer from instability in air, ⁶ low reusability due to metal leaching, ⁷ and/or difficult catalyst separation due to their colloidal nature.⁸ Therefore, the development of earth-abundant metal catalysts with high stability, easy separation, and high reusability is of considerable interest. Herein, we report that cobalt ions doped into the TiO₂ surface lattice (denoted as Co/TiO₂) was successfully synthesized by hydrogen (H₂) treatment method. The Co/TiO₂ catalyst has uniquely high stability and showed high activity for the hydrosilylation of various alkenes under solvent-free conditions. The Co/TiO2 catalyst was recoverable from the reaction mixture by simple filtration and reusable without metal leaching.

Results and discussion

Co/TiO₂ was prepared as follows. TiO₂ was soaked in an aqueous solution of Co $(NO_3)_2$. After stirring for 2 min, the mixture was adjusted to pH 10.0 with aqueous NaOH solution and then stirred at room temperature in air for 6 h. 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

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and then treated under H_2 at atmospheric pressure and 250 °C for 2 h (H_2 treatment) to give Co/TiO₂ as a pale green powder.

We initially investigated the catalytic activity of Co/TiO₂ in the hydrosilylation of 1-octene (1) with dimethylphenylsilane (2) under solvent-free conditions at 100 °C. Co/TiO₂ efficiently promoted this hydrosilylation, affording corresponding organosilicon product dimethyl(1-octyl)phenylsilane (3) in 93% yield without any byproduct formation (Table 1, entry 1). Co/TiO₂ without H₂ treatment also showed activity but gave lower yield of 3 compared with H₂-treated Co/TiO₂ (Table 1, entry 2). Co species immobilized on various supports prepared in a similar manner to Co/TiO2 were also tested in the hydrosilylation. Only Co/hydroxyapatite achieved a low yield of 3, while other Co catalysts, such as Co/Al₂O₃, Co/CeO₂, Co/SiO₂, and Co/MgO, showed almost no activity (Table 1, entries 3–7). Neither bulk CoO nor TiO₂ showed any catalytic activity (Table 1, entries 8 and 9). Next, metal effect on the hydrosilylation of 1 was investigated using TiO₂-supported base metals. Interestingly, Co/TiO₂ showed the highest activity among the TiO₂-supported base metals, including Ni/TiO₂, Fe/TiO₂, and Cu/TiO₂ (Table 1, entries 10–12). These results showed that Co/TiO2 exhibited high activity, and the combination of Co and TiO₂ induced specific catalysis among the supported base metals. To the best of our knowledge, this is the first example of a heterogeneous Co catalyst for alkene hydrosilylation.

The substrate scope of the Co/TiO₂-catalyzed hydrosilylation

Table 1 Solvent-free hydrosilylation of 1 with 2 using heterogeneous base metal catalysts^a

Ph Me-Si-H + Me 2	C ₆ H ₁₃ Catalyst (M: 1 mol%)	− Me Me Si 3
entry	catalyst	yield (%) ^b
1	Co/TiO ₂	93
2 ^{<i>c</i>}	Co/TiO ₂	73
3	Co/hydroxyapatite	32
4	Co/Al ₂ O ₃	<1
5	Co/CeO ₂	<1
6	Co/SiO ₂	<1
7	Co/MgO	<1
8 ^{<i>d</i>}	CoO	<1
9 ^e	TiO ₂	<1
10	Ni/TiO ₂	69
11	Fe/TiO ₂	66
12	Cu/TiO ₂	16

^{*a*}Reaction conditions: catalyst (0.12 g), dimethylphenylsilane (3.6 mmol), 1-octene (3 mmol), Ar. ^{*b*}Determined by NMR spectroscopy using biphenyl as an internal standard. ^{*c*}Without H₂ treatment. ^{*d*}CoO (0.10 g). ^{*c*}TiO₂ (0.12 g)

under solvent-free conditions was investigated, as summarized in Table 2. Base metal catalysts are known to officiable ineffective for hydrosilylation using tertiary silanes.⁹ In contrast, Co/TiO₂ showed high efficiency in the hydrosilylation of various alkenes with **2**, affording the corresponding products without any side reactions, such as alkene isomerization and Markovnikov-type hydrosilylation. In fact, the catalytic performance of the Co/TiO₂ catalyst was superior to that of the traditional Co carbonyl cluster catalyst $[Co_2(CO)_8]^{10}$: Co/TiO₂ gave a 90% yield with >99% selectivity for **3** from the hydrosilylation of **1** with **2** at 40 °C for 14 h, while $[Co_2(CO)_8]$ gave a low yield of **3** (32%) together with the formation of alkene isomerization product 2-octene in 57% yield. Interestingly, Co/TiO₂ was active toward alkenes bearing a hydroxyl, which was not tolerated by previously reported Ni¹¹ and Fe¹² catalysts (Table 2, entry 6). Other alkenes containing amide and

Table 2 Co/TiO₂-catalyzed hydrosilylation of various alkenes under solvent-free conditions^a

R ₂ -	$\begin{array}{cccc} R_1 & & & \\ R_2 - Si - H & + & & \\ R_3 & & & \\ \end{array} \xrightarrow{Catalyst (Co : 1 mol\%)} & & \\ R_2 - Si & & \\ R_3 & & & \\ \end{array} \xrightarrow{R_1} \\ R_3 & & & \\ \end{array}$						
entry	hydrosilane	alkene	temp. (°C)	time (h)	conv. (%) ^{b,c}	yield (%) ^b	
1	Me ₂ PhSiH	(CH ₂) ₅ CH ₃	100	0.5	94	93	
2	Me ₂ PhSiH	(CH ₂) ₁₃ CH ₃	100	1	>99	92	
3	Me₂PhSiH	\sim	40	30	96	91	
4	Me ₂ PhSiH		100	8	92	92	
5 ^d	Me ₂ PhSiH	Ph Ph	100	36	95	90	
6 ^{<i>d</i>}	Me ₂ PhSiH	∕∕ОН	100	4	95	92	
7 ^e	Me ₂ PhSiH	CH ₂₎₈ 0/0 −	160	18	90	85 ^f	
8 ^g	Me₂PhSiH	<i>⊳</i> N	160	24	99	88 ^f	
9	Me ₂ PhSiH	/─_Si─_	40	36	94	92	
10	Me₂PhSiH	OEt I Si-OEt I OEt	150	36	97	84	
11 ^h	$PhSiH_3$	(CH ₂) ₅ CH ₃	120	4	89	83	
12 ^h	Ph_2SiH_2	(CH₂)₅CH₃	160	6	90	80	
13	Cl₃SiH	(CH ₂) ₅ CH ₃	160	2	<1	0	
14	(MeO)₃SiH	(CH ₂) ₅ CH ₃	160	2	<1	0	

^oReaction conditions: Co/TiO₂ (0.12 g), hydrosilane (3.6 mmol), alkene (3 mmol), Ar. ^bDetermined by NMR spectroscopy using biphenyl as an internal standard. ^cAlkene conversion. ^dCo/TiO₂ (0.18 g). ^eAlkene (0.6 mmol). ^fIsolated yield. ^gAlkene (0.3 mmol). ^hHydrosilane (6 mmol).

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Fig. 1 Recycling experiments of Co/TiO $_{2}$ in hydrosilylation of 1 with 2.



Fig. 2 Hot filtration experiment of Co/TiO $_2$ in hydrosilylation of 1 with 2.

ester groups were also good substrates to give the desired products (entries 7 and 8). Co/TiO₂ also promoted the hydrosilylation of primary and secondary silanes with **1** (entries 11 and 12). On the other hand, alkoxyhydrosilane and trichlorohydrosilane were inactive in the Co/TiO₂-catalyzed hydrosilylation (entries 13 and 14).

After the catalytic reaction, Co/TiO_2 was easily recovered from the reaction mixture by filtration and then reused without any loss of efficiency (Fig. 1). To determine whether the hydrosilylation proceeded heterogeneously, Co/TiO_2 was removed from the reaction mixture by hot filtration when the yield of **3** was ca. 40% (Fig. 2). Further treatment of the resulting filtrate under similar reaction conditions did not afford any products, clearly showing that hydrosilylation proceeded on the Co/TiO_2 surface. On the other hand, the yield of **3** continued to rise after removing Co/TiO_2 without H₂ treatment, which indicated that leaching of Co ions from Co/TiO_2 occurred during the reaction (see Fig. S1, ESI). These results clearly show that H₂ treatment of Co/TiO_2 plays a crucial role in providing high durable catalyst.

The practicality of the Co/TiO₂ catalyst on a preparative scale was investigated with experiment on 30 mmol scale of **1** (Scheme 1). The corresponding product was obtained in 92% isolated yield (6.8 g) which provides the basis for large-scale implementation of Co/TiO₂-catalyzed hydrosilylation reactions. Furthermore, Co/TiO₂ promoted the hydrosilylation of **1** with **2** in air, demonstrating the high stability of Co/TiO₂ (Scheme 2). This is the first report of a heterogeneous base metal catalyst operating in air.





Scheme 2 Co/TiO₂-catalyzed hydrosilylation of **1** with **2** in air.

To gain insights into the unique catalysis with high stability of Co/TiO₂, Co/TiO₂ was characterized using several methods. Powder X-ray diffraction (XRD) measurements showed that the diffraction pattern of Co/TiO₂ was similar to that of the parent TiO₂ and no diffraction peaks derived from crystalline Co oxides, such as CoO and Co₃O₄, were observed (see Fig. S2, ESI). The transmission electron microscopy (TEM) image of Co/TiO2 showed that no recognizable Co aggregates were formed (detection limit, ~1 nm) (see Fig. S3, ESI). These results suggested that Co/TiO₂ contained subnanometer-scale Co species that were highly dispersed on TiO₂. The atomic-scale structure of the Co species in Co/TiO₂ was then investigated using Co K-edge X-ray absorption analysis (Fig. 3). The X-ray absorption near-edge structure (XANES) spectrum of Co/TiO₂ showed that the edge energy value of Co/TiO₂ was consistent with that of CoO (Fig. 3A (a) and (b)). The Fourier transform (FT) of the k³-weighted Co K-edge extended X-ray absorption fine structure (EXAFS) spectrum of Co/TiO₂ showed two main peaks at around 1.8 and 2.5 Å (Fig. 3B (a)). These peak positions were similar to but different from those of bulk CoO (Fig. 3B (b)). Furthermore, the intensities of these peaks were much lower than those of reference CoO, suggesting the formation of very small Co species on TiO₂. The inverse FT of these peaks was well fitted to Co-O, Co-Co, and Co-Ti shells (Table 3). The Co-O distance (2.02 Å) was shorter than that of bulk CoO (reference sample) and similar to that of Ti-O (1.94-2.05 Å) (see Table S1, ESI), indicating that Co ions entered the lattice of TiO_2 to form a solid solution. On the other hand, the curve fitting results of Co/TiO₂ without H₂ treatment suggested that these peaks were well fitted to Co-O and Co-Co shell and no formation of Co-Ti bond. These results clearly showed the H₂ treatment was crucial for the formation of the solid solution of Co in TiO₂.

The formation of a Co solid solution state on the TiO₂ surface was further investigated by ultraviolet/visible (UV–Vis) spectroscopy (see Fig. S4, ESI). UV–Vis spectrum of Co/TiO₂ without H₂ treatment has three absorption peaks in the range of 200–1000 nm. The strong absorption below 400 nm was attributed to TiO₂. Another two broad peaks around 460 nm and 700 nm in the visible light region were assigned to the adsorption of low-spin Co³⁺ in octahedral sites and Co³⁺ \rightarrow Co²⁺ charge transfer transition.¹³ After H₂ treatment, the two peaks in the visible light region disappeared and a new peak around 620 nm appeared. This newly generated absorbance peak is from the Co²⁺ \rightarrow Ti⁴⁺ charge-transfer transition

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Fig. 3 (A) Co K-edge XANES spectra of (a) Co/TiO₂, (b) CoO, (c) Co/TiO₂ without H₂ treatment, and (d) Co₃O₄; (B) Co K-edge EXAFS spectra of (a) Co/TiO₂, (b) CoO, (c) Co/TiO₂ without H₂ treatment, and (d) Co₃O₄.

Table 3 Results of curve-fitting analysis of Co K-edge EXAFS

	shell	CN	R (Å)	DW (Å) ^a
	Co-O	5.4	2.02	0.07
Co/TiO ₂ (H ₂ treatment)	Co–Co	2.8	3.02	0.07
	Co–Ti ^b	2.9	3.06	0.07
	Co–O	6.0	2.13	0.07
600	Co–Co	12.0	3.01	0.07
Co/TiO ₂	Co-O	3.8	1.92	0.08
(without H ₂ treatment)	Co–Co	2.2	2.88	0.08
	Co–O	6.0	1.93	0.08
CO_3O_4	Co–Co	6.0	2.87	0.08

^aDebye–Waller factor. ^bTheoretical value

that resulted from the formation of an ilmenite $CoTiO_3$ species, confirming the formation of a solid solution of $CoTiO_3$ species on the TiO₂ surface.¹⁴ The high stability and reusability of Co/TiO₂ in alkene hydrosilylation can be explained by the strong interaction between Co and TiO₂ resulting from the formation of CoTiO₃ species on the TiO₂ surface.

Conclusions

In conclusion, we have developed an easily recoverable and reusable heterogeneous base metal catalyst. A newly synthesized Co ion-doped TiO_2 by H_2 treatment method was active and selective for alkene hydrosilylation under solvent-free conditions. After the reaction, the Co/TiO₂ catalyst was recovered from the reaction mixture and reused without any loss of activity. This catalyst also showed high stability in the hydrosilylation, even in air for the first time. The detailed characterization of Co/TiO₂ showed that Co ions were doped

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into the TiO₂ lattice to form CoTiO₃ species on the I_1 in O_2 is ufface by the H₂ treatment. The strong interaction between Co and TiO₂ in the solid solution led to the high stability and reusability of Co/TiO₂ in alkene hydrosilylation.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- (a) L. N. Lewis, J. Stein, Y. Gao, R. E. Colborn and G. Hutchins, *Platin. Met. Rev.*, 1997, **41**, 66; (b) I. Ojima, *In the Chemistry of Organic Silicon Compounds*, ed. S. Patai and Z. Rappoport, Wiley Interscience, New York, 1989, 1479; (c) B. Marciniec, *Hydrosilylation: A Comprehensive Review on Recent Advances*. Springer, Berlin, 2009.
- For homogeneous precious metal catalysts, see: (a) I. E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant and J. P. Declercq, *Science*, 2002, **298**, 204; (b) O. Buisine, G. Berthon-Gelloz, J. F. Brière, S. Stérin, G. Mignani, P. Branlard, B. Tinant, J. P. Declercq and I. E. Markó, *Chem. Commun.*, 2005, 3856; (c) M. V. Jiménez, J. J. Pérez-Torrente, M. I. Bartolomé, V. Gierz, F. J. Lahoz and L. A. Oro, *Organometallics*, 2008, **27**, 224; (d) L. Busetto, M. C. Cassani, C. Femoni, M. Mancinelli, A. Mazzanti, R. Mazzoni, R. Mazzoni and G. Solinas, *Organometallics*, 2011, **30**, 5258; (e) J. L. Speier, J. A. Webster and G. H. Barnes, *J. Am. Chem. Soc.*, 1957, **79**, 974; (f) B. D. Karstedt, General Electric Company, US Pat., US3775452 (A), 1973.
- For heterogeneous catalysts based on precious metals, see:
 (*a*) K. Motokura, K. Maeda and W. J. Chun, *ACS Catal.*, 2017,
 7, 4637; (*b*) X. Cui, K. Junge, X. Dai, C. Kreyenschulte, M. M. Pohl, S. Wohlrab, F. Shi, A. Brückner and M. Beller, *ACS Cent. Sci.*, 2017, 3, 580.
- 4 A. J. Holwell, *Platin. Met. Rev.*, 2008, **52**, 243.
- 5 For homogeneous base metal catalysts, see: (a) A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis and J. G. P. Delis, *Science*, 2012, **335**, 567; (b) L. B. Junquera, M. C. Puerta and P. Valerga, *Organometallics*, 2012, **31**, 2175; (c) C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix and P. L. Holland, *J. Am. Chem. Soc.*, 2015, **137**, 13244; (d) J. H. Docherty, J. Peng, A. P. Dominey and S. P. Thomas, *Nat. Chem.*, 2017, **9**, 595; (e) C. Wang, W. J. Teo and S. Ge, *ACS Catal.*, 2017, **7**, 855; (f) M. Y. Hu, Q. He, S. J. Fan, Z. C. Wang, L. Y. Liu, Y. J. Mu, Q. Peng and S. F. Zhu, *Nat. Commun.*, 2018, **9**, 221.
- L. Cao, Z. Lin, F. Peng, W. Wang, R. Huang, C. Wang, J. Yan,
 J. Liang, Z. Zhang, L. Long, J. Sun and W. Lin, *Angew. Chem. Int. Ed.*, 2016, 55, 4962.
- 7 (a) W. Jondi, A. Zyoud, W. Mansour, A. Q. Hussein and H. S.
 Hilal, *React. Chem. Eng.*, 2016, 1, 194; (b) H. S. Hilal, M. A.
 Suleiman, W. J. Jondi, S. Khalaf and M. M. Masoud, *J. Mol. Catal. A: Chem.*, 1999, 144, 47.

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- Published on 31 July 2019. Downloaded by KEAN UNIVERSITY on 7/31/2019 9:01:08 AM.
- (a) R. Azuma, S. Nakamishi, J. Kimura, H. Yano, H. Kawasaki, T. Suzuki, R. Kondo, Y. Kanda, K. Shimizu, K. Kato and Y. Obora, *ChemCatChem*, 2018, **10**, 2378; (b) I. Buslov, F. Song and X. Hu, *Angew. Chem. Int. Ed.*, 2016, **55**, 12295.
- 9 A. D. Ibrahim, S. W. Entsminger, L. Zhu and A. R. Fout, *ACS Catal.*, 2016, **6**, 3589.
- (a) A. J. Chalk and J. F. Harrod, J. Am. Chem. Soc., 1965, 87, 1133 (b) N. Chatani, T. Kodama, Y. Kajikawa, H. Murakami, F. Kakiuchi, S. Ikeda and S. Murai, Chem. Lett., 2000, 29, 14.
- 11 I. Buslov, J. Becouse, S. Mazza, M. Montandon-Clerc and X. Hu, *Angew. Chem. Int. Ed.*, 2015, **54**, 14523.
- D. Peng, Y. Zhang, X. Du, L. Zhang, X. Leng, M. D. Walter and Z. Huang, J. Am. Chem. Soc., 2013, 135, 19154.
- 13 (a) Z. Shi, L. Lan, Y. Li, Y. Yang, Q. Zhang, J. Wu. G. Zhang and X. Zhao, ACS Sustainable Chem. Eng., 2018, 6, 16503; (b) L. Lan, Z. Shi, Q. Zhang, Y. Li, Y. Yang, S. Wu and X. Zhao, J. Mater. Chem. A., 2018, 6, 7194.
- (a) M. W. Li, X. M. Gao, Y. L. Hou and C. Y. Wang, J. Nano-Electron. Phys., 2013, 5, 3022; (b) R. Ye, H. Fang, N. Li, Y.
 Wang and X. Tao, ACS Appl. Mater. Inter., 2016, 8, 13871.

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