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Introduction

During the last few decades, noble metal-based organometallic and heterogeneous catalysts have been proven to be effective for a large number of organic reactions. One area of recent progress is the oxidation of alcohols to carbonyl compounds.¹⁻⁴ To meet environmental and economical acceptability, much effort has been devoted to develop heterogeneous catalysts, mainly based on noble metals¹⁻⁴ (such as Pd,⁵ Ru,^{6,7} Pt,⁸ and Au^{9,10}) which are highly effective for the aerobic oxidation of alcohols. Non-noble metal based heterogeneous catalysts also catalyze the aerobic oxidation of alcohols,1-3,11-16 but their efficiencies are generally lower than the noble metal catalysts in terms of activity and substrate scope. From the viewpoint of atom efficiency and safety of the reaction, an oxidant-free catalytic dehydrogenation of alcohols to carbonyl compounds and molecular hydrogen is ideal. This process is also of current interest as a potential method for hydrogen production from biomass products.^{17,18} Several systems for the dehydrogenative oxidation of alcohols using homogeneous Rh,¹⁹ Ru,²⁰⁻²⁵ and Ir²⁶⁻²⁸ catalysts were reported, but most of them suffer from requirements of acid or base additives, difficult catalyst

Heterogeneous cobalt catalysts for the acceptorless dehydrogenation of alcohols†

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A series of transition metal(M)-loaded TiO₂ catalysts (M/TiO₂) and Co-loaded catalysts on various support materials were prepared by an impregnation method, followed by *in situ* H₂-reduction at 400 °C, and tested for the acceptor-free oxidation of cyclododecanol in the liquid phase. Among the catalysts including noble metal catalysts, Co/TiO₂ showed the highest activity. In the presence of Co/TiO₂ (0.1–3 mol%) the dehydrogenation of various aliphatic secondary alcohols proceeded to afford the corresponding ketones. The catalyst was recoverable and was reused after the H₂-reduction treatment. Based on the spectroscopic characterization of the catalyst combined with the studies on the effect of the Co oxidation states on the catalytic activity, it is clarified that the surface metallic Co sites with electron deficiency are the catalytically active species.

> synthesis and manipulation, difficulties in catalyst reuse and high price. To overcome these problems, heterogeneous Ru,²⁹⁻³¹ Ag,^{32,33} and Au³⁴ catalysts have been recently developed, but these systems require the use of noble metals. From environmental and economic viewpoints, use of first-row transition-metal catalysts for this reaction is ideal. There are a few examples based on Ni,35-37 Co38 and Cu39 based heterogeneous catalysts, but they suffer from drawbacks such as high catalyst loading, a limited scope³⁵⁻³⁷ or high reaction temperature (200 °C).37,38 Although a few cobalt (Co) catalysts are known to be effective for the aerobic oxidation of alcohols,^{11–15} to the best of our knowledge, Co catalyzed acceptor-free oxidation of alcohols is not known. Our ongoing interest in the catalysis of supported metal nanoparticles (NPs) in organic synthesis40 motivated us to investigate possibilities of supported Co metal NPs as cheaper alternatives to the well established noble-metal catalysts. We report herein our findings on the Co-based heterogeneous catalyst for the acceptor-free alcohol dehydrogenation of secondary alcohols to ketones. The effect of Co oxidation state on the activity is studied to clarify the structure of active Co species.

Experimental

General

Commercially available organic and inorganic compounds (from Tokyo Chemical Industry, Wako Pure Chemical Industries, Kishida Chemical, or Mitsuwa Chemicals) were used without further purification. The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out

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with an Ultra ALLOY capillary column UA⁺-5 (Frontier Laboratories Ltd) or an Rtx-65 capillary column (Shimadzu) using nitrogen as the carrier gas.

Catalyst preparation

TiO₂ (JRC-TIO4, 50 m² g⁻¹), MgO (JRC-MGO-3, 19 m² g⁻¹), CeO₂ (JRC-CEO3, 81.4 m² g⁻¹), and SiO₂–Al₂O₃ (JRC-SAL-2, Al₂O₃ = 13.75 wt%, 560 m² g⁻¹) were supplied from Catalysis Society of Japan. γ -Al₂O₃ (with a surface area of 124 m² g⁻¹) was prepared by calcination of γ -AlOOH (Catapal B Alumina purchased from Sasol) for 3 h at 900 °C. SiO₂ (Q-10, 300 m² g⁻¹) was supplied from Fuji Silysia Chemical Ltd. Active carbon (296 m² g⁻¹) was purchased from Kishida Chemical. Hydroxides of Zr or Sn were prepared by hydrolysis of zirconium oxynitrate 2-hydrate or SnCl₄·6H₂O in distilled water by gradually adding an aqueous NH₄OH solution (1.0 mol dm⁻³), followed by filtration of the precipitate, washing with distilled water three times, drying at 100 °C for 12 h. Nb₂O₅·*n*H₂O was commercially supplied (CBMM). ZrO₂, Nb₂O₅, and SnO₂ were prepared by calcination of these hydroxides at 500 °C for 3 h.

Co₃O₄/TiO₂ was prepared by an impregnation method; a mixture of TiO₂ and an aqueous solution of Co(NO₃)₂·6H₂O was evaporated at 50 °C, followed by drying at 90 °C for 12 h and calcination in air at 300 °C for 1 h. Before each catalytic experiment, a pre-reduced catalyst (Co/TiO₂) was prepared by in situ pre-reduction of Co₃O₄/TiO₂ in a glass (pyrex or quartz) tube under a flow of H_2 (20 cm³ min⁻¹) at the reduction temperature $(T_{\rm H_2})$ of 400 °C for 0.5 h. Co (5 wt%)-loaded CeO₂, ZrO₂, Nb₂O₅, SiO₂-Al₂O₃, SnO₂, SiO₂, and C were prepared by the impregnation method in the same manner as the preparation of Co/TiO₂. Al₂O₃- or MgO-supported Co (5 wt%) catalysts were prepared by the impregnation method, followed by drying at 90 °C for 12 h, and by in situ pre-reduction of the precursor under H₂ at 400 °C. TiO₂- or Al₂O₃-supported metal (Ni, Cu, Ru, Pd, Rh, Ag) catalysts with a metal loading of 5 wt% were prepared by the impregnation method in a similar manner to the preparation of Co/TiO2 using an aqueous solution of metal nitrates (Ni, Cu), RuCl₃, or an aqueous HNO₃ solution of Rh (NO₃)₃ and Pd(NO₃)₂. Au/TiO₂ synthesized by a deposition-precipitation procedure (Au = 1.5 wt%, average Au particle size = 3.6 ± 0.28 nm) was purchased from the World Gold Council and used in the catalytic experiment without any pretreatment.

Catalytic reactions

The catalysts, *e.g.*, Co/TiO₂ (Co loading = 5 or 10%), were prereduced to Co_3O_4/TiO_2 in the glass tube under a flow of H_2 (20 cm³ min⁻¹) at 400 °C for 0.5 h. After the pre-reduction, we carried out catalytic tests without exposing the catalyst to air as follows. The mixture of *o*-xylene (1 g), alcohol (1 mmol), and *n*-dodecane (0.5 mmol) was injected onto the pre-reduced catalyst inside a reactor (cylindrical glass tube) through a septum inlet, followed by filling with N₂. Then, the resulting mixture was stirred under reflux; the reaction temperature was *ca*. 144 °C and the heating temperature was 155 °C. Conversion and yields of products were determined by GC using *n*dodecane as an internal standard. Progress of the reaction was monitored by GC analysis of aliquots (*ca.* 0.05 g). The initial rate of the reaction was measured under the conditions where the conversion was below 40%. The products were identified by GC-MS equipped with the same column as GC and by comparison with commercially pure products. GC analysis of the gas phase product (H_2) was carried out by a Shimadzu GC-6A instrument with a TCD detector, molecular sieve 5A column and an Ar carrier.

Characterization

Temperature programmed reduction under H_2 (H_2 -TPR) was carried out with BELCAT (BELL Japan Inc.). The sample, Co_3O_4/TiO_2 (Co loading = 5 wt%, 20 mg), was mounted on a quartz tube and was heated with a temperature ramp-rate of 5 °C min⁻¹ in a flow of 5% H_2/Ar (20 cm³ min⁻¹). The effluent gas was passed through a trap containing MS4A to remove water, then through the thermal conductivity detector. The amount of H_2 consumed during the experiment was detected by a thermal conductivity detector.

X-ray diffraction (XRD) patterns of the powdered catalysts were recorded under ambient conditions with a Rigaku Mini-Flex II/AP diffractometer with Cu Kα radiation.

Co K-edge X-ray absorption measurements were performed in transmission mode at the BL01B1 in the SPring-8 (Hyogo, Japan, proposal no. 2012A1734). The storage ring energy was operated at 8 GeV with a typical current of 100 mA. The catalyst pre-reduced in a flow of 100% H_2 (20 cm³ min⁻¹) for 0.5 h at various temperatures was cooled to room temperature in the flow of H₂ and was sealed in cells made of polyethylene under N2, and then the XAFS spectrum was taken under ambient conditions. The analysis of X-ray absorption near-edge structures (XANES) and extended X-ray absorption fine structure (EXAFS) was performed using the REX version 2.5 program (RIGAKU). The Fourier transformation of the k^3 -weighted EXAFS oscillation from k space to r space was performed over the range 24-157 nm⁻¹ to obtain a radial distribution function. The inversely Fourier filtered data were analyzed with a usual curve fitting method in the k range of 24–157 nm^{-1} . The parameters for the Co-O and Co-Co shells were provided by the FEFF6. The number of free parameters for curve fitting can be estimated as $P_{\text{free}} = 2\Delta k \ \Delta R/\pi \approx 13$, indicating that we can model the EXAFS data with three shells.

IR spectra were obtained by use of a Jasco Fourier transform infrared (FT-IR) 4100 spectrometer equipped with an MCT detector at a 4 cm⁻¹ resolution. 64 scans were collected to obtain each spectrum. The real temperature of the sample was estimated from a calibration curve of temperatures measured inside and outside the IR cell. The catalyst precursor (Co₃O₄/ TiO₂) was pre-reduced under H₂ (20 kPa) at 500 °C for 0.5 h, followed by evacuation at the same temperature for 0.5 h. IR spectra of clean samples before CO adsorption experiments were measured under evacuation at -180 °C and were used as background spectra. Subtracted IR spectra of adsorbed CO were measured after the sample was exposed to CO (500 Pa) at -180 °C. Table 1 Dehydrogenation of cyclododecanol^a

$\begin{array}{c} & \overset{OH}{\longrightarrow} & \text{cat.(1 mol\%)} \\ & & & & \\ 1.0 \text{ mmol} & 1 & 144 ^{\circ}\text{C}, 0.5 \text{ h} \end{array} \qquad $						
Entry	Catalyst	Conv. (%)	Yield (%)			
1 ^{<i>b</i>,<i>c</i>}	Co_2O_4	1	0			
$2^{b,c}$	CoO	-	1			
3 ^b	Copowder	20	12			
4^c	Co_3O_4/TiO_2	0	0			
5	Co/TiO ₂	39	37			
6^d	Co/TiO ₂ -air	1	1			
7	Co/Al_2O_3	15	15			
8	Co/CeO ₂	12	12			
9	Co/C	10	9			
10	Co/ZrO_2	9	9			
11	Co/SiO ₂	9	9			
12	Co/SiO ₂ -Al ₂ O ₃	9	2			
13	Co/SnO ₂	2	1			
14	Co/Nb ₂ O ₅	2	1			
15	Co/MgO	2	2			
16	Ni/TiO ₂	5	5			
17	Cu/TiO ₂	2	2			
18	Ag/TiO_2	2	2			
19	Pd/TiO ₂	5	5			
20	Ru/TiO ₂	3	3			
21^c	Au/TiO_2	11	11			
22	Ag/Al_2O_3	5	1			
23	Pd/Al_2O_3	4	1			
24	Rh/Al ₂ O ₃	4	4			
25	Ru/Al_2O_3	6	1			

^{*a*} Catalysts were pre-reduced in H₂ at 400 °C. Conversion and yields were determined by GC. ^{*b*} Catalyst = 10 mol%. ^{*c*} Catalysts were not pre-reduced. ^{*d*} Pre-reduced Co/TiO₂ was exposed to air at room temperature for 0.5 h.

Results and discussion

Catalyst screening

As summarized in Table 1, catalyst screening tests were first carried out to investigate the effect of various catalyst parameters on the catalytic activity for the dehydrogenation of cyclododecanol 1 to cyclododecanone 2 under the same reaction conditions (under N_2 in reflux conditions for 0.5 h). The metal-loaded catalysts, prepared by H2-reduction (400 °C) of metal oxide-loaded precursors, were used in the catalytic tests without exposing the catalyst to air. First, commercial Co compounds (10 mol% with respect to 1) and supported Co catalysts (1 mol%) were tested (entries 1-15). Among various support materials (MgO, Al₂O₃, CeO₂, ZrO₂, TiO₂, Nb₂O₅, SiO₂-Al₂O₃, SiO₂, SnO₂, C), the TiO₂-supported Co catalyst showed the highest yield of 2. Use of a large amount (10 mol%) of commercial Co compounds (entries 1-3) resulted in lower yield than Co/TiO₂. Co/TiO₂ with different Co loadings (1-20 wt%) were also prepared. Under the standard conditions shown in Table 1, the initial formation rate of 2 was measured under the conditions where the conversion of 1 was below 40%, and the turnover frequency (TOF) of these catalysts (based on the total number of Co atoms) was estimated. Fig. 1 shows the effect of Co loading on the TOF of Co/TiO2 catalysts for the



Fig. 1 Effect of Co loading of Co/TiO₂ (T_{H_2} = 400 °C) on TOF (based on the total number of Co atoms) for the dehydrogenation of cyclododecanol at 144 °C.

dehydrogenation of **1**. It is found that the loading of 5–10 wt% is the optimal value. A series of transition metal-loaded TiO_2 and noble metal-loaded Al_2O_3 catalysts were also tested for the dehydrogenation of **1**. Among the first-row transition metals (entries 5, 16, 17), Co/TiO₂ showed the highest yield of **2**. Notably, Co/TiO₂ showed higher yield than noble metal (Ag, Pd, Ru, Au)-loaded TiO₂ catalysts (entries 18–21) and noble metal (Ag, Pd, Rh, Ru)-loaded Al_2O_3 catalysts (entries 22–25). From the above results, TiO₂-supported Co (5 or 10 wt%) catalysts were found to be the optimal catalysts.

Structure of active Co species

Next, we studied the effect of oxidation states of Co on the activity. The catalytic results in Table 1 showed that the catalyst precursor (Co₃O₄/TiO₂) and commercial cobalt oxides (CoO and Co_3O_4) exhibited no activity when they were tested without H_2 -reduction pretreatment (entries 1, 2, 4). The TiO₂ support showed no activity even after the H2-reduction pretreatment. These results indicate that the support itself and cobalt oxides are completely inert. By changing the H2-reduction temperature ($T_{\rm H_2}$ = 300–600 °C) of Co₃O₄/TiO₂, we prepared a series of Co/TiO₂ catalysts with various Co oxidation states. Under the conditions shown in Table 1, the initial formation rates of 2 by these Co/TiO₂ catalysts were measured, and the TOF based on the total number of Co atoms was estimated. Fig. 2 shows the effect of T_{H_2} on the TOF. The TOF value steeply increased with $T_{\rm H_2}$ in the $T_{\rm H_2}$ range from 300 °C to 400 °C and then gradually decreased with further increase in $T_{\rm H_2}$.

The structure of Co species in a series of Co/TiO₂ catalysts reduced at various temperatures was studied by various characterization methods. The crystal phase was confirmed by XRD (Fig. 3). In the XRD pattern of the as-calcined sample, lines due to CoO and Co metal were absent, and a broad line due to Co_3O_4 was observed. Thus the sample is referred to as Co_3O_4 / TiO₂. The degree of reduction can be estimated from the TPR profile of Co_3O_4/TiO_2 under a flow of H₂/Ar (Fig. 4). Two different regions of reduction were observed: a lower temperature region (200–340 °C) and a higher temperature region located between 340 and 520 °C. XRD result shows that



Fig. 2 Effect of H₂-reduction temperature of Co/TiO₂ (Co = 5 wt%) on TOF (based on the total number of Co atoms) for the dehydrogenation of cyclododecanol at 144 °C and fractions of Co species (XANES analysis).



Fig. 3 XRD patterns of Co/TiO₂ (Co = 5 wt%) after H₂-reduction at various temperatures.



Fig. 4 H_2 -TPR profile of Co₃O₄/TiO₂ (Co = 5 wt%)

 H_2 -reduction at 300 °C resulted in complete reduction of Co_3O_4 to CoO. XRD patterns of the samples after the H_2 -reduction at higher temperatures (400–600 °C) resulted in complete reduction of CoO to metallic Co. These results suggest that the reduction of Co_3O_4 species in the catalyst precursor proceeds in a two step process, Co_3O_4 to CoO (at 200–340 °C) and CoO to Co (at 340–520 °C).

Fig. 5A shows the XANES spectra of representative samples, and Fig. 6 shows the XANES spectra of the Co/TiO₂ catalysts reduced at various temperatures. The XANES feature of Co3O4/ TiO_2 is nearly identical to that of Co_3O_4 , indicating that Co_3O_4 is the predominant Co species in the precursor. The spectral features gradually change with increase in the reduction temperature. The XANES spectrum of Co/TiO₂ reduced at 600 °C was nearly identical to that of Co foil. These results are qualitatively in agreement with the XRD and TRP results. Curvefitting analysis of XANES spectra is a well established method to quantify the ratio of several metal species in different oxidation states. As illustrated in Fig. S1 (in the ESI[†]), we obtained the fractions of the Co metal, CoO, and Co₃O₄ by the leastsquares fitting of the XANES spectrum of the Co/TiO₂ sample with a linear combination of XANES spectra of Co foil, CoO, and Co₃O₄/TiO₂. The fraction of metallic Co, CoO and Co₃O₄ species in each catalyst is plotted in Fig. 2 as a function of the reduction temperature. The result is qualitatively consistent with the XRD result except for the result of the sample reduced at 400 °C. The XRD result showed that the Co metal is the only Co species in this sample, but the XANES result showed the co-presence of CoO and the Co metal. This conclusion is supported by the following EXAFS result (Fig. 5B, Table 2). The EXAFS of the sample reduced at 400 °C consists of a Co-O shell (CN = 2.2 at R_{CO-O} of 2.13 Å) and a CO-Co shell (CN = 6.3 at $R_{\text{Co-Co}}$ of 2.49 Å). The Co–O distance is consistent with that of CoO, and the Co-Co distance is consistent with that of Co foil, indicating the co-presence of CoO species and the Co metal. The absence of CoO diffraction lines for this sample may be due to the presence of X-ray amorphous CoO species such as highly dispersed CoO species or ionic Co(II) species. Finally, a comparison between structural and catalytic results in Fig. 2 shows that the steep increase in the activity in the $T_{\rm H_2}$ range from 300 °C to 400 °C corresponds to the formation of metallic Co species. This suggests that the metallic Co species are the active species.

The catalyst named Co/TiO₂-air (Table 1, entry 6) was prepared by exposing the Co/TiO₂ catalyst, pre-reduced at 400 °C, to the ambient conditions for 0.5 h. This catalyst showed no activity. This suggests that the metallic Co atoms on the surface of Co particles are the active species and their re-oxidation by O₂ under ambient conditions results in the catalyst deactivation. This hypothesis is confirmed by the following results. Upon exposure to the ambient conditions, the percentage of CoO species in the Co/TiO₂ ($T_{H_2} = 400$ °C) sample, estimated by the H₂-TPR experiment, increased from 37% to 54%. EXAFS results (Table 2) showed that air-exposure of the Co/TiO₂ catalyst pre-reduced at 400 °C resulted in an increase in the Co-O coordination number from 2.2 to 3.4. These



Fig. 5 (A) XANES and (B) EXAFS Fourier transforms at Co K-edge for Co/TiO₂ (Co = 5 wt%) and reference compounds.



Fig. 6 Co K-edge XANES spectra of Co/TiO₂ (Co = 5 wt%) after H₂-reduction at various temperatures.

	5 ,		5		
Sample	Shell	\mathbf{N}^{a}	$R^b/ m \AA$	$\sigma^c/{ m \AA}$	$R_{\rm f}^{\ d}/\%$
Co ₃ O ₄ /TiO ₂	0	6.0	1.92	0.064	2.5
	Со	3.6	2.85	0.045	
	Со	5.9	3.34	0.064	
Co/TiO ₂	0	2.2	2.13	0.050	0.6
	Со	6.3	2.49	0.069	
Co/TiO2-air	0	3.4	2.10	0.094	1.8
	Со	5.2	2.52	0.094	
	Со	1.6	3.09	0.105	
Co foil	Со	11.7	2.49	0.075	0.7
CoO	0	4.9	2.14	0.083	2.0
	Со	8.8	3.00	0.069	
Co_3O_4	0	4.5	1.92	0.054	0.4
	Со	3.6	2.85	0.049	
	Со	5.1	3.35	0.057	
^a Coordination	numbers.	^b Bond	distance.	^c Debye–Waller	factor

Table 2 Curve-fitting analysis of Co K-edge EXAFS

^{*d*} Residual factor.

results indicate that metallic Co species on the surface of Co metal NPs are the active species and these Co species are reoxidized by O_2 under ambient conditions to yield inactive CoO species.

The presence of surface Co^0 species in the Co/TiO₂ catalyst (Co loading = 10 wt%) was confirmed by a CO adsorption IR study. IR spectra of adsorbed CO species on the catalyst after



Fig. 7 IR spectra of CO adsorbed on various catalysts at -180 °C: (a) TiO₂, (b) Co/TiO₂ (Co loading = 10 wt%, $T_{H_2} = 500$ °C), (c) Co/TiO₂ after re-oxidation in 20 kPa O₂ at room temperature.

H₂-reduction at 500 °C are shown in Fig. 7. Adsorption of CO on the reduced Co catalysts leads to the appearance of peaks in the region of 1800-2200 cm⁻¹ which can be attributed to adsorbed CO species on different sites. The intense peak at 2179 cm^{-1} can be due to the CO adsorbed on TiO₂ and oxidized Co species. In the spectrum of Co/TiO₂ bands in a range of 2000-2100 cm⁻¹ generally assigned to linearly adsorbed CO on metallic Co are observed, while those in a range of 1800-2000 cm⁻¹ due to bridge-type CO adsorption on large Co⁰ crystallites are nearly absent. For metal oxide-supported Co metal NPs, peaks centered around 2070 cm⁻¹ have been assigned to CO linearly adsorbed on metallic Co sites with electron deficiency $(Co^{\delta^+} \text{ sites})^{41-43}$ at the support interface or near unreduced cobalt ions. CO adsorbed on the ideal metal surface is expected to be observed at lower wavenumbers. The spectrum of Co/TiO₂ below 2079 cm⁻¹ shows an absorption maximum at 2070 cm⁻¹. Upon exposure to O₂ (20 kPa) at room temperature for 0.5 h, the band due to CO adsorbed on the $\operatorname{Co}^{\delta^+}$ sites disappeared. Combined with the result of catalytic tests, the result indicates that the surface metallic Co sites with electron deficiency are the catalytically active species.

OH $R_1 \qquad R_2$ 1 mmol O Co/TiO ₂ (x mol%) o-xylene (1 g), 144 °C R ₁ R_2 + H ₂								
Entry	Alcohol	Co (mol%)	t/h	Conv. (%)	Yield (%)			
1	Cyclooctanol	1	6	98	98			
2	1st reuse	1	6	100	95			
3	2nd reuse	1	6	99	99			
4	3rd reuse	1	6	95	95			
5	Cyclooctanol	0.2	6	97	97			
6^{b}	Cyclooctanol	0.1	48	88	88			
7	Cyclododecanol	0.2	24	96	96			
8	Cycloheptanol	3	24	78	78			
9	Cyclohexanol	1	24	67	64			
10	Cyclopentadecanol	3	24	92	90			
11	exo-Norborneol	0.5	24	96	96			
12	4-Octanol	0.5	24	98	96			
13	2-Octanol	1	12	85	78			
14	1-Octanol	1	24	12	10			
15^{c}	Benzylalcohol	1	24	19	8			

^{*a*} Co/TiO₂ (Co = 10 wt%) pre-reduced at 400 °C was used. Conversion and yields were determined by GC. ^{*b*} Solvent-free conditions: cyclooctanol (10 mmol) was heated at 155 °C in a flow of N₂ (10 mL min⁻¹) in the presence of Co/TiO₂ (Co = 5 wt%) pre-reduced at 400 °C. ^{*c*} T = 80 °C. Toluene (4% yield) was produced as a byproduct.

Catalytic properties

Next, we examined the catalytic properties of Co/TiO_2 (10 wt%) Co) under the conditions shown in Table 3. The dehydrogenation of cyclooctanol by Co/TiO₂ (1 mol%) for 6 h resulted in 98% yield of cyclooctanone. After 1 h of the reaction the yields of gas phase H_2 (27%) and cyclooctanone (29%) were nearly identical to the alcohol conversion (30%), indicating that H_2 was generated quantitatively. The reaction was completely terminated by a removal of the catalyst from the reaction mixture after 1 h; further heating of the filtrate for 5 h under the reflux conditions did not increase the yield. ICP analysis of the filtrate confirmed that the content of Co in the solution was below the detection limit. These results confirm that the reaction is attributed to the heterogeneous catalysis of Co/TiO₂. After the reaction, the catalyst was easily separated from the reaction mixture by centrifugation. The filtered catalyst was washed with acetone, followed by drying in air at 90 °C for 12 h, and by reducing in H_2 at 400 °C for 0.5 h. As shown in Table 3 (entries 2-4), the recovered catalyst was reused at least three times.44 In the low catalyst loading condition (Co = 0.2 mol%), the catalyst showed 97% yield of the product after 6 h corresponding to a TOF of 81 h^{-1} . Even under solventless conditions, the reaction with 0.1 mol% of the catalyst for 48 h resulted in 88% yield of the product, corresponding to the turnover number (TON) of 880. These values are higher than those for previous Co-based catalysts¹¹⁻¹⁵ for the liquid phase aerobic oxidation of alcohols.

The scope of the Co/TiO₂-catalyzed dehydrogenation of various alcohols is shown in Table 3. In the presence of Co/TiO₂ (0.2-3 mol%), various aliphatic secondary alcohols were

selectively converted to the corresponding ketones with good to high yields (64–96%). For example, *exo*-norborneol was converted to the corresponding ketone in 96% yield by 0.5 mol% of the catalyst, corresponding to a TON of 192. For the reaction of primary alcohols (benzylalcohol and 1-octanol), yields of the corresponding aldehydes were low (10–14%). To the best of our knowledge, this study represents the first example of acceptorfree oxidation of various secondary alcohols by a Co catalyst. It should be noted that the previous examples of the Co-based heterogeneous catalysts for the aerobic alcohol oxidation were effective for activated (benzyl) alcohols but not generally effective for less activated aliphatic alcohols.^{11–15} Therefore, this study represents the rare example of a Co-based catalyst effective for the oxidation of aliphatic secondary alcohols to ketones.

Conclusions

In summary, we have shown that TiO_2 -supported Co metal NPs heterogeneously catalyze the acceptor-free oxidation of secondary alcohols. The catalyst, readily prepared from commercial compounds, is easily recoverable and reused, and shows higher activity in the oxidation of less activated aliphatic alcohols than the previous Co-based catalysts. Studies on the structure–activity relationship showed that the surface metallic Co sites with electron deficiency are the catalytically active species.

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- 44 A Catalyst recycle experiment without re-activation treatment was also carried out for the reaction of cyclooctanol (t = 6 h) under the conditions in Table 3. Yields of cyclooctanone for the first and second reuse experiments were 95% and 5%, respectively. It is found that the re-activation treatment is necessary.