Abstract: Various decarbonylation reactions via oxidative addition of carbonyl compounds to metal catalysts can be applied to late-stage modification and have been actively studied to date; however, several inherent problems derived from the oxidative addition are difficult to be solved, such as toxic CO production, deactivation of catalysts by CO adsorption, intolerance of some functional groups, or air-sensitivity of catalysts. In this context, formal decarbonylation, which eliminates CO as other compounds without involving oxidative addition, is attractive but hardly reported, especially using heterogeneous catalysts. Herein, formal decarbonylation of diaryl 1,2-diketones to afford monoketones using CeO$_2$ as a reusable heterogeneous catalyst and O$_2$ in air as the terminal oxidant was developed, generating CO$_2$ as the only byproduct. The results revealed that the reaction was enabled by the synergistic catalytic effect of the Lewis acid–base pairs and redox properties in CeO$_2$.

Owing to the numerous carbonyl functionalities in carbonyl compounds, studies have been focusing on their decarbonylation as a new methodology for functional group transformation while preserving the carbon frameworks, and thus, decarbonylation can be applied to late-stage modification.$^{[1]}$ Recently, various carbonyl compounds underwent novel molecular transformations via decarbonylation, which generally proceeds via oxidative addition of coordinated carbonyl compounds to metal catalysts, carbon monoxide (CO) deinsertion, and reductive elimination to produce decarbonylated products followed by CO desorption to achieve the catalytic cycle (Scheme 1a).$^{[1a]}$ However, there are several inherent problems in decarbonylation via oxidative addition: (i) a stoichiometric amount of toxic CO is produced, (ii) The generation of CO causes deactivation of the metal catalysts in some cases due to its strong $\pi$-backdonation,$^{[2a-d]}$ (iii) some functional groups including halogens cannot be applied because of the competitive oxidative addition,$^{[2e]}$ and (iv) most of the reported catalytic systems required inert atmosphere because of the use of air-sensitive low-valent metal catalysts.$^{[1]}$ Additionally, despite the great potential of heterogeneous catalysts for developing environmentally friendly synthetic methodologies including facile product separation, catalyst reusability, and scale-up potential for continuous production, most reports on decarbonylation depended on homogeneous catalysts; the application of heterogeneous catalysts have been limited to decarbonylation of reactive carbonyl compounds such as aldehydes and acyl chlorides.$^{[3]}$

Scheme 1. Study background and overview.
Diaryl ketones are widely present in nature and pharmaceuticals, and utilized as versatile organic synthetic building blocks. There are many reports on diaryl ketone synthesis as represented by cross-coupling reactions using aryl halides, organometallics, and/or CO gas; however, prefunctionalization of substrates is indispensable, and a stoichiometric amount of base, excessive amounts of toxic CO gas, and/or harmful halogenated byproducts are problematic. On the other hand, diaryl ketone synthesis from diaryl 1,2-diketones without using prefunctionalized substrates or CO gas is potentially a green alternative to the aforementioned conventional ketone synthesis and provides more versatile methodologies applicable to late-stage modification based on the fact that diaryl 1,2-diketones also widely exist in natural products and useful organic materials and can be synthesized from different fundamental starting materials including ketones, aldehydes, alkenes, alkynes and so on (Scheme 1b). In spite of its utility, there are limited studies on the decarbonylation of diaryl 1,2-diketones to produce diaryl ketones. We previously reported the first practical diaryl 1,2-diketone decarbonylation via oxidative addition using a supported Au–Pd alloy nanoparticle catalyst. However, a stoichiometric amount of CO and considerable amount of biphenyl byproducts were inevitably produced during the process owing to the Pd-catalyzed oxidative addition step (Scheme 1c). Additionally, the catalyst was hardly reused due to the sintering of Au–Pd alloy nanoparticles and/or organic compound adsorption to cover the active sites.

Formal decarbonylation is a decarbonylation method from carbonyl compounds that does not involve oxidative addition and that eliminates CO as other compounds, which is possible to solve the aforementioned problems of direct decarbonylation derived from requirement of the oxidative addition step. In fact, formal diaryl 1,2-diketone decarbonylation has been developed via a benzilic acid rearrangement mainly using Cu catalysts, however, (super)stoichiometric amounts of oxidants, bases, and/or anilines were required for the reaction (Scheme 1c). Although there are studies on diaryl ketone formation from benzoin/benzil catalyzed by an Al2O3-based catalyst or using a high-temperature water system, they require high temperature (>300°C), which is difficult to apply to liquid-phase organic synthesis. To our knowledge, versatile formal decarbonylation of diaryl 1,2-diketones without using (super)stoichiometric amounts of reagents have not been reported. Also, there are no reports on heterogeneously catalyzed formal decarbonylation applicable to liquid-phase organic synthesis to date.

Herein, CeO2-catalyzed formal decarbonylation of a variety of diaryl 1,2-diketones to afford diaryl ketones with various substituents including halogen groups intact without any additives was conducted using O2 in air as the terminal oxidant and generating CO2 as the only byproduct (Scheme 1d). CeO2 worked as a heterogeneous catalyst and was reused several times with no fear of the aforementioned sintering of active species. A series of control experiments combined with characterization of the catalysts revealed that the present formal decarbonylation was achieved by the synergistic catalysis of CeO2: Lewis acid–base pairs synergistically catalyzed efficient benzilic acid rearrangement following by aerobic oxidative decarbonylation via redox of CeO2. Moreover, a tandem reaction starting from benzoins to produce diaryl ketones via aerobic oxidative dehydrogenation followed by formal decarbonylation using only the CeO2 catalyst was achieved.

First, the effect of metal oxide catalysts on the decarbonylation of diaryl 1,2-diketones was investigated using benzil 1a as the substrate under the reaction conditions listed in Table 1. Only when CeO2 was used, a high yield of the desired decarbonylated product benzophenone 2a was obtained (Table 1, entry 1). Other metal oxides, such as acidic metal oxides, basic metal oxides, and redox-active metal oxides (Table 1, entries 2–5, 6–8, and 9–12, respectively), hardly exhibited any catalytic effect on the reaction. The failure to detect the decarbonylated product 2a without using CeO2 (Table 1, entry 13) and the considerable decrease in its yield under Ar atmosphere (Table 1, entry 14) confirm the essential roles of CeO2 and O2 in the 1,2-diketone decarbonylation. The optimized reaction conditions (Table 1, entry 1) were determined after investigating the effect of solvents (Table S1), temperatures (Table S2), and atmospheres (Table S3).

The decarbonylation of 1a was immediately stopped after the hot filtration of CeO2 during the reaction (Figure S1). Moreover, Ce leaching into the reaction solution was hardly observed using inductively coupled plasma–atomic emission spectroscopy (ICP–AES) (Ce: 0.006% of Ce used for the reaction), indicating a heterogeneous catalysts process. CeO2 could be reused at least three times after filtration and washing with Et2O followed by drying in vacuo (Figure S2). Although the final 2a yields gradually decreased with the repeated use of the catalyst, the catalyst could be easily regenerated by calcination at 300 °C for 3 h under air atmosphere for removing adsorbed organic compounds (Figures S2, S3, and S4).

To clarify the reaction mechanism, control experiments were conducted. CeO2 was stirred with 1a at room temperature.

![Table 1. Effects of metal oxide catalysts on 1a decarbonylation](https://orcid.org/0000-0001-5504-4762 Content not peer-reviewed by ChemRxiv. License: CC BY-NC-ND 4.0)
(−25 °C) (CeO$_2$-1a), and its attenuated total reflection−infrared (ATR−IR) spectra were obtained. The mixture exhibited peaks around 1605, 1495, and 1445 cm$^{-1}$, corresponding to the asymmetric (1605 and 1495 cm$^{-1}$) and symmetric (1445 cm$^{-1}$) stretching bands, respectively, of the carboxylate adsorbents on the metal oxides (Figure 1a).[15,16] Thus, 1a is likely to be converted into benzoic acid (1a$'$) via benzoic-acid rearrangement on CeO$_2$. In fact, the three peaks were also observed in the ATR−IR spectra of CeO$_2$ stirred with 1a$'$ (CeO$_2$-1a$,'$ Figure 1a), and the 2a yield of the reaction starting from 1a$'$ was comparable to that of the reaction starting from 1a, confirming that 1a$'$ was a reaction intermediate (Scheme 2a, b). These results suggest that the proposed decarbonylation proceeded via benzoic-acid rearrangement of 1,2-diketones followed by decarbonylation to afford diaryl ketones. The 1a conversion and 2a production were suppressed in the presence of benzoic acid (PhCOOH) (Scheme 2c), whereas the 2a yield did not considerably decrease with 1a$'$ as the substrate under the same reaction conditions (Scheme 2d), indicating the involvement of benzoic-acid rearrangement catalyzed by the basicity of CeO$_2$. Since the formal decarbonylation slightly proceeded using CeO$_2$ under Ar atmosphere (Table 1, entry 14) and CO$_2$ was generated while CO was not (Figure S5), the oxidative decarbonylation step likely proceeds owing to the oxidizing ability of CeO$_2$ itself. In fact, when using CeO$_2$ reduced by sodium naphthalenide (CeO$_2$-NaNaph), of which the X-ray photoelectron spectra (XPS) indicated an increase in the Ce$^{3+}$/Ce$^{4+}$ ratio compared with that of purchased CeO$_2$ (CeO$_2$-fresh, Figures 1b and S6), the 2a production from 1a or 1a$'$ under Ar atmosphere hardly occurred (Scheme 2e, f). Moreover, the XPS spectrum of CeO$_2$ after being used in the formal decarbonylation of 1a under Ar atmosphere (CeO$_2$-used-Ar) indicated an increase in Ce$^{3+}$ compared with that of CeO$_2$-fresh (Figures 1b and S6), which confirmed that the oxidizing ability of CeO$_2$ contributed to the oxidative decarbonylation. To complete the catalytic cycle, O$_2$ should be involved in the reoxidation of Ce$^{4+}$ into Ce$^{4+}$. To confirm the role of O$_2$ in the reaction, formal 1a decarbonylation was conducted under $^{18}$O$_2$ atmosphere. Only under $^{18}$O$_2$ atmosphere, the ratio of $^{46}$CO$_2$ and $^{48}$CO$_2$ to $^{44}$CO$_2$ increased with the increase in the 2a yield (Figure 1c and Table S4), indicating that the catalyst regeneration occurring using O$_2$ via the Mars–van Krevelen mechanism.

The products of the formal 1a decarbonylation under $^{18}$O$_2$ atmosphere were observed by gas chromatography−mass spectrometry (GC−MS) to be $^{18}$O-labeled 1a and 2a as well as $^{48}$CO$_2$ (Figures 1d and S7), possibly because the O−atom exchange between the substrates and lattice oxygen occurs through a reverse nucleophilic-addition reaction from the lattice oxygen (blue color, Figure 1e). This suggests the involvement of the Lewis acid sites near the lattice oxygen (Lewis base sites) in the decarbonylation. The addition of 4-dimethylaminopyridine (DMAP), which acts as the Lewis base, also reduced the initial rate of the 1a formal decarbonylation (Figure S8).[18] Moreover, the difference between the symmetric and asymmetric stretching vibrations of the carboxylate adsorbents ($\Delta$as−s) at $\Delta$as−s = 50 cm$^{-1}$ and $\Delta$as−s = 160 cm$^{-1}$ in the ATR−IR spectra of CeO$_2$ stirred with 1a (Figure 1a) can be assigned to the bidentate carboxylates and bridged ones, respectively (Figure S9).[19] This observation confirmed the role of the Lewis acid sites on CeO$_2$ in carboxylate-intermediate stabilization. To further clarify the origin of the exceptional catalytic activity of CeO$_2$, the ATR−IR spectra of CeO$_2$-1a was compared with those of MgO, Nb$_2$O$_5$, and supports with classical Lewis pairs (CLPs) including Al$_2$O$_3$, TiO$_2$, and ZrO$_2$[19] after stirring with 1a at room temperature. The three peaks assignable to the carboxylate adsorbents in CeO$_2$-1a were not observed in the other metal oxide cases (Figure 1a), suggesting that the benzoic-acid rearrangement only occurs efficiently on CeO$_2$. Because the basicity of MgO is higher than CeO$_2$,[20] the Lewis acid sites on CeO$_2$ considerably contribute to the carboxyl group activation and intermediate stabilization. In contrast, Nb$_2$O$_5$ (with stronger acidic sites than CeO$_2$) did not catalyze the benzilic-acid rearrangement step. These results and the fact that metal oxides with Lewis acid and base sites reported to act as CLPs did not induce the rearrangement step show that the exceptional catalytic performance of CeO$_2$ is possibly due to the concerted
activation of diaryl 1,2-diketones by surface-defect-induced Lewis acid-base pairs like heterogeneous frustrated Lewis pairs (FLPs) composed of lattice oxygen as the Lewis base and Ce$^{3+}$ as the Lewis acid.[21,22]

Therefore, the following reaction mechanism was proposed (Figure 1f): (i) lattice oxygen addition to the diaryl 1,2-diketones via carbonyl group activation by Ce$^{3+}$ Lewis acid sites to form nucleophilic adducts on CeO$_2$ (intermediate A),[20,23] (ii) benzilic-acid rearrangement of intermediate A to afford the corresponding carboxylate coordinated to the Lewis acid sites on CeO$_2$ in a bidentate/bridging manner (intermediate B), (iii) oxidative decarboxylation to form diaryl ketones and CO$_2$ by reducing Ce$^{4+}$.

Figure 1. Characterization of the catalysts and the proposed reaction mechanism: (a) ATR–IR spectra of metal oxides stirred with 1a, (b) XPS spectra of CeO$_2$, (c) gas-phase analyses under $^{16}$O$_2$ or $^{18}$O$_2$ atmosphere, (d) ratios of $^{18}$O-labeled compounds under $^{18}$O$_2$ atmosphere, (e) proposed mechanism of O-atom exchange between the carbonyl compounds and CeO$_2$, and (f) proposed mechanism of the formal 1,2-diketone decarbonylation.
The exceptional catalytic performance of CeO$_2$–mesitylene (2 mL) at 150°C in open air for 24 h with respect to the decarbonylation of iodo benzil, exhibited good tolerance without producing benzils. The halogenated yields were 72% and 68%, respectively. Halogenated diaryl ketones, regardless of the positions of the methyl groups, underwent formal decarbonylation to afford diaryl ketones. The methyl withdrawing group was also found to efficiently and heterogeneously catalyze the formal decarbonylation of diaryl 1,2-diketones with wide substrate scope and functional group tolerance and could be reused several times. The exceptional catalytic performance of CeO$_2$ is due to its redox properties and Lewis acid–base pairs. This work provides a novel methodology for additive-free and environmentally friendly diaryl ketone synthesis and enables the exploration of new organic synthetic reactions by utilizing characteristics specific to heterogeneous catalysts.

**Supporting Information**

The authors have cited additional references within the Supporting Information.[81–112]

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metal species, such as Cu, Rh, and Pd, reported to catalyze the ICP-MS reaction could not be applied to diaryl 1,2-dehydrogenations. Studies reported, but these systems demonstrated limited substrate scopes and a high level of selectivity for the formal decarbonylation, whereas DMAP only decreases the production rate of 1a. Moreover, conjugate PhCOOH bases can coordinate to metal oxygen complexes (CeO₂), used for the formal decarbonylation. The observed peaks correspond to the 1,2-dehydrogenation reaction products. In the benzilic-acid rearrangement mechanism, Lewis base sites are directly involved in the rearrangement step, whereas Lewis acid sites act as a cocatalyst. Moreover, conjugate PhCOOH bases can coordinate to Lewis acid sites, resulting in completely suppressing the formal 1a to 2a decarbonylation, whereas DMAP only decreases the production rate of 2a.


Even at the surface of the fresh CeO$_2$, the XPS spectrum around the Ce 3d region revealed a considerable presence of Ce$^{3+}$ species (31%) (Figure S6).

The limitations of the proposed formal decarbonylation are summarized in Scheme S2.


[24] The limitations of the proposed formal decarbonylation are summarized in Scheme S2.


We report CeO₂-catalyzed formal decarbonylation of diaryl 1,2-diketones to afford diaryl ketones by utilizing molecular oxygen as the terminal oxidant without any additives, which was enabled by the synergistic catalysis of the Lewis acid–base pairs and redox properties in CeO₂. Additionally, a tandem reaction starting from benzoins to produce diaryl ketones via oxidative dehydrogenation followed by formal decarbonylation is also highlighted.