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CeO₂ as a versatile and reusable catalyst for transesterification of esters with alcohols under solvent-free conditions†

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 CeO_2 acted as an efficient and reusable heterogeneous catalyst for transesterification of esters with alcohols under the solvent-free conditions at 160 °C. Among the 11 kinds of metal oxides, CeO_2 is the most suitable catalyst in terms of catalytic activity, leaching-resistance and reusability. This catalytic system tole-rates various esters and alcohols, and valuable esters such as heteroaromatic esters and benzyl benzoates are produced, demonstrating a practical utility of the system. On the basis of kinetic analysis and *in situ* IR studies of adsorbed species, a reaction mechanism is proposed, in which proton abstraction of alcohol by a Lewis base site of CeO_2 to yield alkoxide species is the rate-limiting step.

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Introduction

The ester moiety presents one of the most ubiquitous functional groups in chemistry such as in polymers, drugs and biologically relevant compounds, playing an important role in biology and serving both as a key intermeditate and/or a protecting group in organic transformation.¹ Traditionally esters were synthesized from carboxylic acids and alcohols with highly reactive acylating reagents such as acyl halides and acid anhydrides. In view of atom-economy, the catalytic transesterification of esters, especially methyl esters, with higher and/or functionalized alcohols is desirable for the synthesis of diverse esters. In addition, the transesterification of esters is more advantageous than the condensation reaction of carboxylic acids with alcohols owing to the ease of handling and high stability of esters, and their high solubility in most organic solvents.^{1,2} In general, the transesterification reaction is catalyzed by protic acids,3 Lewis acids,4 and basic catalysts such as DMAP,⁵ metal alkoxides,⁶ or metal carbonates.⁷ Recently, various efficient homogeneous catalysts such as Lewis acids including Zn clusters,⁸ Sn,⁹ Ti,¹⁰ Zr,¹¹ Fe,¹² Pd,¹³ La¹⁴ or Ce¹⁵ metal complexes, ammonium triflates,¹⁶ N-heterocyclic carbenes,17 Zn-I2,18 I2,19 zwitterionic salts20 have been developed. However, these homogeneous catalysts suffer from drawbacks such as difficulties in catalyst reuse and products separation. Solid bases²¹ (mostly CaO or MgO-based oxides²²) and solid acids (acidic resins,²³ zeolites,²⁴ SO₄²⁻-ZrO₂,²⁵ polyoxometalates,²⁶ MoO₃/TiO₂²⁷ or clays²⁸) were reported as heterogeneous catalysts for the preparation of biodiesel, monoglyceride, or β -ketoester. Among them, Ca-based catalysts are the most effective catalysts. However, they were not stable during the reaction and suffered from tremendous leaching of Ca species into the reaction media.^{22b} To suppress the metal leaching, CaO-CeO₂^{22a,b} and CaO-La₂O₃^{22a} were developed, but these systems still suffer from metal leaching, narrow substrate scope and necessity of solvent. To the best of our knowledge, there are no reports on heterogeneous catalysts for transesterification with wide substrate scope and high stability (leaching-resistance and reusability). A versatile and reusable heterogeneous catalyst applicable for various methyl esters and alcohols should be developed.

Our research group reported a series of CeO_2 -catalyzed organic reactions in a liquid phase:²⁹ substrate-specific hydration of nitriles,^{29b} one-pot esterification of nitriles with alcohols,^{29c} one-pot *N*-alkyl amidation of nitriles with amines^{29d} and transamidation of amides with amines.^{29e} In these reports, we demonstrated that the Lewis acid–base pair site on CeO₂ is a catalytically important species. We report herein that CeO₂ acts as a versatile, reusable and leaching-resistant catalyst for solvent-free transesterification of esters with alcohols. Kinetic and *in situ* IR studies will show a possible mechanism, in which the Lewis base site of CeO₂ plays an important role.

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Experimental section

General

The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out using N₂ and He as the carrier gas, respectively, with an Ultra-ALLOY capillary column UA^+ -5 (Frontier Laboratories Ltd). All the chemicals for organic reactions were analytic reagents from chemical products corporation and were used without further purification.

Catalyst

CeO₂ (JRC-CEO3, surface area = 81 m² g⁻¹) pre-calcined at 600 °C before being supplied from the Catalysis Society of Japan was used as a standard catalyst. Other metal oxides, commercially available or supplied from the Catalysis Society of Japan, were calcined at 500 °C for 3 h. These metal oxides were stored under air and used without any pretreatments.

Typical procedures for transesterification

A typical procedure for transesterification of methyl benzoate with *n*-octyl alcohol is as follows. For the catalytic tests in Table 1, CeO₂ (50 mg, 11.6 mol% Ce with respect to methyl benzoate) was added to the mixture of methyl benzoate (2.5 mmol), *n*-octyl alcohol (3.0 mmol) in a reaction vessel equipped with a condenser under N₂ (using a trap to remove MeOH). For the other catalytic tests, the reaction was carried out in a reaction vessel without a condenser under an open system in air; the small amounts of alcohol as a byproduct can be released out of the reactor *via* a needle inserted into the rubber on the top of the vessel. The mixture was stirred at 160 °C. The reaction mixture was analyzed by GC. Conversion and yield of the products were determined based on methyl

Table 1 Transesterification by various metal oxides^a

	DMe + HO	Meta	al oxide	о ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
Catalyst	$S_{\rm BET} \left({{{\rm{m}}^2}\;{{\rm{g}}^{ - 1}}} ight)$	<i>t</i> (h)	Yield (%)	$V^b \text{ (mmol h}^{-1} \text{ m}^{-2}\text{)}$
CeO ₂	81	0.08	13.6	1.04
CaO	22	0.25	56.1	5.10
MgO	19	1	42.2	1.11
ZnO	12	3	15.4	0.21
La_2O_3	18	1	24.1	0.67
Y_2O_3	69	1	29.6	0.21
TiO ₂	47	24	29.1	0.01
ZrO_2	73	24	18.5	0.01
Nb ₂ O ₅	54	24	35.8	0.01
Al_2O_3	124	24	13.1	0.002
SiO ₂	300	24	27.9	0.002
Blank	_	24	3.5	_

^{*a*} Reaction conditions: methyl benzoate (2.5 mmol), *n*-octyl alcohol (3.0 mmol), metal oxide (50 mg), T = 160 °C, under N₂. Yield of *n*-octyl benzoate was determined by GC. ^{*b*} Initial formation rate of *n*-octyl benzoate per catalyst surface area measured under the conditions in which the yield of *n*-octyl benzoate was below 60%.

benzoate and *n*-octyl benzoate using pentadecane as an internal standard. The products were identified by GCMS.

In situ IR

In situ IR spectra were recorded at room temperature on a JASCO FT/IR-6100 equipped with a quartz IR cell connected to a conventional flow reaction system. A CeO₂ powder was pressed into a 40 mg of self-supporting wafer and mounted on the quartz IR cell with CaF₂ windows. Spectra were measured accumulating 35 scans at a resolution of 4 cm⁻¹ in a flow of He. A reference spectrum of the catalyst wafer under He was subtracted from each spectrum. For the introduction of methyl acetate and methanol into the IR disc, the liquid compounds were injected under a He flow preheated at 150 °C, which was fed to the *in situ* IR cell. Then, the IR disk was purged with He, and IR measurement was carried out.

Results and discussion

First, we examined the catalytic activity of various metal oxides for transesterification of methyl benzoate with 1.2 equivalents of n-octyl alcohol (Table 1). The reaction was carried out under solvent-free conditions in N2 at 160 °C. Transesterification hardly proceeded without a catalyst (Table 1, blank). For various metal oxides, the rate of n-octyl benzoate formation per catalyst weight was measured under the conditions in which conversions were below 60%. Using a specific surface area of metal oxides, the rate per catalyst surface area was calculated (Table 1). Basic metal oxides such as CaO, MgO and CeO₂ showed a higher rate than the other metal oxides, and the rate changed in the following order: CaO > MgO > CeO₂. These three metal oxides were tested for the reaction under the open system to vaporize the methanol (Table 2). Among these oxides, CeO₂ showed the highest yield (97%) after 24 h. ICP analysis of the solution after the reaction showed that the content of Ce in the solution was below the detection limit. In contrast, serious leaching was observed for CaO and MgO. A gram-scale experiment of this reaction (Scheme 1) was carried out using 1.7 g (12.5 mmol) of methyl benzoate and 2.0 g (15.0 mmol) of *n*-octyl alcohol by CeO_2 (50 mg, Ce = 2.3 mol%)





^{*a*} Reaction conditions: methyl benzoate (2.5 mmol), *n*-octyl alcohol (3.0 mmol), metal oxide (50 mg), T = 160 °C, under open system. Yield of *n*-octyl benzoate was determined by GC.

204

MgO

24

94



Scheme 1 A gram-scale transesterification by CeO₂.

at 160 °C in 96 h to give 92% yield of the ester. Under the same conditions. CaO showed a lower yield (85%) as shown in Fig. S1 (in the ESI⁺). Based on the number of Ce cations on the surface of CeO₂ (1.067 mmol g⁻¹),³⁰ CeO₂ showed a turnover number (TON) of 216. To the best of our knowledge, this is the highest TON for the transesterification of alkyl benzoate with alcohol among the previous systems including Zn clusters⁸ (TON = 78), carbenes¹⁷ (TON = 19), I_2^{19a} (TON = 23) and zwitterionic salts²⁰ (TON = 48). Next, we studied the reuse of CeO_2 and CaO for the transesterification of methyl benzoate with *n*-octyl alcohol (Fig. 1). For each successive use, the recovered catalyst was retrieved from the reaction mixture by centrifugation, washed with acetone three times to remove the products, and dried in air at 90 °C for 1 h. CeO2 was reused at least three times without any indication of catalyst deactivation. These results indicate that CeO₂ is a reusable and heterogeneous catalyst for transesterification. In contrast, the recovered CaO was significantly deactivated. Adsorption of CO₂ onto the metal oxide surface might be remarkable on CaO because the basicity of CaO was higher than that of CeO₂. From these results, it is concluded that, among the metal oxides tested, CeO2 is the most effective catalyst for transesterification in terms of activity, leaching-resistance and reusability. This result will be explained from the following properties of the metal oxides. In general, CeO₂ is practically used for the abrasive preparation and automotive catalysts under a hightemperature steam because CeO2 is stable due to its high lattice enthalpy (-4850 kJ mol⁻¹).³¹ Moreover, CeO₂ is less soluble than CaO or MgO under an acidic solution (in a possible coexistence of carboxylic acid) due to its isoelectric point $(CeO_2:^{32} pH = \sim 7.5, CaO:^{33} pH = 12-13, MgO:^{34} pH = 12-13).$

Next, we investigated the substrate scope in CeO₂-catalyzed transesterification. Transesterification of various esters with n-octyl alcohol or n-hexyl alcohol was examined (Table 3). Methyl benzoates (entries 1, 2), methyl phenylacetate (entry 3), alkyl alkylates (entries 4-6) reacted to afford the corresponding esters in good to high yields (72-97%). Methyl esters with a heteroaromatic ring (entries 7-11), which are not tolerated by homogenous catalysts due to their high coordinating property to the metal center, can be transformed into the corresponding esters in high yields (85-99%). Owing to pharmaceutical importance of heteroaromatic alkyl ester structure,³⁵ the present method is important from a practical viewpoint. A long chain amylester (entries 12, 13) and a bulky ester (tertiarybutylester) (entries 14, 15) also selectively underwent transesterification with primary (n-octyl alcohol) and secondary alcohols (2-octanol) to give the corresponding esters in good to excellent yields (88-99%). Transesterification of methyl benzoate with various alcohols was also examined (Table 4). n-Alkyl alcohols (entries 1-3), branched alkyl



Fig. 1 Recycle tests of CeO₂ (A) and CaO (B) for the transesterification of methyl benzoate (2.5 mmol) with *n*-octyl alcohol (3.0 mmol). Conditions: 50 mg catalyst, 160 °C, 24 h, under an open system.

alcohols (entry 4, 5), cinnamyl alcohol (entry 6) and benzyl alcohols having an electron-donating or an electron-withdrawing group (entries 7–11), and a secondary alcohol (entry 12) reacted to afford the corresponding esters in moderate to high yields (64–99%). Benzyl benzoates are known to show inhibitory effects on angiotensin II-induced hypertension.³⁶ These examples demonstrate that CeO_2 is a versatile catalyst for producing various esters including the pharmacologically valuable ones.

The above reactions under solvent-free conditions require high temperature (typically 160 °C) to evaporate the small amount of alcohol. We also tested the standard reaction of methyl benzoate with *n*-octyl alcohol under reflux conditions in hexane (at *ca*. 69 °C) under an open system, in which methanol can be released out of the reactor *via* a needle inserted into the rubber on the top of the vessel. After 48 h, nearly quantitative yield of the product was obtained (Scheme 2), which indicates that high temperature is not critical. \cap

 Table 3
 Transesterification with various esters by CeO2^a

 \cap

	$R^1 \xrightarrow{\downarrow} O^2 R^2 + R^3 OH \xrightarrow{CeO_2} R^1 \xrightarrow{\downarrow} O^2 R^3 + R^2 OH$					
Entry	Ester	Alcohol	<i>t</i> (h)	Yield (%)		
1	OMe	<i>n</i> -Octyl alcohol	24	97 (94)		
2	OMe	<i>n</i> -Octyl alcohol	48	91		
3	OMe	<i>n</i> -Octyl alcohol	24	75		
4	OMe	n-Octyl alcohol	24	72		
5^b	OMe	<i>n</i> -Hexyl alcohol	24	85		
6 ^{<i>b</i>}	OPr	<i>n</i> -Hexyl alcohol	32	88		
7	OMe	<i>n</i> -Octyl alcohol	48	91		
8 ^b	O OEt	<i>n</i> -Octyl alcohol	48	94		
9	O M OMe	<i>n</i> -Octyl alcohol	48	85		
10	OMe	<i>n</i> -Octyl alcohol	48	85		
11	OMe OMe	<i>n</i> -Octyl alcohol	48	99		
12 ^{<i>c</i>}		<i>n</i> -Octyl alcohol	36	93 (87)		
13 ^c		2-Octanol	36	88 (83)		
14 ^c	C Lok	<i>n</i> -Octyl alcohol	15	99 (98)		
15 ^c	r lok	2-Octanol	18	99 (97)		

^{*a*} Reaction conditions: ester (2.5 mmol), alcohol (3.0 mmol), CeO₂ (50 mg), T = 160 °C, under an open system. Yield of the product was determined by GC. Isolated yields are in the brackets. ^{*b*} Reaction conditions: ester (2.5 mmol), alcohol (5.0 mmol), CeO₂ (50 mg), T = 160 °C. ^{*c*} Reaction conditions: ester (2.5 mmol), alcohol (5.0 mmol), CeO₂ (50 mg), T = 180 °C.

To clarify the reaction mechanism, we measured *in situ* IR (Fig. S2[†]) spectra of the adsorption complexes formed by introduction of methyl acetate (a model ester compound) or methanol (a model alcohol compound) into CeO₂ at 30 °C. The samples were first preheated in He flow at 600 °C, followed by cooling to 30 °C. Then, 1 μ L of methyl acetate or methanol was injected into He flow preheated at 150 °C, which was fed to the CeO₂ disc. The spectrum of adsorbed methyl acetate shows the bands due to adsorbed acetate species (1556, 1421 and 1340 cm⁻¹) and adsorbed methoxy species (1102, 1045 cm⁻¹), which indicates that methyl ester is dissociated on the CeO₂



	OMe + R-C	DH $\xrightarrow{CeO_2}$ \xrightarrow{O}^R	+ СН ₃ ОН	
Entry	Alcohol	Product	<i>t</i> (h)	Yield (%)
1	ОН		24	97 (94)
2	ОН		24	97 (92)
3	ОН		24	91
4	ОН		48	92
5	ОН		24	93
6	ОН		24	64
7	ОН		48	83
8	ОН		48	89
9	МеО	O O O Me	24	97
10	O ₂ N OH		48	97
11	Р		48	97
12 ^{<i>b</i>}	OH	Colored and the second	36	99 (96)

^{*a*} Reaction conditions: ester (2.5 mmol), alcohol (3.0 mmol), CeO_2 (50 mg), T = 160 °C, under an open system. Yield of the product was determined by GC. Isolated yields are in the brackets. ^{*b*} Reaction conditions: methyl benzoate (2.5 mmol), alcohol (5.0 mmol), CeO_2 (50 mg), T = 180 °C.



Scheme 2 Low temperature transesterification by CeO₂.

surface to form the acetate and methoxy species (Scheme 3a). The spectrum of adsorbed methanol shows the bands due to methoxy species (1105, 1046 cm⁻¹). According to the literature,³⁷ the methoxy species are formed by the mechanism in Scheme 3b; the Lewis base site (exposed $O^{\delta-}$) on CeO₂ abstracts a proton from methanol to produce the methoxy species. Then, we carried out kinetic studies for liquid phase catalytic reactions. We examined the effect of the substrate concentration on the initial rate for the transesterification of methyl benzoate with *n*-octyl alcohol using *o*-xylene as a



 $\label{eq:scheme 3} \begin{array}{l} \mbox{Dissociative adsorption of (a) methyl acetate and (b) methanol on CeO_2.} \end{array}$

solvent. The reaction rate increased with initial alcohol concentration, and the reaction order (n) of 1.2 was obtained (Fig. S3⁺). On the other hand, the rate showed nearly zero order dependence (n = -0.1) on the initial methyl ester concentration (Fig. S4⁺). These results suggest that alcohol is involved in a rate-limiting step, while methyl ester is not involved in a rate-limiting step and is strongly adsorbed onto the CeO₂ surface. Summarizing IR and kinetic results, it can be concluded that the abstraction of a proton from an alcohol by basic sites of CeO₂ is the rate-limiting step. The following mechanism can be proposed (Scheme 4); (1) dissociative adsorption of ester to adsorbed carboxylate species, (2) dissociative adsorption of alcohol to alkoxide species assisted by the base sites of CeO_2 and (3) nucleophilic substitution reaction of alkoxide species to carboxylate species and desorption of the corresponding esters.

Fig. 2 plots the reaction rate for various metal oxide catalysts as a function of the averaged electronegativity of the metal oxide. It is shown that basicity of metal oxides increases with decrease of the electronegativity.^{38,39} The result shows that the reaction rate increases with decrease in the electronegativity, indicating that the catalytic activity increases with increase in the basicity of metal oxides. This tendency is consistent with the proposed mechanism, in which the abstraction of a proton from alcohol by basic sites of metal oxides is the rate-limiting step.

Conclusion

Among the 11 kinds of metal oxides, CeO_2 was the most suitable catalyst in terms of catalytic activity, leaching-resistance and reusability for transesterification of esters with alcohols under the solvent-free conditions. Various esters, including a





Scheme 4 A proposed mechanism of transesterification by CeO₂.



Fig. 2 Reaction rate as a function of averaged electronegativity of metal oxide.

sterically-hindered ester (*tertiary*-butylester), and various alcohols (primary and secondary) were transformed into the corresponding esters, including the pharmacologically valuable esters such as heteroaromatic esters and benzyl benzoates. On the basis of mechanistic studies, a reaction mechanism is proposed, in which proton abstraction of alcohol by the Lewis base site of CeO_2 to yield alkoxide species is the rate-limiting step. The mechanism is consistent with the observed increase in the catalytic activity with increase in the basicity of metal oxides.

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