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Recyclable Lewis acid catalysts by tuning supercritical vs liquid carbon dioxide phases: lanthanide catalysts with tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide

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Abstract—Lanthanide tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide catalysts are shown to be continuously employed in supercritical carbon dioxide by changing supercritical vs. liquid carbon dioxide phases. The lanthanide complexes are thus extremely efficient Lewis acid catalysts even in supercritical carbon dioxide phase by virtue of the highly electron-withdrawing and solubilizing effect of tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide without any hydrocarbon spacer. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

A wide variety of Lewis acid catalysts have been developed on the basis of the Lewis acid–base complexation in organic polar solvents.[1] However, the Lewis acid complexes have often been employed and then wasted after the reactions in more than a stoichiometric amount. Therefore, it is desirable to decrease the amount of a Lewis acid complex in catalytic by developing a stronger Lewis acid catalyst and the recycle process thereof. The replacement of conventional liquid solvents by supercritical fluids as reaction media for homogeneous catalysis has been known to provide the opportunity to control the reaction in terms of the reactivity and selectivity because of high gas miscibilities, greater diffusivities, clustering effects, and tunable solvent power by changing their densities along with the pressure.[2] Supercritical fluids have been employed as an environmentally benign reaction media in late transition metal catalysis for hydroformylation[3] and hydrogenation.[4] By contrast, the design and immobilization of strong Lewis acid catalysts are essentially remained as a challenging problem in this unorthodox non-polar media for Lewis acid catalysis.[5]

We have developed lanthanide(III) tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide as a new Lewis acid catalyst. Numerous and long-enough (perfluorooctyl, C_8F_{17}) perfluoroalkyl ligands[6] can be attached directly without any hydrocarbon spacer for increasing the Lewis acidity. These lanthanide catalysts can be employed for fluorous biphase catalysis (FBC) to be soluble in fluorous solvent.[7,8] FBC has been of concern as an environmentally benign reaction system to have the advantage that fluorous catalysts are immobilized in fluorous solvent and recycled. However this FBC method is not yet completely green reaction system in the use of an organic solvent such as 1,2-dichloroethane and toluene. To solve this drawback, we investigated the use of supercritical carbon dioxide ($scCO_2$) in place of an organic solvent (Fig. 1(a)).[9] Since fluorous compounds are soluble in $scCO_2$,[3a,f,4c,e,5a,e] homogeneous phase with fluorous solvent immobilizes fluorous lanthanide catalysts. After the reaction, fluorous solvent remains in the reaction vessel by releasing liquid carbon dioxide with product. In addition, we tried to reuse the lanthanide catalysts by changing from $scCO_2$ to liquid carbon dioxide (Fig. 1(b)). Lanthanide catalysts are insoluble in liquid carbon dioxide even in the presence of reaction substrate or product. We report here the completely recyclable use of lanthanide(III) tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl) amide complexes in $scCO_2$.

2. Results and discussion

First, we examined the catalytic activities of the lanthanide

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Keywords: supercritical carbon dioxide; liquid carbon dioxide; environmental benignity; lanthanide; Lewis acid catalysis; tris(perfluorooctanesulfonyl)methide; bis(perfluorooctanesulfonyl)amide.

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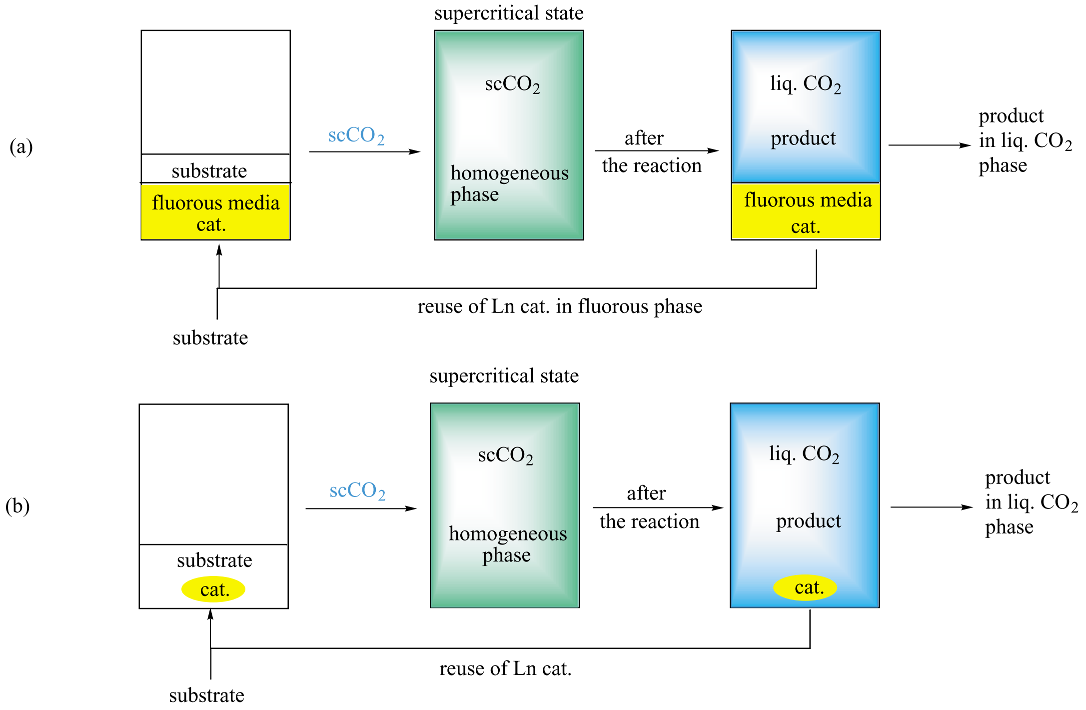
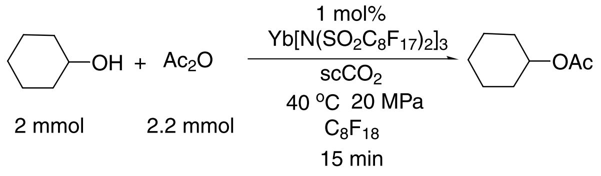


Figure 1. The recycle methods of fluorous lanthanide catalysts using $scCO_2$ as a reaction media. (a) fluorous/$scCO_2$ biphase reaction, (b) without fluorous solvent.

complexes for alcohol acylation as a probe reaction in $scCO_2$/fluorous solvent (perfluorooctane). The ester formation of cyclohexanol (2 mmol) with acetic anhydride (2.2 mmol) underwent in homogeneous phase involving soluble fluorous phase immobilized lanthanide catalyst above critical point. After the reaction, lanthanide catalyst was soluble in fluorous phase and the product separated from fluorous phase was obtained by extracting with organic solvent. The isolated yield of the product was 98% (Table 1). By contrast, the yield of esterification in $scCO_2$ without lanthanide catalyst was 3%. Therefore lanthanide catalyst is very effective Lewis acid in $scCO_2$. Fluorous phase immobilized lanthanide catalyst was recycled in five times and no loss of activity was observed for the recovered catalyst.

We examined the esterification of cyclohexanol catalyzed lanthanide complexes without fluorous solvent in $scCO_2$. The ester formation of cyclohexanol (2 mmol) with acetic anhydride (2.2 mmol) underwent in homogeneous phase involving soluble fluorous lanthanide catalyst above critical point (Photo 1). However heterogeneous phase appeared with solid catalyst below critical temperature even in the presence of products. Taking this advantage of fluorous lanthanide catalyst with respect to temperature-dependent solubility,[10] we examined to reuse these complexes. The liquid carbon dioxide was evacuated with products, after the reaction completed within 10 min in the homogeneous phase at 40°C with 1 mol% of scandium and ytterbium complexes (Fig. 1(b)). The lanthanide tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide complexes were insoluble in carbon dioxide liquid phase and the residual lanthanide complexes remained in the autoclave and were reused without isolation. The reaction product could be isolated into the carbon dioxide liquid phase after completing the reaction and lowering the temperature (−20°C). Cyclohexyl acetate was thus obtained in quantitative yield as calculated by GC analysis (Table 2). Scandium and ytterbium complexes were completely remained in the reaction vessel as determined by atomic emission spectrometry. No loss of activity was observed for

Table 1. Esterification in $scCO_2/C_8F_{18}$ catalyzed by $Yb[N(SO_2C_8F_{17})_2]_3$

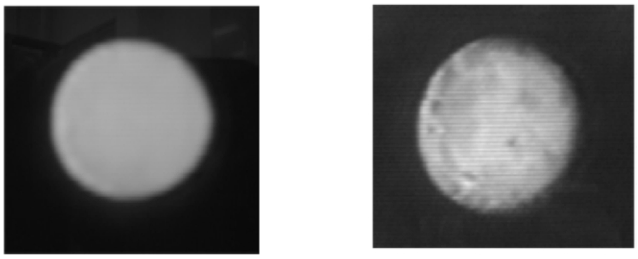


Cycle[a]	%Yield[b]
1	99 (98)[c]
2	99
3	99
4	99
5	99

[a] The catalyst in the fluorous phase was recycled.

[b] Calculated by GC analysis using *n*-nonane as an internal standard.

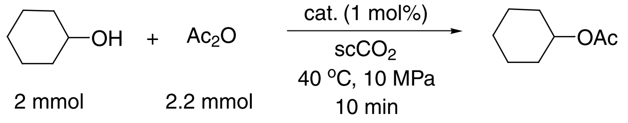
[c] Value in parenthesis refers to the isolated yields.



(a) (b)

Photo 1. Esterification in (a) homogeneous phase under supercritical carbon dioxide (b) heterogeneous phase under liquid carbon dioxide.

Table 2. Esterification in $scCO_2$ catalyzed by Yb and Sc complexes



Cycle[a]	%Yield[b]	
	$Yb[N(SO_2C_8F_{17})_2]_3$	$Sc[C(SO_2C_8F_{17})_3]_3$
1	99 (98)[c]	99 (98)[c]
2	99	100 (98)[c]
3	98	99

[a] The residual catalyst was recycled.

[b] Calculated by GC analysis using *n*-nonane as an internal standard.

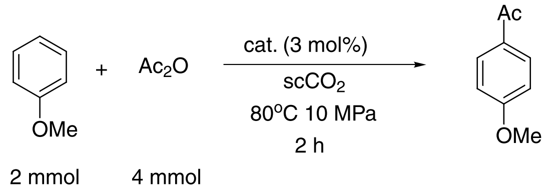
[c] Values is parenthesis refer to the isolated yields.

the catalyst recovered. The isolated yield of the product was 98%. Thus, the reaction of cyclohexanol (2 mmol) with acetic anhydride (2.2 mmol) was carried out at 40°C for 10 min, in the presence of 1 mol% of lanthanide complexes. Then, the liquid carbon dioxide was evacuated. Cyclohexyl acetate was obtained in good isolated yield. The remaining scandium and ytterbium complexes were completely recovered and reused in $scCO_2$ without isolation (Table 2).

Then, the catalytic activities and recyclable use of the lanthanide complexes were examined for C–C bond forming (CCF) reactions. Friedel–Crafts(F–C) reaction constitutes one of the most useful processes in organic synthesis.[11] The F–C acylation reaction of anisol (2 mmol) with acetic anhydride (4 mmol) was also carried out at 80°C for 2 h, in the presence of a catalytic amount (3 mol%) of scandium and ytterbium complexes. The remaining scandium and ytterbium complexes were completely (>99%) recovered and reused in the supercritical carbon dioxide phase without isolation (Table 3).

In summary, we have disclosed lanthanide tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl) amide complexes as efficient and recyclable Lewis acid catalysts by tuning supercritical ($scCO_2$) vs liquid carbon dioxide. The lanthanide complexes are thus extremely efficient Lewis acid catalysts even in $scCO_2$ by virtue of the highly electron-withdrawing effect of tris(perfluorooctanesulfonyl)methide and bis(perfluorooctanesulfonyl)amide ligands without any hydrocarbon spacer.

Table 3. Friedel–Crafts reaction in $scCO_2$ catalyzed by Yb and Sc complexes



Cycle[a]	% Yield[b]	
	$Yb[N(SO_2C_8F_{17})_2]_3$	$Sc[C(SO_2C_8F_{17})_3]_3$
1	79 (77)[c]	82 (79)[c]
2	77	80
3	77	79

[a] The residual catalyst was recycled.

[b] Calculated by GC analysis using *n*-decane as an internal standard.

[c] Values is parenthesis refer to the isolated yields.

3. Experimental

3.1. General

^1H and ^{13}C NMR spectra were measured on a JEOL JNM-EX400 (400 MHz) spectrometers. Chemical shifts of ^1H NMR were expressed in parts per million relative to chloroform (δ 7.26) or tetramethylsilane (δ 0.00) as an internal standard in chloroform-*d*. Chemical shifts of ^{13}C NMR were expressed in parts per million relative to chloroform-*d* (δ 77.0) as an internal standard. GC analysis was carried out on SHIMADZU GC-1700AF and GC–MS analysis was taken by Hewlett–Packard G1800 A GLS. Atomic emission spectrometer is of IRIS/AP Nippon Jarrell Ash Co. 1,2-Dichoroethane was distilled from phosphorous pentaoxide.

3.2. Ester formation of cyclohexanol with acetic anhydride by using fluorous solvent

A 20 ml stainless steel autoclave equipped with magnetic stirring bar was charged with cyclohexanol (0.20 g, 2 mmol), acetic anhydride (0.22 g, 2.2 mmol), and ytterbium (III) tris[bis(perfluoroocatanesulfonyl)amide] (1 mol% based on cyclohexanol) as a Lewis acid catalyst in perfluorooctane (5 ml). After adding carbon dioxide to apply pressure of 20 MPa to the autoclave, the reaction mixture was stirred for 15 min at 40°C. After cooling below 0°C, the pressure in the autoclave was slowly released. The autoclave was opened at room temperature, and dichloroethane (5 ml) was added to the autoclave and stirred for 15 min to extact the product. Then, the reaction mixture was allowed to stand for 5 min, so that the reaction mixture could separate into the upper organic phase and the lower fluorous phase. As a result of the gas chromatographic analysis of the dichloroethane layer dissolving the product, the yield of cyclohexyl acetate was 99% using *n*-nonane as an internal standard. Cyclohexyl acetate was obtained from dichloroethane layer after evaporation under reduced pressure and silica gel chromatography (0.280 g, 98% isolated yield).

After removing the dichloroethane layer, to which cyclohexanol (0.2 g, 2 mmol) and acetic anhydride (0.22 g, 2.2 mmol) were added. After adding carbon dioxide to apply pressure of 20 MPa to the autoclave, the reaction mixture was stirred for 15 min at 40°C. After cooling below 0°C, the pressure in the autoclave was slowly released. The autoclave was opened at room temperature, and dichloroethane (5 ml) was added to the autoclave and stirred for 15 min to extract the product. As a result of the gas chromatographic analysis of the dichloroethane layer dissolving the product, the yield of cyclohexyl acetate was 99% using *n*-nonane as an internal standard. The similar manner was repeated further three times, and the yields of cyclohexyl acetate were 99, 99 and 99%, respectively.

Ytterbium complexes were completely (>99%) remained in perfluorooctane layer as determined by atomic emission spectrometry. Thus, the catalyst can be reused, since the catalytic activity was not lowered.

3.3. Ester formation of cyclohexanol with acetic anhydride without fluorous solvent

A 20 ml stainless steel autoclave equipped with magnetic stirring bar was charged with cyclohexanol (0.20 g, 2 mmol), acetic anhydride (0.22 g, 2.2 mmol), and ytterbium (III) tris[bis(perfluorooctanesulfonyl)amide] (1 mol% based on cyclohexanol) as a Lewis acid catalyst. After adding carbon dioxide to apply pressure of 10 MPa to the autoclave, the reaction mixture was stirred for 10 min at 40°C. After cooling to −20°C, liquid carbon dioxide was successively introduced to the autoclave at the flow rate of 1 ml/min for 1 h under 6 MPa. The product was extracted with dichloroethane (5 ml). As a result of the gas chromatographic analysis of the dichloroethane layer dissolving the product, the yield of cyclohexyl acetate was 99% using *n*-nonane as an internal standard. Cyclohexyl acetate was obtained from dichloroethane layer after evaporation under reduced pressure and silica gel chromatography (0.279 g, 98% isolated yield).

After successive introduction of liquid carbon dioxide, the pressure in the autoclave was released to give the catalyst, to which cyclohexanol (0.2 g, 2 mmol) and acetic anhydride (0.22 g, 2.2 mmol) were added. After adding carbon dioxide to apply pressure of 10 MPa to the autoclave, the reaction mixture was stirred for 10 min at 40°C. After cooling to −20°C, liquid carbon dioxide was successively introduced to the autoclave at the flow rate of 1 ml/min for 1 h under 6 MPa. The product was extracted with dichloroethane (5 ml). As a result of the gas chromatographic analysis of the dichloroethane layer dissolving the product, the yield of cyclohexyl acetate was 99% using *n*-nonane as an internal standard. The similar manner was repeated, and the yields of cyclohexyl acetate at third attempts were 98%. Ytterbium complexes were completely (>99%) remained in the reaction vessel as determined by atomic emission spectrometry. Thus, the catalyst can be reused, since the catalytic activity was not lowered.

3.4. Friedel–Crafts acylation of anisol with acetic anhydride without fluorous solvent

A 20 ml stainless steel autoclave equipped with magnetic stirring bar was charged with anisol (0.22 g, 2 mmol), acetic anhydride (0.41 g, 4 mmol), and ytterbium(III) tris[bis(perfluorooctanesulfonyl)amide] (3 mol% based on anisol) as a Lewis acid catalyst. After adding carbon dioxide to apply pressure of 10 MPa to the autoclave, the reaction mixture was stirred for 2 h at 80°C. After cooling to −20°C, liquid carbon dioxide was successively introduced to the autoclave at the flow rate of 1 ml/min for 1 h under 6 MPa. The product was extracted with dichloroethane (5 ml). As a result of the gas chromatographic analysis of the dichloroethane layer dissolving the product, the yield of *p*-methoxyacetophenone was 79% using *n*-decane as an internal standard. *p*-Methoxyacetophenone was obtained from dichloroethane layer after evaporation under reduced pressure and silica gel chromatography (0.231 g, 77% isolated yield).

After successive introduction of liquid carbon dioxide, the pressure in the autoclave was released to give the catalyst, to which anisol (0.22 g, 2 mmol) and acetic anhydride (0.41 g, 4 mmol) were added. After adding carbon dioxide to apply pressure of 10 MPa to the autoclave, the reaction mixture was stirred for 2 h at 80°C. After cooling to −20°C, liquid carbon dioxide was successively introduced to the autoclave at the flow rate of 1 ml/min for 1 h under 6 MPa. The product was extracted with dichloroethane (5 ml). As a result of the gas chromatographic analysis of the dichloroethane layer dissolving the product, the yield of *p*-methoxyacetophenone was 77% using *n*-decane as an internal standard. The similar manner was repeated, and the yields of at third attempts were 77%. Ytterbium complexes were completely (>99%) remained in the reaction vessel as determined by atomic emission spectrometry. Thus, the catalyst can be reused, since the catalytic activity was not lowered.

3.5. Experimental data

3.5.1. Cyclohexyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20–1.44 (m, 5H), 1.52–1.58 (m, 1H), 1.70–1.74 (m, 2H), 1.84–1.87 (m, 2H), 2.03 (s, 3H), 4.71–4.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.45, 23.81, 25.37, 31.65, 72.61, 170.40; MS (EI, 70 eV): *m/z* 127 ($C_6H_{11}CO_2^+$), 99 ($C_6H_{11}O^+$), 82 ($C_6H_{10}^+$), 67, 43 (CH_3CO^+); Elemental analysis (%) calcd for $C_8H_{14}O_2$: C 67.57, H 9.92, found: C 67.40, H 9.94.

3.5.2. *p*-Methoxyacetophenone. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (s, 3H), 3.87 (s, 3H), 6.93 (d, J=9.8 Hz, 2H), 7.94 (d, J=9.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.36, 55.44, 113.57, 130.22, 130.46, 163.31, 196.55; MS (EI, 70 eV): *m/z* 150 (M^+), 135 ($MeOPhCO^+$), 107 ($MeOPh^+$), 92, 77, 64, 63, 43 (CH_3CO^+); Elemental analysis (%) calcd for $C_9H_{10}O_2$: C 71.98, H 6.71, found: C 72.07, H 6.66.

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