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Heterogeneous catalysis of novel polymeric rare earth complexes under solvent-free conditions: Zero-emission synthesis of β-amino alcohols

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Abstract

Novel polymeric rare earth complexes, $RE_2(BPDS)_3$ (RE = rare earth metal, BPDS = biphenyl-4,4′-disulfonate), in which the metal ions are homogeneously dispersed, were synthesized by the self-organization of the metal ion and the corresponding aryldisulfonate and successfully used as a reusable Lewis acid catalyst for the ring-opening reaction of epoxides with amines to give the desired β-amino alcohols in excellent yields under solvent-free heterogeneous conditions. The catalysts can be quantitatively recovered and reused more than five times without decreasing their activities. The catalytic activity of $Sc(OPf)_3$ ($Pf = SO_2C_8F_{17}$) for the same reaction under solvent-free conditions was also examined.

Keywords: Heterogeneous catalyst; Coordination polymer; Self-organization; Solvent-free conditions; Reusable catalyst

1. Introduction

The development of efficient heterogeneous catalysts that can be easily prepared, recovered and reused without losing their activities has received much attention from a practical and environmental point of view. Many recoverable and reusable heterogeneous catalysts such as inorganic material-supported [1], insoluble polymer-supported [2] and dendritic catalysts [3] have been developed. In general, however, they show lower activities and selectivities, compared to the corresponding homogeneous ones, and the syntheses of them are often tedious.

β-Amino alcohols are versatile synthetic intermediates for a wide rage of biologically active natural and unnatural products [4–6]. They can also serve as good chiral ligands of some asymmetric metal complex catalysts [7]. The nucleophilic ring-opening of epoxides with an amine is recognized as an important route to obtain such β-amino alcohols with 1,2-*trans* stereochemistry. Therefore, various methodologies have been developed for this purpose, which include the use of alumina [8], metal alkoxides [9], metal triflates [10–12], transition metal halides [13], alkali metal perchlorates [14], rare earth metal halides [15], silica under high pressure [16,17], montmorillonite cley under microwave irradiation [18]. However, these methodologies suffer from one or more disadvantages such as long reaction time, high reaction temperature, moderate yield, use of air or moisture sensitive catalysts, and requirement of the stoichiometric amount of catalyst. Recently, Curini et al. succeeded in the ring-opening of epoxides with aromatic amines using zirconium sulfophenylphosphonate as a heterogeneous catalyst under solvent-free conditions [19]. More recently, Chakraborti and Kondaskar [20] and Chakraborti et al. [21] reported that $ZrCl_4$ and LiBr can also be an effective catalyst for the conversion under solvent-free conditions. Here, we report porous coordination polymer-type rare earth complexes as a novel heterogeneous catalyst that can effectively work under

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solvent-free conditions and can be recovered and reused many times.

2. Experimental

2.1. General methods

IR spectra were obtained with a JASCO FT/IR-420 instrument. Elementary analyses were accomplished at Center of Elementary Analysis, Faculty of Sciences, Kyushu University. Column chromatography was conducted on Fuji Silysia Chemical, Chromatorex® NH silica gel, 100–200 mesh. Tetrahydrofurane (THF) was distilled from sodium 9-fluorenone ketyl [22]. Rare earth triisopropoxides were purchased from Kojundo Chemical Laboratory Co., Ltd.

2.2. Typical procedure for the preparation of $RE_2(BPDS)_3$: scandium(III) biphenyl-4,4′-disulfonate $[Sc_2(BPDS)_3]$

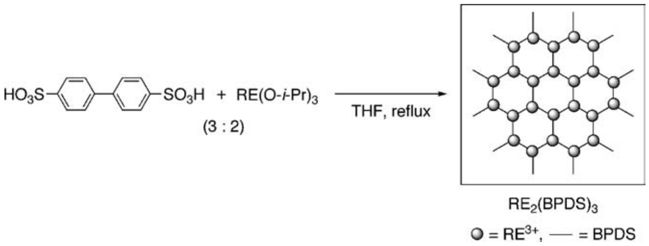
To a refluxing solution of Sc(O-*i*-Pr)$_3$ (444 mg, 2.0 mmol) in THF was slowly added a solution of biphenyl-4,4′-disulfonic acid (943 mg, 3.0 mmol) in THF, and the resulting mixture was stirred for 18 h under the same conditions. After cooling the suspension to room temperature, the precipitate was filtered and washed with THF. The colorless solid was dried at 200 °C for 24 h in vacuo to give the complex $Sc_2(BPDS)_3$ (911 mg, 83%). IR (KBr): 3399, 1599, 1388, 1279, 1161, 1112, 1048, 997, 818, 728 and 610 cm^{-1}. Anal. calcd. for $C_{36}H_{24}O_{18}S_6Sc_2 \cdot 4H_2O$: C, 39.35; H, 2.94. Found: C, 39.48; H, 2.89.

2.3. Ring-opening reaction of cyclohexene oxides with benzylamine: synthesis of trans-2-benzylamino-1-cyclohexanol

To a flask containing $Sc_2(BPDS)_3$ (10.3 mg, 0.02 mmol) was added cyclohexene oxide (39.3 mg, 0.40 mmol) and benzylamine (47.2 mg, 0.44 mmol), and the mixture was stirred for 12 h at room temperature. The reaction mixture was added Et_2O (3 ml) and subjected to centrifugation. The supernatant was collected and the precipitate was washed with Et_2O (three times, total 12 ml). The combined solution was concentrated under reduced pressure and subjected to column chromatography on NH silica gel (acetone/hexane 1:19) to give the desired product (81.7 mg, 99.5%). The recovered catalyst was drying at room temperature in vacuo and used again for the next round of reaction.

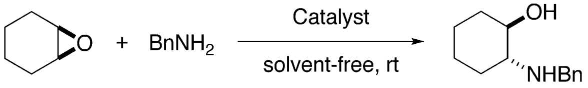
3. Results and discussion

The polymeric rare earth complexes were prepared in one step by refluxing RE (O-*i*-Pr)$_3$ (RE = Sc, Yb, Y, La) and biphenyl-4,4′-disulfonic acid in THF as shown in Scheme 1. The complexes were dried at 200 °C under vacuum before use.



Scheme 1. Preparation of the polymeric rare earth complex.

Table 1
Catalytic ring-opening reaction of cyclohexene oxide with benzylamine



Entry	Catalyst	(mol%)	Time (h)	Yield (%)[a]
1[b]	$Sc(OPf)_3$	2.5	24	30
2[b]	$Sc_2(BPDS)_3$	5.0	40	40
3	$Sc(OPf)_3$	2.5	2	99
4	$Sc_2(BPDS)_3$	5.0	12	99
5	$Yb_2(BPDS)_3$	5.0	12	99
6	$Y_2(BPDS)_3$	5.0	12	89
7	$La_2(BPDS)_3$	5.0	12	38

[a] Isolated yield.

[b] Toluene was used as the solvent.

The catalytic activity of $RE_2(BPDS)_3$ as well as $Sc(OPf)_3$ ($Pf = SO_2C_8F_{17}$), which was previously prepared in this laboratory [23], was tested for the ring-opening reaction of cyclohexene oxide with benzylamine. When the reactions were carried out by using 2.5 mol% of $Sc(OPf)_3$ or 5 mol% of $Sc_2(BPDS)_3$ in toluene at room temperature under heterogeneous conditions, the desired amino alcohol was obtained in only low yield, respectively (Table 1, entries 1 and 2). On the other hand, under solvent-free conditions the reaction proceeded smoothly to give the product in excellent yields (entries 3 and 4). The catalytic activity of $Yb_2(BPDS)_3$ complex was found to be as effective as $Sc_2(BPDS)_3$ (entry 4), but the activity was generally decreased as the ionic radius of the metal complex increased; thus, the yield of the product catalyzed by $La_2(BPDS)_3$ complex was very low (entry 7).

As the reaction catalyzed by $Sc_2(BPDS)_3$ complex proceeded under heterogeneous conditions, we checked the reusability of the catalyst. Although the recovered $Sc(OPf)_3$, which was dried at 100 °C for 10 h before use, seriously lost the original activity, the recovered $Sc_2(BPDS)_3$ did not lose the activity; it could be successfully reused for five times (5th run; 97% yield).

4. Conclusion

We have developed a novel rare earth coordination polymer catalysts $RE_2(BPDS)_3$ that can be prepared from rare earth triisopropoxides RE(O-*i*-Pr)$_3$ and a two-way ligand biphenyl-4,4′-disulfonic acid in one step. These catalysts, $Sc_2(BPDS)_3$ and $Yb_2(BPDS)_3$ in particular, effectively promote the ring-opening reaction of cyclohexene oxide with benzylamine under solvent-free heterogeneous conditions. Furthermore, they can be stored at room temperature, quantitatively recovered after the reaction and reused more than five times without losing their original catalytic activities.

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