



Efficient, stable, and reusable Lewis acid–surfactant–combined catalyst: One-pot Biginelli and solvent-free esterification reactions



Yunfeng Qiu^a, Hongnan Sun^a, Zhuo Ma^b, Wujiong Xia^{a,*}

^a State Key Lab of Urban Water Resource and Environment (SKLUWRE) & Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, Harbin, Heilongjiang 150080, China

^b School of Life Science and Technology, Harbin Institute of Technology, Harbin, Heilongjiang 150080, China

ARTICLE INFO

Article history:

Received 24 February 2014

Received in revised form 21 April 2014

Accepted 22 April 2014

Available online 2 May 2014

Keywords:

Lewis acid–surfactant combined catalyst

Biginelli

Esterification

Micro reactor

Solvent-free

ABSTRACT

Cerium(III) trislaurylsulfonate ($\text{Ce}(\text{LS})_3$), a Lewis acid and surfactant combined catalyst, was prepared and characterized by SEM, SEM-EDX, XRD, NMR, FT-IR, TG, and elemental analysis. $\text{Ce}(\text{LS})_3$ was found to be stable and efficient to catalyze one-pot Biginelli and solvent-free esterification reactions. Furthermore, $\text{Ce}(\text{LS})_3$ is easy to recycle after reaction by pouring into cold water and filtration. Present work will shed deep insight into the understanding of the catalytic nature of LASCs, and extend its application in important organic transformations.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Homogeneous catalytic systems usually exhibit high activity in organic reactions, however, suffer from the difficulty of recovery whereas heterogeneous catalysts are easily separated from the reaction mixture and show high catalytic activity by rational design of novel structures or components [1]. Nevertheless, heterogeneous catalytic systems still have to face the low efficiency of mass transfer in multiphase reaction [2]. To address the drawbacks of both homogeneous and heterogeneous catalysts, it is appealing to design a novel catalytic system, e.g. colloidal dispersion or reverse micelles formed by Lewis acid–surfactant combined catalysts (LASCs) [3–6].

With the unique characteristics in multifunctional catalytic property, LASCs firstly developed by Kobayashi [5,7], as one of the most widely investigated catalytic system, has attracted increasing attentions during the past decades. Not only LASCs act as a Lewis acid to activate substrate molecules, but also serve as a surfactant to form stable colloidal dispersion systems with organic substrates. It is worth noting that the self-assembled process of LASCs will concentrate acid catalysts at the interface of the micelles to enhance the catalytic efficiency. To realize the best functions, exploration of LASCs designed to have specific catalytic sites, fascinating stability and practical reusability has fueled research

on tailoring the combination of Lewis acids and surfactants with expectations of achieving novel or enhanced catalytic properties. So far, most studies on LASCs focused on their application in aldol [7], Diels–Alder [8,9], allylation of aldehydes [10,11], propargylamines reactions [12,13], and also in asymmetric hydroxylation [14], hydroxymethylation [15], ring-opening reactions and so on [16]. However, some of the reported LASCs are trivial to separate from the reaction system after reaction, and some have severe hygroscopicity, which would make it inconvenient for practical application [17,18]. Therefore, room still exists for developing novel LASCs and extending its application in a wider range of reactions. Additionally, few papers are addressed on the characterization of catalysts in detail. Therefore, the systematic study on the characterization of LASCs would provide deep insight into the understanding of catalytic nature, and it is also of great significance to develop a new strategy to build functional LASCs with satisfied efficiency, stability and reusability to enhance the catalytic performance in important organic transformations.

Recently, Biginelli reaction has attracted considerable attentions owing to its usefulness for the synthesis of dihydropyrimidines (DHPMs) and their derivatives [19]. DHPMs are important class of compounds exhibiting pharmacological activities such as calcium channel blockers, anti-inflammatory, antitumor, α -1a-adrenergic receptor antagonist, and antihypertensive agents [20–22]. Traditional approach for HCl-catalyzed three-component cyclocondensation reaction of aldehyde, β -ketoester and urea in reflux ethanol was firstly described by Biginelli in 1893, however,

* Corresponding author. Tel.: +86 451 86403760; fax: +86 451 86403760.
E-mail address: xiawj@hit.edu.cn (W. Xia).

there existed some drawbacks including lower yields (20%–60%), particularly for substituted aromatic and aliphatic aldehydes and long reaction time from 24 to 36 h [23]. Subsequently, more complex multistep approaches could lead to higher overall yields but lack the simplicity of one-pot cyclocondensation protocols [24–26]. Previous work found that Lewis acids could catalyze one-pot Biginelli reactions, however, some of the reagents are expensive, harmful, and difficult to recover due to homogeneous phase, and some nanocomposites needed sophisticated preparation procedure [27–30].

It has been widely recognized that organic esters prepared from carboxylic acids and alcohols are important fine chemicals due to their practical application in the production of fragrances, polymers, plasticizers, biofuels, and emulsifiers [31–33]. The pioneering work of polyesterification catalyzed by dodecylbenzene sulfonic acid (DBSA) was reported by Saam et al. [34,35]. Subsequently, Landfester et al. and Takasu et al. reported that DBSA and scandium trisdodecylsulfate [Sc(DS)₃] could catalyze polyesterification, respectively [36,37]. And another representative work on esterification is systematically studied by Kobayashi et al. [38]. Additionally, DBSA, copper dodecylbenzene sulfonate (CDBS) and cerium(III) trisdodecylsulfate trihydrate [Ce(DS)₃·3H₂O] could also effectively catalyze the solvent-free esterification reaction [17,18]. It is worth mentioning that DBSA or CDBS is trivial to separate from the reaction system after reaction, and Ce[DS]₃·3H₂O has severe hygroscopicity, which make it inconvenient for practical application.

Herein, we present the work on synthesis and characterization of Ce(III) trislaurylsulfonate, an air stable LASCs, and its application in catalyzing one-pot Biginelli reaction and solvent-free esterification reaction.

2. Experimental

2.1. Chemicals

All reagents and solvents were commercially available and were used as such.

2.2. General remarks

Morphologies and components of catalysts were performed on a field-emission scanning electron microscope (FE-SEM) (Model S-4300, Hitachi, Japan). Small angle X-ray diffraction (SAXRD) patterns were analyzed by Glancing-angle X-ray diffraction (GA-XRD; Philips X'Pert, Holland) using a CuK α radiation. Fourier transform infrared spectroscopy (FTIR) was recorded on a Perkin-Elmer 1710 Fourier transform spectrometer. Metal content in catalysts were measured by inductively coupled plasma-optical (ICP) emission spectroscopy (Optima 5300DV). ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained on Bruker AV-400 instrument, using CDCl₃ as solvent and TMS as reference. High resolution mass spectra were recorded in an Accurate Mass Q-TOF, LC/MS, Agilent Technologies 6520. Analyses of esters were measured by gas chromatography (GC) on a Tianmei GC-5790 chromatograph with FID detector, equipped with a polar polyethylene glycol column BP 20, 12 m, 0.32 i.d. and film thickness of 0.25 μ m. Oven temperature ranged from 200 to 250 °C, using a heating rate of 2 °C min⁻¹.

2.3. Catalysts preparation

Cerium(III) trislaurylsulfonate monohydrate (Ce[SO₃C₁₂H₂₅]₃ or denoted as Ce[LS]₃) was synthesized according to a published procedure as follows [39]. (i) 2.94 g of sodium laurylsulfonate (SLS, Aladdin, 98%) were added to 50 mL of distilled water and dissolved

Table 1
FT-IR assignments for SLS, as-prepared Ce[LS]₃, and recycled Ce[LS]₃ after four runs.

Item	Wavenumber (cm ⁻¹)			Assignments
	SLS	Ce[LS] ₃	Ce[LS] ₃ recycled	
Alkyl chain	2957, 2873	2956, 2873	2956, 2872	ν (CH ₃)
	2921, 2851	2918, 2850	2917, 2849	ν (CH ₂)
	1468	1468	1468	δ (CH ₂)
	1415	1413	1413	α -CH ₂
	1378	1377	1377	δ (CH ₃)
	722	722	722	—CH ₂ —
SO ₃ ⁻	533, 553,	522, 544,	522, 545,	SO ₃ ⁻
	619	605, 621	604, 621	
	1065, 1180,	1069, 1081,	1069, 1081,	SO ₃ ⁻
	1204	1166, 1186	1167, 1186	

at 60 °C in a water bath; (ii) 5.59 g of cerium(III) chloride heptahydrate (CeCl₃·7H₂O, Aladdin, 99%) were completely dissolved in 50 mL of distilled water at room temperature and warmed up at 60 °C in a water bath; (iii) after dissolution, the CeCl₃ solution was added under stirring, and the resulted slurry was stirred for 30 min. The white precipitate was filtered, recrystallized with hot distilled water for 3 times, and dried in vacuum at room temperature (25 °C) overnight.

Other catalysts were prepared following the similar procedure, and denoted as La[LS]₃, Fe[LS]₃, Co[LS]₃, Ni[LS]₂, Cu[LS]₂, Zn[LS]₂, and Mn[LS]₂. Ce[DS]₃ was also synthesized by the similar procedure except using sodium dodecylsulfate (SDS) instead of sodium laurylsulfonate (SLS) as starting material.

2.4. General procedure for the synthesis of 3,4-dihydropyrimidinones/thiones

To a mixture of aldehyde **1** (1 mmol), ethyl acetoacetate **2** (1.5 mmol) and urea or thiourea **3** (1.5 mmol) in a round-bottomed flask (10 mL), M[LS]_x (10 mol%) and one drop concentrated HCl in ethanol (3 mL) was added. The reaction mixture was stirred at 80 °C for 6 h in an oil-bath (Table 1). At the end of reaction (monitored by TLC), the mixture was poured into crushed ice/water mixture. Stirring was maintained for 5 min, and the solid mixture was filtered, washed with cold water (2 × 15 mL). Subsequently, the solid cake was dissolved in acetone, and the undissolved catalyst could be easily filtered. The acetone phase was collected and dried by rotavap, then the crude powder was recrystallized from ethyl acetate/*n*-hexane or ethanol to afford pure product. All products were identified by comparing their spectral and physical data with those of authentic samples. Used acetone could be recycled for next experiment, which was found to have no influence on reaction yield.

2.5. General procedure for the synthesis of esters

Carboxylic acid (1 mmol), alcohol (6 mmol) and 5 mol% catalyst were added to a 10 ml round-bottom flask with a reflux condenser. The reaction mixture was continuously stirred using a magnetic stirrer (800 rpm) at 80 °C in an oil-bath for an appropriate time, and the progress of reaction was monitored by TLC. At the end of reaction, the mixture was cooled to room temperature and poured into water. Afterwards, the filtered cake was purified by chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as eluent to give the pure product.

Download English Version:

<https://daneshyari.com/en/article/65138>

Download Persian Version:

<https://daneshyari.com/article/65138>

[Daneshyari.com](https://daneshyari.com)