

Conversion of Amides to Esters via Selective Cleavage of Amide C–N Bonds over a CeO₂ Catalyst

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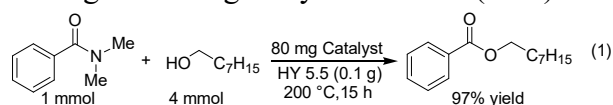
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Amide groups are present in a broad range of natural and synthetic compounds. Despite its importance as key building blocks for such compounds, synthetic application of amide is limited owing to poor electrophilic nature and resonance stability of amide bond. As a consequence of the difficulties, cleaving C–N bond of amide still remains challenging and attracts much interests. In particular, so much effort has been devoted to alcoholysis reactions of amides. Although various non-catalytic methods of amide alcoholysis have been reported, they suffer from use of excess amount of promoters such as HCl and NaNO₂ as well as generation of resultant wastes. There has been substantial progress by utilizing homogeneous catalytic systems in recent years that enables conversion of amides to esters via alcoholysis reactions [1-2]. In these cases, however, the processes require additives and/or the use of elaborate catalytic ligand such as NHC, and difficulties are encountered with catalyst recycling [2]. In order to realize environmentally benign processes and large-scale applications, catalyst employed for these transformation reactions should be readily prepared, heterogeneous, and recyclable [3]. We herein report a general catalytic system for direct C–N bond cleavage to one-pot esterification of several tertiary amides with alcohols under additive-free condition using CeO₂ as reusable heterogeneous catalyst.

CeO₂ (JRC-CEO2) supplied from the Catalysis Society of Japan was calcined at 600 °C for 3 h and used as a catalyst. Typical catalytic reactions condition is as follows: amide (1.0 mmol), alcohol (4.0 mmol), CeO₂ (80.0 mg) and *n*-dodecane (0.3 mmol) as an

internal standard were added to a Pyrex reaction tube (18.0 ml). HY zeolite (0.1 g) wrapped by a filter paper was also placed at the upper portion of the reaction tube for removal of formed amine as a byproduct. The reaction mixture was heated at 200 °C and stirred for 15 h under N₂ atmosphere. After completion of the reaction, the products were analyzed by GC, GC-MS and ¹H-NMR.

The catalyst was screened with the following model reaction (1). Among various metal oxide and solid acid catalysts tested (metal oxides: CeO₂, CaO, MgO, ZnO, TiO₂, ZrO₂, Nb₂O₅, Al₂O₃, SiO₂, Fe-mont, solid acids: Amberlyst-15, HBEA-150, Niobic acid, Nafion-SiO₂), CeO₂ gave the highest yield of ester (97%).



Subsequently, substrate scope was investigated to show potential applicability of the CeO₂-catalyzed system. Various alcohols containing cyclic, linear, aliphatic and aromatic moieties were efficiently converted to give the esters. In addition to the scope of alcohols, amide substrate scope was also investigated by employing 1-octanol (Fig. 1). The obtained results indicate that the proposed catalytic system is applicable to various amides.

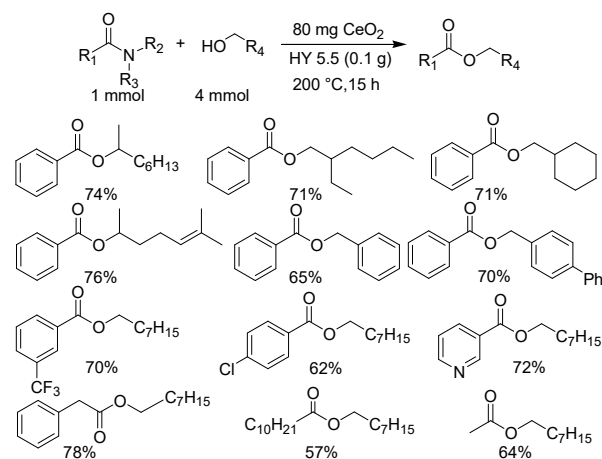


Fig.1 Substrate scope for CeO₂-catalyzed ester formation reaction from various amides and alcohols.

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