



Short Communication

Supported cobalt oxide nanoparticles as efficient catalyst in esterification and amidation reactions

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ABSTRACT

Co/SBA-15 nanoparticle catalysts (CoNP) were prepared using a commonly adapted synthetic route and then utilised for esterification and amidation reactions using aromatic and linear chain compounds for the production of long chain esters and amides. The study shows that the use of CoNP catalysts favours the use of aromatic reactants with electron donating substituents specifically in the *para* position. For the amidation reaction, good to excellent yields were obtained demonstrating tolerance towards differently substituted aromatic compounds. Overall, the synthesized catalysts proved to be efficient and highly versatile, and recyclable under the investigated conditions.

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1. Introduction

Biodiesel is a form of biofuel mainly composed of long chain methyl esters. Derived usually from triglycerides, biodiesel is a good substitute of traditional fossil fuels [1]. Studies have shown that carbon emissions from biodiesel are significantly lower than that of fossil fuels [2]. Biodiesel can be easily derived from renewable sources (such as plants, animal fat), although because of food security [3] (e.g. food vs fuel), issues on the cost of separation, and downstream processing, alternative biodiesel feed stocks and biofuels are currently being explored. The industrially adapted method for the preparation of biodiesel involves a homogeneous base catalysed process which generates soap by-products which are hard to separate. Downstream processing is even more difficult for two reasons: 1) the final products should be neutralized to remove the residual catalyst base, and 2) the soap formed also has surfactant properties that allow them to adhere to the methyl ester fraction during liquid–liquid separation [4].

Many solid acid catalysts have already been proposed for esterification reactions, more specifically for the synthesis of long chain ester compounds (e.g. biodiesel-like biofuels). Solid acid catalysts include –SO₃H functionalized ionic liquid catalysts for biodiesel conversion of rapeseed oil. In this study, hexamethylene triamine and butane sulfonates were mixed together to form a zwitterionic catalyst that is easily

separable from the organic phase of the liquid mixture [5]. Another type of solid catalysts is water-tolerant heteropolyacid catalysts (Cs_{2.5}H_{0.5}PW₁₂O₄₀) with metals possessing Lewis acidity which work with free fatty acids at low temperatures [6]. Aside from heterogeneous acid catalysts, basic metal oxides are also used to kinetically favour the reaction, having been shown to perform the conversion at much shorter times. An example of a metal-oxide catalyst that is able to provide yields >90% of methyl esters is alkali-doped metal oxide (CaO and MgO) [7]. Other innovations for esterification/transesterification processes include the use of supercritical conditions in order to easily separate products from reactants [8]. Metal-layered hydroxides have also been reported for biodiesel synthesis because of their crystalline structure and surface basicity [9,10]. Efficient enzymatic catalysts have also been used in both esterifications and transesterification reactions but sparingly utilised in some cases due to their deactivation at higher temperatures and difficult separation (only improved in immobilized biocatalysts— i.e. lipases) [11,12].

The synthesis of amides, on the other hand, is one of the most fundamental and significant subjects in organic chemistry. Amides play vital roles in versatile biological systems such as proteins and peptides as well as pharmaceuticals, natural products, material chemistry, and polymers [13]. Syntheses of amides are traditionally carried out through the reaction of carboxylic acids [13, 14] and activated carboxylic acids derivatives such as chlorides [15], anhydrides [16], esters [17] and acyl azides [18] with amines. Alternative approaches such as the Staudinger ligation [19], Beckmann rearrangement [20] and the Schmidt–Abue rearrangement [21] have also been developed. Despite considerable progress in this area, most procedures suffer from

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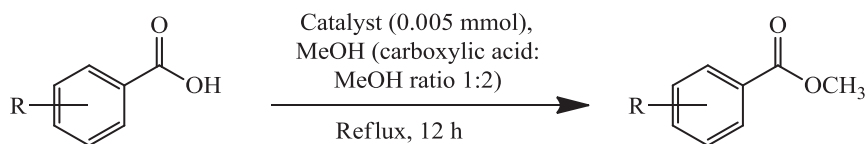


Fig. 1. Overall catalytic reaction scheme for the esterification reactions.

drawbacks including harsh reaction conditions, the use of costly transitional metal catalysts, a limited substrate scope and/or toxic solvents. Most of the developed catalytic systems are homogeneous and cannot be efficiently separated from the product; thus contaminating final products.

Following recent efforts from the group in the design of heterogeneous catalysts for oxidation reactions [22], we report herein the catalytic activities of novel supported heterogeneous catalytic nanomaterial (Co/SBA-15, CoNP) in esterification and amidation reactions. We performed oxidation reactions of aldehydes by adding oxygen and nitrogen groups to the carbonyl carbon. The esterification reactions will be of primary importance for the synthesis of biodiesel and similar fuel substitutes, while the amidation reaction will prove useful for the synthesis of Weinreb amide, which is an industrial precursor of ketones. In this paper, we mainly show that metal-supported catalysts can be used for different oxidation reactions in very good yields under non-conventional reaction conditions such as microwave, ball-milling, and solvent-less medium. Unlike other catalysts, nanomaterials are attractive catalysts due to their large surface area and excellent properties (different from bulk metals) that can interact with more reactant molecules at one time [23]. To demonstrate the versatility of the catalyst, we show here that it is possible to add cyclic nitrogen precursors to aldehydes with the catalyst.

2. Experimental procedure

Unless otherwise stated, all reagents and chemicals in this study were used as received and were not further purified (from Sigma Aldrich Co.). Nitrogen adsorption/desorption experiments were carried out using a Coulter SA3100 surface area analyser.

Prior to analysis, samples were de-gassed at 130 °C for 5 h. Surface areas were determined using the BET equation. The metal

content in the materials and filtrate after reuse were determined using inductively coupled plasma (ICP) in a Philips PU 70000 sequential spectrometer equipped with an Echelle monochromator (0.0075 nm resolution). Solid samples were digested in HNO₃ and subsequently analyzed by ICP.

2.1. Material preparation

Co/SBA-15 (CoNP) catalyst was prepared according to the procedure previously reported by our research group [23]. This method is also used in many similar syntheses and is therefore highly reproducible. Briefly, 2 mmol 3-aminopropyl (trimethoxy) silane was added to a mixture of salicylaldehyde (2 mmol) and excess MeOH. Then, 1 mmol of Co precursor, Co(OAc)₂·2H₂O, was added to the solution with stirring. The new mixture was stirred for 3 h until the color changed from pink to olive green. In parallel, SBA-15 was prepared according to previously reported methods used by our lab [24] where 750 mL of 6 M HCl was added to P123-coated Teflon bottles till complete dissolution, followed by the addition of tetraethyl orthosilicate (TEOS). The mixture was left stirring and subsequently aged at 100 °C for 24 h. The complex and the SBA-15 were eventually mixed with stirring overnight. The resulting solution was subjected to rotary evaporation, and the solids were dried twice in the oven (80 °C).

2.2. Esterification reactions

Esterification reactions in this study were performed using CoNP catalysts. In a typical reaction, 0.005 mmol of CoNP (0.5 mol.%) was added to a mixture of carboxylic acid precursor (1 mmol) and excess MeOH (molar ratio 1:2) under reflux conditions for 12 h. As soon as the reaction was judged complete using thin-layer chromatography (TLC), the catalyst was separated from the mixture through filtration and then washed with portions of 20 mL ethyl acetate. The product was isolated using a liquid–liquid extraction procedure and dried using Na₂SO₄.

2.3. Amidation reactions

The amidation reaction was first conducted between benzaldehyde, piperidine, CoNP (0.5 mol.%) as catalyst, and hydrogen peroxide as oxidant. The reaction was conducted at 70 °C for 1–5 h depending on the substrates. Subsequently, the catalyst was tested with various substrates and nitrogen precursors.

Table 1
Esterification of various carboxylic acids catalysed by supported cobalt nanoparticles.

Carboxylic acid	Ester product	Isolated yield (%)
		98
		98
		96
		90
		88
		92
		94

Reaction conditions: 1 mmol acid, 2 mmol MeOH, 0.5 mol.% CoNP, reflux, 12 h reaction.

Table 2
Effects of substituent position to the esterification reaction.

Carboxylic acid	Ester product	Isolated yield (%)
		95
		90
		98

Reaction conditions: 1 mmol acid, 2 mmol MeOH, 0.5 mol.% CoNP, reflux, 12 h reaction.

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