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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.

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 $-SO_3H$ 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 heterogeneous heteropolyacid catalysts ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) 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 deactivationat 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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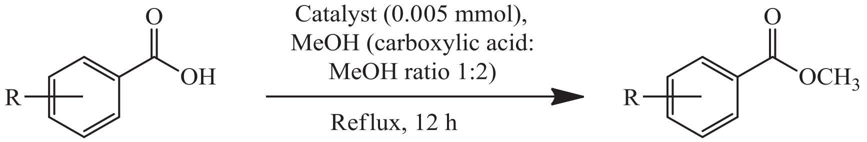


Fig. 1. Overall catalytic reaction scheme for the esterification reactions.

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.

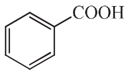
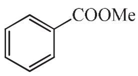
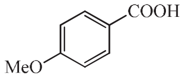
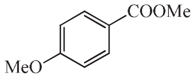
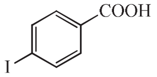
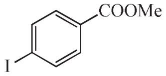
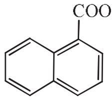
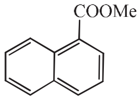
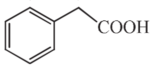
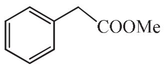
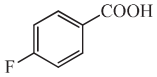
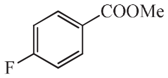
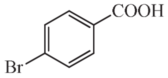
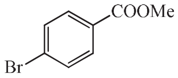
Following recent efforts from the group in the design of heterogeneous catalysts for oxidation reactions [22], we report herein the catalytic activities of novel supported heterogeneous catalytic nanomaterial (Co/SBA-15, CoNP) in esterification and amidation reactions. We performed oxidation reactions 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 excelling 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 HNO_3 and subsequently analyzed by ICP.

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.

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, $Co(OAc)_2 \cdot 2H_2O$, 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).

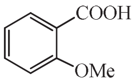
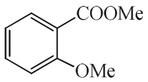
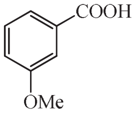
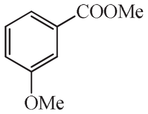
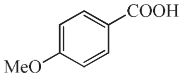
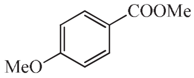
2.2. Esterification reactions

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 Na_2SO_4.

2.3. Amidation reactions

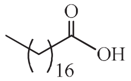
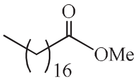
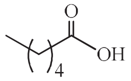
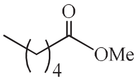
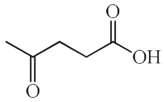
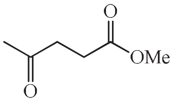
The amidation reaction was first conducted between benzaldehyde, piperidine, CoNP (0.5 mol.%) as catalyst, and hydrogen peroxide as oxidant. The reaction was conducted at 70 °C for 1–5 h depending on the substrates. Subsequently, the catalyst was tested with various substrates and nitrogen precursors.

Table 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.

Table 3
Catalytic activity of the CoNP with linear substrates.

Carboxylic acid	Ester product	Isolated yield (%)
		92
		90
		84

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

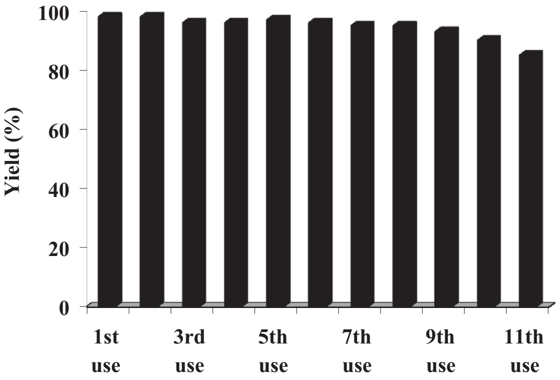


Fig. 2. Reuses of the CoNP catalyst in the esterification of benzoic acid with methanol. Reaction conditions (each run): 1 mmol benzoic acid, 2 mmol MeOH, 0.5 mol.% CoNP, reflux, 12 h reaction.

3. Results and discussion

3.1. Esterification reactions

Surface and textural properties of CoNP have already been reported [24]. Cobalt loading was around 0.3 mmol g^{-1}. Further characterization results of the CoNP indicated a surface area of 450 $m^2\ g^{-1}$, with a pore size of 3.6 nm and 0.77 $cm^3\ g^{-1}$ mesoporous pore volume, with an excellent homogeneous dispersion of the cobalt oxide species on the SBA-15 support.

The catalyst was tested using different aromatic and linear-chain carboxylic acids. Based on Table 1, the esterification yield was found to increase with increasing electron-donating ability of the substituent in the aromatic ring (Fig. 1). This trend is mainly because of the ability of the electron donating substituents to stabilize reaction intermediates [25,26]. Additionally *ortho*- and *para*-methoxylated aromatic rings produced almost identical yields as compared to *meta*-substituted carboxylic acids. These findings indicate that the position of the substituent does not play a significant role in product formation (Table 2).

Esterification reactions were then conducted with straight chain carboxylic acid reactants (Table 3) to investigate the possibility of extending the scope of the reaction to biodiesel-like molecules and related esters derived from biomass (e.g. levulinic acid). The increased number of carbons affects the yield of the esterification by reducing the amount of dissolved methanol that interacts with the substrate [28]. Normally, high fatty acid:methanol ratios are utilised to drive the reaction equilibrium to product formation for longer chain fatty acids. The proposed method appears to favour substrates with electron donating properties that stabilize the ion complex formed [26]. Notably, the yield decreased considerably when a keto-acid such as levulinic acid was used. We believe that this could be due to the competing nucleophilic addition reaction which affects the esterification equilibrium.

Table 4
Screening of reaction conditions in the oxidative amidation of benzaldehyde and piperidine.

Entry	Catalyst loading (mol.%)	Oxidant	Solvent	T (°C)	Yield (%)[a]
1	–	H_2O_2	CH_3CN	RT	11[b]
2	0.3	–	CH_3CN	RT	12[b]
3	0.3	H_2O_2	CH_3CN	RT	22
4	0.3	H_2O_2	CH_3CN	70	38
5	0.3	TBHP	CH_3CN	RT	56
6	0.3	TBHP	CH_3CN	70	48
7	0.3	TBHP	CH_2Cl_2	70	41
8	0.3	TBHP	Solvent free	60	40
9	**0.5**	$\mathbf{H_2O_2}$	**Solvent free**	**70**	**96**
10	**0.5**	$\mathbf{H_2O_2}$	$\mathbf{CH_3CN}$	**70**	**98**
11	0.5	TBHP	H_2O	70	65
12	0.5	TBHP	CH_3CN	70	96

[a] Isolated yield.
[b] Only benzoic acid was detected.

Upon reaction completion, the catalyst was recovered by filtration, washed and finally dried at 70 °C. A new reaction was then performed with fresh reactants under identical conditions. As seen in Fig. 2, one remarkable property of CoNP is its reusability (Fig. 2). The catalyst was repeatedly used ten times (i.e. using benzoic acid as starting carboxylic acid) without any significant loss in activity, demonstrating the stability of the catalyst under the employed conditions. No cobalt was found in solution upon successive reuses as measured by ICP/MS.

3.2. Amidation reactions

The oxidative amidation of aldehydes with amines was subsequently explored using Co-SBA-15 (Fig. 3).

Results in Table 4 show that the nature of the solvent played a significant effect on the yield of the model reaction. Aprotic polar solvents such as acetonitrile proved to be suitable for this oxidative addition reaction. Among the oxidants examined, TBHP (*tert*-butylhydroperoxide) and H_2O_2 proved to be highly efficient for the model reaction (entries 9–11). Increased amounts of catalyst up to 0.5 mol.% also provided improved results (Table 4, entries 9–12). Interestingly, the reaction could still afford an excellent yield of amide products under solvent-free conditions (entry 9).

Encouraged by the promising results obtained for the amidation of benzaldehyde and piperidine, the scope and utility of the protocol were extended to a variety of aldehydes and amines under solvent-free conditions. Results included in Figs. 4 and 5 prove that CoNP is also a highly active catalyst for the oxidative addition of aldehydes to amines, providing good to excellent yields of amides. The reaction also

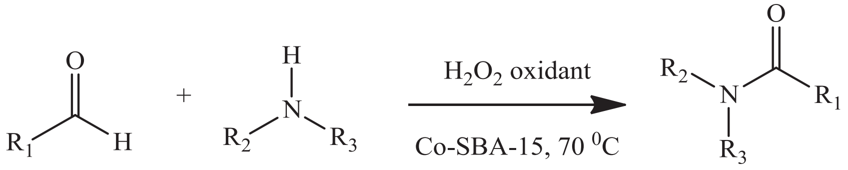


Fig. 3. Oxidative amidation of aldehydes with amines using CoNP.

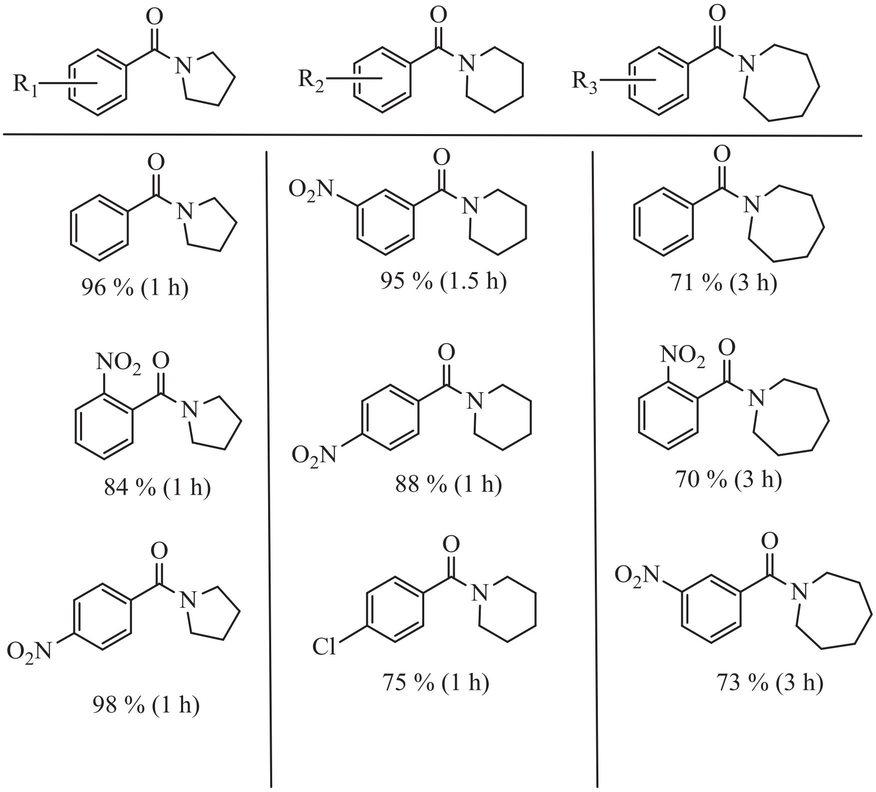


Fig. 4. Amide yields and time of reaction in the oxidative addition of aldehydes to cyclic amines.

showed great tolerance towards electron-withdrawing and donating substituents in the aromatic ring of the starting aldehydes. Particularly, aryl aldehydes bearing an electron-withdrawing group such as $-NO_2$, $-Cl$ gave relatively higher product yields. Changing the position of the nitro-group on the benzene ring from *para*- to *meta*- did not affect the yield of the desired products. However, the oxidative coupling reaction afforded a moderate yield of the corresponding amide in the case of 2-nitrobenzaldehyde. Aliphatic aldehydes including phenylpropanal, 2-

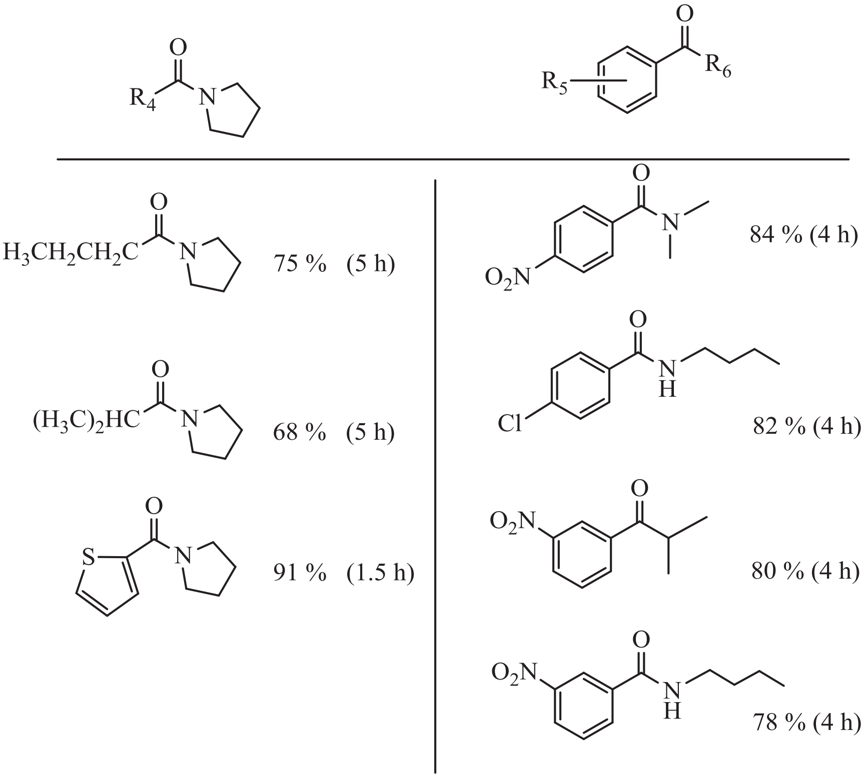


Fig. 5. Amide yields and time of reaction in the oxidative addition of aldehydes to cyclic and aliphatic amines.

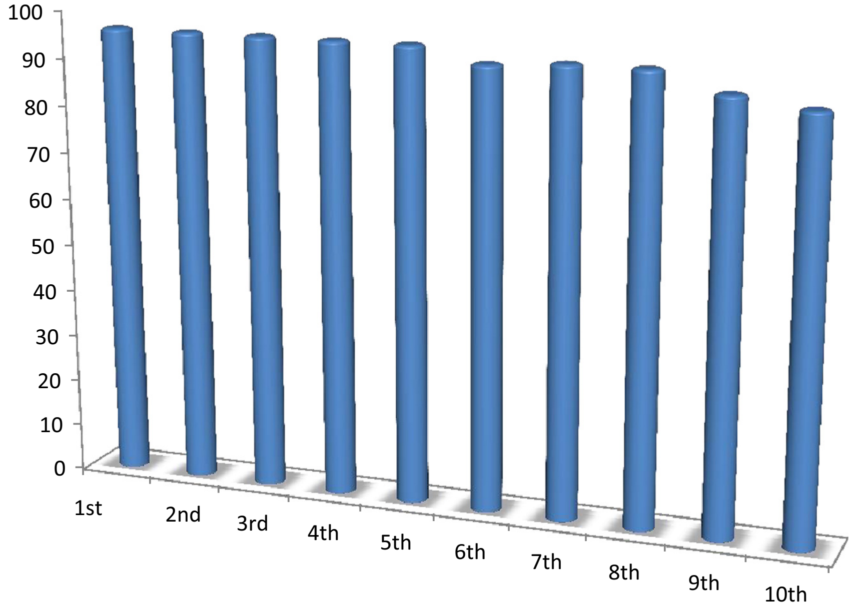


Fig. 6. Reusability studies of CoNP [conversion (mol.%) vs number of reuses] in the oxidative amidation under solvent-free conditions. Reaction conditions: 1 mmol benzaldehyde, 1 mmol piperidine, 0.3 mL H_2O_2 30%, 0.017 g catalyst, 70 °C, 1 h.

methylpropanal, and butanal could be converted into the corresponding aliphatic amides in good yields (Fig. 5).

It is also important to note that the kinetics of the reaction tend to be higher when aromatic aldehydes and cyclic amines are used, as observed in increased reaction times when aliphatic amines were used. This observation could be due to the ability of aromatic aldehydes to stabilize (through the aromatic system) the resulting intermediate, which leads to the formation of both kinetically and thermodynamically favored product.

Reusability results are depicted in Fig. 6 which clearly demonstrate the high stability and reusability of the nanocatalyst after several uses. Upon completion of the first reaction to afford an excellent yield of the corresponding amide, the catalyst was recovered by filtration, washed and finally dried at 70 °C. A new reaction was then performed with fresh reactants under identical conditions. We found that CoNP (0.5 mol.%) could be successfully recycled in ten successive amidation runs to afford the corresponding amide in an average 95% isolated yield. ICP-MS analysis of the reaction mixture indicated no detectable cobalt leaching (<0.05 ppm) under the investigated conditions, in good agreement with reusability data with the high stability and activity of the supported CoNP catalyst. However, due to the aggregation and sintering, catalyst deactivation was gradually observed after 10 runs.

4. Conclusions

This study presents a highly efficient method for esterification reactions which can be in principle further translated to a more complex transesterification process. Using the proposed Co-supported system, ester yields up to 98% could be achieved for a range of products from the esterification of linear to aromatic carboxylic acids and methanol. Furthermore, kinetic considerations seem to be predominantly affecting yields based on esterification trends. Recycling of the catalyst also proved its stability up to 10 runs of reaction for both esterifications and amidations. The recyclability of the catalyst clearly shows its promising role as heterogeneous catalyst in acid-catalysed processes.

Acknowledgments

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References

[1] A. Murugesan, C. Umarani, R. Subramanian, N. Nedunchezhian, Renew. Sust. Energ. Rev. 13 (2009) 653–662.
[2] A. Monyemand, J.H. Van Gerpen, Biomass Bioenergy 20 (2001) 317–325.
[3] D. Boddiger, Lancet 370 (2007) 923–924.
[4] J.H. Van Gerpen, Fuel Process. Technol. 86 (2005) 1097–1107.
[5] X. Liang, J. Yang, Green Chem. 12 (2010) 201–204.
[6] F. Chai, F. Cao, F. Zhai, Y. Chen, X. Wang, Z. Su, Adv. Synth. Catal. 347 (2007) 1057–1065.
[7] C.S. MacLeod, A.P. Harvey, A.F. Lee, K. Wilson, Chem. Eng. J. 135 (2008) 63–70.
[8] S.J. Yoo, H. Lee, B. Veriansyah, J. Kim, J. Kim, Y. Lee, Bioresour. Technol. 101 (2010) 8686–8689.
[9] J. Shumaker, C. Crofcheck, S.A. Tackett, E. Santillan-Jimenez, T. Morgan, Y. Ji, M. Crocker, T.J. Toops, Appl. Catal. B 82 (2008) 120–130.
[10] D.G. Cantrell, L.J. Gillie, A.F. Lee, K. Wilson, Appl. Catal. A 287 (2005) 183–190.
[11] H. Noureddini, X. Gao, R.S. Philkana, Bioresour. Technol. 96 (2005) 769–777.
[12] M. Iso, B. Chen, M. Eguchi, T. Kudo, S. Shrestha, J. Mol. Catal. B 16 (2001) 53–58.
[13] E. Valeur, M. Bradley, Chem. Soc. Rev. 38 (2009) 606–631.
[14] R. Luque, V. Budarin, J.H. Clark, D.J. Macquarrie, Green Chem. 11 (2009) 459–461.
[15] A. Brennführer, H. Neumann, M. Beller, Angew. Chem. Int. Ed. 121 (2009) 4176–4196.
[16] G.E. Veitch, K.L. Bridgwood, S.V. Ley, Org. Lett. 10 (2008) 3623–3625.
[17] Z. Fu, J. Lee, B. Kang, S.H. Hong, Org. Lett. 14 (2012) 6028–6031.
[18] E. Saxon, C.R. Bertozzi, Science 287 (2000) 2007–2010.
[19] N.A. Owston, A.J. Parker, J.M.J. Williams, Org. Lett. 9 (2007) 3599–3601.
[20] K. Tani, B.M. Stoltz, Nature 441 (2006) 731–734.
[21] R. Luque, J.H. Clark, ChemCatChem 3 (2011) 594–597.
[22] J.M. Campelo, D. Luna, R. Luque, J.M. Marinas, A.A. Romero, ChemSusChem 2 (2009) 18–45.
[23] F. Rajabi, R. Luque, J.H. Clark, B. Karimi, D.J. Macquarrie, Catal. Commun. 12 (2011) 510–513.
[24] M. Ojeda, A.M. Balu, V. Barrón, A. Pineda, Á.G. Coleto, A.Á. Romero, R. Luque, J. Mater. Chem. A 2 (2014) 387–393.
[25] G.A. Olah, Acc. Chem. Res. 4 (1971) 240–248.
[26] J.Y. Cho, C.N. Iverson, M.R. Smith, J. Am. Chem. Soc. 122 (2000) 12868–12869.