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Published in:
Catalysis Science and Technology

Link to article, DOI:
[10.1039/c9cy00271e](https://doi.org/10.1039/c9cy00271e)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Modvig, A. E., & Riisager, A. (2019). Selective formation of formic acid from biomass-derived glycolaldehyde with supported ruthenium hydroxide catalysts. *Catalysis Science and Technology*, 9(16), 4384-4392. <https://doi.org/10.1039/c9cy00271e>

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Selective Formation of Formic Acid from Biomass-derived Glycolaldehyde with Supported Ruthenium Hydroxide Catalysts

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Abstract

Ceria-supported ruthenium hydroxide catalysts, $\text{Ru}(\text{OH})_x/\text{CeO}_2$, comprising micro- and nanoparticle supports were prepared, characterized and examined for the catalytic aerobic oxidation of glycolaldehyde (GAD) to formic acid (FA) in water under mild and base-free conditions. Under optimized reaction conditions, both of the examined catalyst types gave high FA yield around 80% at full GAD conversion with low CO_2 formation (>95% carbon balance), while intermediate oxidation products were obtained at milder conditions and humins dominated at more harsh conditions. The nanoparticle catalysts were more active than analogous catalysts based on microparticle ceria, which had lower BET surface area and lower content of surface $\text{Ru}(\text{OH})_x$ species relatively to other Ru-species. Notably, the superior nanoparticle-based catalyst also proved reusable in three consecutive reaction runs with essentially unchanged catalytic performance. The study demonstrate a benign and green protocol to convert GAD - a versatile platform molecule obtainable from biomass-derived carbohydrates – into the large-volume commodity chemical FA which has multiple industrial applications.

Keywords: Formic acid; glycolaldehyde; oxidation; ruthenium hydroxide; heterogeneous catalysis

1. Introduction

Increasing environmental concerns and more strict legislation require development of sustainable chemical processes relying on alternatives to fossil feedstock. In this context, the high carbon-content of lignocellulosic biomass comprised in polymeric carbohydrates and lignin (44-53%) render forestry, agro- and agricultural biomass promising renewable sources for production of carbon-containing bulk and fine chemicals.^{1,2}

Thermal degradation of biomass-derived carbohydrates result in formation of the smallest α -hydroxy sugar, glycolaldehyde (GAD), as a by-product. Alternatively, GAD can be produced in higher yields from glucose in critical water and from bio-oils.³⁻⁵ GAD is reactive and can be transformed into several other chemicals with important applications, including diamines or ethanolamines by direct amination (polymers and pharmaceuticals),⁶ C6 and high-value C4 sugars by aldol condensation (food and pharmaceuticals),^{7,8} lactic acid and ethylene glycol by hydrothermal treatment and hydrogenation (polymer building blocks)⁹⁻¹¹ and glyoxal/glycolic acid/glyoxylic acid by oxidation.¹²⁻¹⁴ This large reaction diversity makes GAD a versatile biomass-derived platform molecule with potential to be explored also as starting material for other attractive commodity chemicals like formic acid (FA).

FA is globally produced on an annual scale of 0.6 Mt and used in several industries and products, including leather, agricultural, pharmaceutical, chemical, textile, rubber and catalysis.¹⁵⁻¹⁷ More recently, FA has also been found feasible for hydrogen storage due to its fast and selective release of H₂ and CO₂ under mild conditions.^{18,19} Currently, FA is predominantly produced in industry by a two-step gas-phase process involving formation of methyl formate from methanol and CO followed by hydrolysis of methyl formate, affording FA and methanol which is recycled.¹⁶ However, a liquid-phase oxidation process using water as solvent where carbohydrates and other forms of biomass affords FA in high yields has recently been commercialized using a vanadium-substituted heteropolyacid catalyst.^{20,21} The catalyst system is homogeneous, but easy catalyst separation and reuse would be obtained by use of a heterogeneous catalyst.

Heterogeneous ruthenium-based catalysts have been widely applied for oxidations,²²⁻³⁰ hydrogenations³¹⁻³⁴ amination,³¹ C-C bond formation,^{35,36} etc. Additionally, catalytic upgrading of biomass and derived compounds have been reported over various supported ruthenium oxide catalysts.^{16,36-42} The many applications of ruthenium in catalysis has rendered it a very well-studied metal in both homogeneous and heterogeneous systems.⁴³⁻⁵⁴ More recently, Mizuno and Yamaguchi reported high activity of supported ruthenium hydroxide catalysts (Ru(OH)_x/support) in liquid-phase oxidations of alcohols, aldehydes and amines.⁵⁵⁻⁵⁹ The catalysts were easily prepared by deposition-precipitation and dried at low temperature without further activation by calcination or reduction, affording highly dispersed ruthenium hydroxide species on the support surface.⁵⁹ The ruthenium hydroxide species provide a Lewis acid site on the ruthenium center and a Brønsted basic site of the hydroxide group within the same catalyst. Oxidation of ethanol to acetic acid has previously been reported by our group over a microparticulate ceria-supported ruthenium hydroxide catalyst, where the ceria support was selected due to its oxygen transfer properties.⁴⁰

In this work, catalysts based on ruthenium hydroxide supported on nano- and microparticulate ceria (*i.e.* Ru(OH)_x/CeO₂) were studied for the oxidative conversion of GAD into FA under mild conditions with oxygen as oxidant in a base-free aqueous media (Scheme 1). Water was selected as solvent since biomass-derived GAD typically is produced by aqueous-phase reforming, and because aerobic oxidation is safe to perform in aqueous media, which is not the case for many organic solvents. The formation of FA with supported Ru(OH)_x is proposed to proceed via a mechanism involving oxidative dehydrogenation of the hydrated aldehyde (geminal diol) of

GAD, which is dominant in aqueous solution, with the ceria support providing stabilization for intermediate surface Ru-species. The introduced catalytic process demonstrate a benign and green route to produce the versatile commodity chemical FA from a feedstock derived from biomass.

Scheme 1: Aerobic oxidation of glycolaldehyde (GAD) to formic acid (FA) with ruthenium hydroxide supported on ceria nano- or microparticles.

2. Experimental

2.1 Materials

Ruthenium(III) chloride (purum, ~41% Ru, Sigma-Aldrich), cerium(IV) oxide (<50 nm “nano”, ≥99.9%, Sigma-Aldrich), cerium(IV) oxide (<5 μm “micro”, ≥99.9%, Sigma-Aldrich), sodium hydroxide (≥98%, Sigma-Aldrich), glycolaldehyde dimer (GAD, Sigma-Aldrich), formic acid (FA, ≥98%, Sigma-Aldrich), oxygen (99.5%, Air Liquide Denmark), pressurized air (Air Liquide Denmark). All reagents were used without further purification.

2.2 Catalyst Preparation

Supported ruthenium hydroxide catalysts based on ceria nanoparticles (Ru1) and microparticles (Ru2) were prepared by deposition-precipitation according to published procedures.^{40,54,56,58,62,63} RuCl₃ (246.8 mg, 1.2 mmol) was dissolved in MilliQ water (143 mL) affording a solution with a ruthenium concentration 8.3 mM. Nano- or microparticulate CeO₂ support (9.76 g) was added to the solution which was left stirring for 15 min before the pH was adjusted to 13.5 by addition of 1M NaOH (~28 mL) and the mixture left stirring for additionally 18 h. Then, the catalyst was removed by filtration, washed thoroughly with MilliQ water until neutral pH of the filtrate was obtained and finally oven dried at 140 °C for 40 h.

2.3 Catalyst Characterization

Surface areas were determined from nitrogen physisorption at liquid nitrogen temperature on a Micrometrics ASAP 2020 apparatus. Samples were outgassed in vacuum at 150 °C for 6 h prior to measurements. The total surface areas were calculated according to the Brunauer–Emmett–Teller (BET) method. Transmission electron microscopy (TEM) images were recorded on a FEI Tecnai Transmission Electron Microscope operated at 200 kV. Samples were dispersed on a lacy amorphous carbon support film prior to the imaging. Energy dispersive X-ray spectroscopy (EDX) analysis were performed on an adjacent Oxford INCA system, coupled with a scanning electron microscope (SEM) from Quanta 200 ESEM FEG operated at 10 kV and spot size of 2.0. The ruthenium content was determined from the average of 4-7 measurements on selected areas of the analyzed samples. X-ray powder diffraction (XRPD) patterns were recorded using a Huber G670 powder diffractometer (Cu–Kα radiation, λ = 1.54056 nm) in the 2θ interval 3-100°. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a ThermoScientific system at room temperature with a monochromatic Al Kα X-ray source (1484.6 eV). Survey spectra were acquired by accumulating four sweeps in the range 0-1400 eV at a pass energy of 200 eV. Ru3p scan spectra were acquired by accumulating 40 sweeps in the range 450-510 eV at a pass energy of 50 eV. Spectral processing was carried out using Avantage 4.87 software using a Powell fitting algorithm and a Smart background subtraction for deconvolutions. Sample charging effects were eliminated by correcting the observed spectra with the Ce3d_{3/2} binding energy value of 900.00 eV.

2.4 Catalytic Oxidation of Glycolaldehyde

All oxidation reactions were performed in customized mini high-pressure reactors ($V = 18.4$ mL). The reactors were charged with GAD (5.9 mmol), $\text{Ru(OH)}_x/\text{CeO}_2$ (114.8 mg, corresponding to 0.23 mol% Ru) and MilliQ water (4.62 g). The reactors were then flushed and pressurized with oxygen gas (1-30 bar), heated to the desired temperature (23-150 °C) while constantly stirring at 500 rpm for 1-70 h. After the reaction, the high-pressure vessels were rapidly cooled to room temperature (23 °C) in an ice-bath, and the gas-phase collected for CO_2 analysis by IR (Quantek NDIR detector equipped with a Hammond Drierite drying tube) and the liquid-phase for product analysis by HPLC (Agilent Technologies 1200 equipped with an Aminex HPX-87H column from Bio-Rad, 300 mm x 7.8 mm x 9 μm , solvent: 5 mM H_2SO_4 , 24 °C with a flow rate of 0.3 mL/min).

3. Results and Discussion

3.1 Catalyst Characterization

The BET surface areas of the prepared Ru1 and Ru2 catalysts varied by approximately a ten-fold as a result of the different support particles sizes, and were both comparable to the pristine nano- and microparticulate ceria materials, respectively (Table 1). The metal content in the catalysts was determined from XRF and EDX analyses (Supporting Information, Figures S1-S2 and Table S1), affording ruthenium contents between 1.0-1.4 wt% in very good agreement with the expected value (1.2 wt%) from the catalyst syntheses.

Table 1: BET surface areas and ruthenium content of the prepared catalysts.

Entry	Catalyst	CeO ₂ support	BET Surface Area (m ² /g)		Ru Content (wt%) ^a	
			CeO ₂	Catalyst	XRF	EDX
1	Ru1	Nano	42	39	1.4 (0.6)	1.3 (0.4)
2	Ru2	Micro	3	3	1.0 (0.1)	1.1 (0.3)

^a Standard deviation in parentheses.

Ruthenium metal or ruthenium oxide nanoparticles were not observed on recorded TEM images of the catalysts (Figure 1), which is in line with previous observations for $\text{Ru(OH)}_x/\text{support}$ catalysts.⁶⁰ However, small particles surrounding the ceria support was observed, forming a veil-like constitution around the ceria particles (Figure 1a and 1c). The veil-like substance was most eminent in the images of Ru1, based on ceria nanoparticles.

The XRD diffraction pattern of Ru2 was found to be identical to the pattern recorded for the microparticulate ceria (Supporting Information, Figures S3-S4), revealing no crystallinity of the Ru(OH)_x phase in accordance with literature.⁴⁰ In contrast, difference in the diffraction patterns for Ru1 and the nanoparticulate ceria was observed as additional peaks appeared in the 2θ region 5-45° for Ru1. Notably, the additional peaks were apparently not associated to crystalline ruthenium or ceria species, and the lower 2θ region indicated a (sub)crystalline substance with a larger unit cell compared to that of ceria. Moreover, the peak width was comparable with that of the nanoparticulate ceria suggesting similar particle size of the unidentified crystalline specie (possibly an impurity). The identity of the crystalline specie remains presently unknown, but it could possibly be associated to the veil-like substance observed in TEM.

Figure 1: TEM images of Ru1 (a and b) and Ru2 (c and d) catalysts.

Figure 2: XPS Ru3p scan of Ru1 (top) and Ru2 (bottom) with freshly prepared catalysts (left) and calcined catalysts (350 °C) (right).

From XPS analysis, cerium, oxygen and ruthenium were detected in the survey spectra of Ru1 and Ru2 (Supporting Information, Figure S5). Deconvolution of the $Ru3p_{3/2}$ area afforded four different Ru-containing species typically assigned⁶⁴ to $Ru^{VI}O_3$, hydrous $Ru^{IV}O_2$ (i.e. $Ru(OH)_x$), $Ru^{IV}O_2$ and Ru^0 , which also previously have been identified in supported $Ru(OH)_x$ catalysts.⁶⁵ However, more recent and detailed analysis suggests that the peaks corresponding to the +6 oxidation state may be a satellite peak of hydrated/anhydrous $Ru^{IV}O_2$ and $Ru(OH)_x$ may be a $Ru(OH)_3$ phase with trivalent ruthenium.⁶⁶ The contribution from the Ru-species was compared based on the calculated area under the curves and presented in Figure 3. For the freshly prepared Ru1 and Ru2 catalysts, the predominant Ru-component was found to be $Ru(OH)_x$ (71 and 58%) which decreased to 35 and 22% after calcination, respectively. Instead, the area of RuO_2 increased indicating formation of RuO_2 on the surface induced by calcination, as expected.

Figure 3: XPS convoluted area distributions of the $Ru3p_{3/2}$ area (455-473 eV) of freshly prepared and calcined Ru1 and Ru2 catalysts.

3.2 Oxidation of Glycolaldehyde

Effect of temperature, pressure and reaction time

Aerobic oxidation of GAD was performed with the prepared $Ru(OH)_x/CeO_2$ catalysts Ru1 and Ru2 in base-free, aqueous medium at mild conditions. All reactions were analyzed for GAD, FA, CO_2 , acetic acid (AA), glycolic acid (GA), glyoxylic acid, glyoxal (GLO), oxalic acid (OA), formaldehyde, lactic acid, various tetroses and hexoses, however, only the major products FA, GA, GLO, AA and CO_2 (>2% yield) were quantified (Figure 4).

Figure 4: Major products of the oxidation of GAD to FA.

Initially, the effect of reaction temperature was studied (Figure 5). The GAD conversion and FA product selectivity increased with increasing temperature until reaching full conversion and maximum selectivity at 80 and 90 °C using the Ru1 (88.8% selectivity) Ru2 catalyst (81.7% selectivity), respectively. At these optimal temperatures (and below), an excellent carbon balance >95% was obtained for all reactions, whereas higher temperatures led to gradually decreased FA selectivity due to formation of humins and CO_2 resulting in lower carbon balance.

Figure 5: Effect of reaction temperature on the oxidation of GAD with Ru1 (left) and Ru2 (right) catalysts. Reaction conditions: GAD (356.1 mg, 5.9 mmol), Ru(OH)_x/CeO₂ (114.8 mg, 0.23 mol% Ru from 1.2 wt% Ru(OH)_x/CeO₂), H₂O (4.6 mL), O₂ (30 bar), 16 h, 500 rpm.

Next, the GAD oxidation was examined at various pressures of oxygen at 90 °C (Figure 6). Several condensation products and low FA selectivity was observed using 1 bar of O₂ for both of the Ru catalysts. Likewise, applying 10 bar of air (*i.e.* P_{O₂} ≈ 2 bar) also resulted in low FA selectivity and yield, possibly due to limited availability of oxygen in the aqueous phase under such moderate oxygen pressure due to low gas solubility. In line with this, significantly higher FA selectivity was obtained at higher partial pressure of oxygen reaching a maximum at 10 bar for both catalysts.

Figure 6: Effect of oxygen pressure on the oxidation of GAD with Ru1 (left) and Ru2 (right) catalysts. Reaction conditions: GAD (356.1 mg, 5.9 mmol), Ru(OH)_x/CeO₂ (114.8 mg, 0.23 mol% Ru from 1.2 wt% Ru(OH)_x/CeO₂), H₂O (4.6 mL), 90 °C, 16 h, 500 rpm.

Study of the reaction time showed that essentially full conversion (99.7%) was obtained after 8 h of reaction with the Ru1 catalyst, affording 80.5% yield of FA (Figure 7). Increasing the reaction time did not affect the FA yield (16-70 h), revealing either high product stability over time at the applied reaction conditions or gradual FA formation from the by-products GLO and GA which were almost fully converted over time. Changing the catalyst to the microparticulate-based Ru2 afforded close to full conversion only after 16 h (99.5%) and 81.9% FA selectivity, showing that the Ru2 catalyst was less active than Ru1 in agreement with the trend observed in the temperature study above. Moreover, with Ru2 the FA yield slightly decreased over time implying decreased product stability as the GLO and GA by-products remained largely unconverted. Hence, possibly also in the reaction with Ru1 was FA not entirely stable at prolonged reaction time.

Figure 7: Effect of reaction time on the oxidation of GAD with Ru1 (left) and Ru2 (right) catalysts. Reaction conditions: GAD (356.1 mg, 5.9 mmol), Ru(OH)_x/CeO₂ (114.8 mg, 0.23 mol% Ru from 1.2 wt% Ru(OH)_x/CeO₂), H₂O (4.6 mL), O₂ (10 bar), 90 °C, 500 rpm.

Effect of substrate concentration and catalyst loading

Since the Ru1 catalyst was found to be the most active of the prepared catalysts its catalytic performance was further studied at varied GAD concentrations and catalyst loadings (Figure 8). Relatively low GAD concentrations affected the catalytic activity negatively resulting in decreased GAD conversions and formation of trace amounts of various unidentified condensation products (Figure 8, left). Likewise, formation of humins was prominent at relatively high GAD concentrations, indicating that ~1.3 M was the optimal GAD concentration under the applied conditions (corresponding to the GAD concentration applied in the above-described results). When the Ru1 catalyst amount was increased an increased catalytic activity and FA yield was obtained (as expected), until a maximum was reached in Ru/GAD ratio corresponding to 0.23 mol% Ru (Figure 8, right). At higher catalyst loadings, the FA yield decreased due to humins formation.

Figure 8: Effect of the concentration of GAD (left) and Ru/GAD ratio (right) on the oxidation of GAD with Ru1 catalyst. Reaction conditions: GAD (356.1 mg, 5.9 mmol), Ru(OH)_x/CeO₂ (114.8 mg, 0.23 mol% Ru from 1.2 wt% Ru(OH)_x/CeO₂), H₂O (4.6 mL), O₂ (10 bar), 90 °C, 8 h, 500 rpm.

Varying the Ru loading to either 0.6 or 2.4 wt% in the nanoparticle-based ceria catalysts yielded the catalysts Ru3 and Ru4, respectively (see Supporting Information, Figure S1 and Table S1 for

XRF and EDX analysis). Application of these catalysts resulted in lower selectivity to FA compared to the Ru1 catalyst with 1.2 wt% Ru and formation of humins was pronounced with the low metal loading (Table 2 entries 3-5). Notably, a decreased catalytic activity was observed with the high Ru loading of 2.4 wt%, indicating formation of less active Ru species on the ceria surface. Absence of catalyst or use of ceria nanoparticles alone afforded only low GAD conversions (3.6-7.2%) and corresponding low FA yields (entries 1 and 2), as expected. Moreover, pre-calcination of the Ru1 catalyst led to a significant decrease in the FA selectivity to 56.8% (entry 6), mostly likely due to transformation of active Ru(OH)_x species on the surface to less active or inactive RuO₂ as also observed by the XPS analysis (Figure 3).

Table 2. Effect of ruthenium loading and reuse of nanoparticle-based ceria catalysts for the oxidation of GAD^a

Entry	Ru loading (wt%)	GAD Conversion (%)	FA Selectivity (%)	Product Yield (%)				
				GLO	GA	AA	FA	CO ₂
1	- ^b	3.6	37.6	0.5	0.0	0.0	1.4	0.0
2	- ^c	7.2	9.7	1.5	0.2	0.1	0.7	0.0
3	0.6	98.9	49.3	12.6	7.1	0.3	48.8	2.7
4	1.2	99.7	80.8	6.2	4.2	0.3	80.5	2.6
5	2.4	85.0	59.2	10.9	3.1	0.2	50.3	1.4
6	1.2 ^d	99.2	56.8	12.5	4.3	0.1	56.3	1.6
7	1.2 ^e	98.0	75.6	5.2	3.9	0.3	74.1	1.7
8	1.2 ^f	95.6	81.6	10.0	5.2	0.2	78.0	2.0

^a Reaction conditions: GAD (356.1 mg, 5.9 mmol), Ru(OH)_x/CeO₂ (0.23 mol% Ru), H₂O (4.6 mL), O₂ (10 bar), 90 °C, 8 h, 500 rpm. ^b Without added catalyst. ^c Nanoparticle ceria alone. ^d Pre-calcined Ru1 catalyst (350 °C, 6 h, static air). ^e First recycling of Ru1 catalyst. ^f Second recycling of Ru1 catalyst.

Catalyst reuse

Reusability of the Ru1 catalyst was assessed by performing consecutive reactions runs, where the catalyst between each run was isolated by filtration, thoroughly washed with water (MilliQ) until neutral pH of the filtrate followed by drying (140 °C, 40 h). The catalyst could successfully be recycled twice without any significant decrease in FA yield, which remained around 80% (Table 2 entries 4, 7 and 8). However, a minor decrease in GAD conversion occurred during the reuse suggesting a gradual decrease in catalyst activity, indicating that trace amounts of Ru species leached during recycling due to insufficient immobilization to the support. In line with this, elemental analysis by ICP on the reaction solution after the third catalyst recycle revealed presence of Ru, but reliable quantification was not possible due to concentration measurements close to the detection limit.

Reaction mechanism for GAD oxidation

Aerobic oxidation with supported Ru(OH)_x catalysts in water has been described to occur by a reaction mechanism involving oxidative dehydrogenation.⁶⁰ An analogous mechanism can also be elucidated for the formation of GLO, GA and OA via the hydrated form of GAD (i.e. germinal diol) which dominates in aqueous solution,⁶¹ whereas formation of FA (and AA) involving C-C cleavage is not directly deduced by this mechanism. Instead, a plausible mechanism for the oxidation of GAD to FA could involve condensation of the germinal diol of GAD with surface Ru(OH)_x species (I) affording the bridged Ru specie (II), which by oxidative cleavage releases two molecules of FA (Figure 9). The latter reaction step leaves two partially charged Ru species (III), possibly stabilized by the ceria surface. Finally, hydration of the partially charged Ru species regenerates Ru(OH)_x and a Ru-hydride specie (IV), which is re-oxidized by the oxygen to

regenerate the Ru(OH)_x species (I) via a peroxide intermediate, as also previously proposed with supported Ru(OH)_x catalysts.⁶³

Figure 9: Proposed reaction mechanism for the aerobic oxidation of GAD to FA in water with Ru(OH)_x/CeO₂.

Hydrothermal treatment of GAD under basic conditions can form FA and AA by reaction pathways comprising condensation intermediates such as, e.g. glyceraldehyde, dihydroxyacetone, formaldehyde, lactic acid, threose, lerythrulose, erythrose and acrylic acid (for details see supporting information Figure S1).⁹ In this study, the GAD oxidation reactions were performed without added base and none of the mentioned products were detected by analysis of the liquid reaction mixtures, indicating that such condensations were not dominating. However, since the Ru(OH)_x/CeO₂ catalyst contains both Lewis acidic- and Brønsted basic sites (as previously mentioned) some FA formation by aldol condensations and oxidation of formaldehyde via the Cannizzaro reaction cannot be excluded.

4. Conclusions

Catalysts based on ruthenium hydroxide supported on ceria were applied for selective aerobic oxidation of biomass-based GAD into FA in water under base-free conditions. Optimization of catalyst and reaction parameters, *i.e.* reaction time, temperature, O₂ pressure, GAD concentration, support and catalyst metal loading, resulted in formation of up to 80.8% FA yield at full GAD conversion at relative benign conditions of 10 bar O₂ and 80 °C using a catalyst based on nanoparticle ceria support. This catalyst could also be recycled in three consecutive reaction runs with only minor change in catalytic performance. In comparison, lower activity was generally obtained for catalysts based on ceria microparticles having lower surface area and less surface Ru(OH)_x species relatively to other Ru-species. Interestingly, all reactions performed at 80-90 °C resulted only in minor formation of CO₂ as over-oxidation product making Ru(OH)_x/ceria an useful catalyst system for valorizing biomass-based oxygenates by aerobic oxidation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Bio-Value platform (biovalue.dk) under the SPIR initiative by The Danish Council for Strategic Research and The Danish Council for Technology and Innovation (case number 0603-00522B).

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