

Article

Ru-Catalyzed Oxidative Cleavage of Guaiacyl Glycerol-β-Guaiacyl Ether-a Representative β-O-4 Lignin Model Compound

Mayra Melián-Rodríguez¹, Shunmugavel Saravanamurugan^{1,2}, Sebastian Meier¹, Søren Kegnæs¹, and Anders Riisager^{1,*}

- ¹ Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Building 207, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark; mayra.melian@gmail.com (M.M.-R.); srsaravana78@gmail.com (S.S.); semei@kemi.dtu.dk (S.M.); skk@kemi.dtu.dk (S.K.)
- ² Laboratory of Bioproduct Chemistry, Center of Innovative and Applied Bioprocessing (CIAB), Sector-81 (Knowledge City), Mohali-140 306 Punjab, India
- * Correspondence: ar@kemi.dtu.dk; Tel.: +45-4525-2233

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Abstract: The introduction of efficient and selective catalytic methods for aerobic oxidation of lignin and lignin model compounds to aromatics can extend the role of lignin applications in biorefineries. The current study focussed on the catalytic oxidative transformation of guaiacyl glycerol- β -guaiacyl ether (GGGE)–a β -O-4 lignin model compound to produce basic aromatic compounds (guaiacol, vanillin and vanillic acid) using metal-supported catalysts. Ru/Al₂O₃, prepared with ruthenium(IV) oxide hydrate, showed the highest yields of the desired products (~60%) in acetonitrile in a batch reactor at 160 °C and 5-bar of 20% oxygen in argon. Alternative catalysts containing other transition metals (Ag, Fe, Mn, Co and Cu) supported on alumina, and ruthenium catalysts based on alternative supports (silica, spinel, HY zeolite and zirconia) gave significantly lower activities compared to Ru/Al₂O₃ at identical reaction conditions. Moreover, the Ru/Al₂O₃ catalyst was successfully reused in five consecutive reaction runs with only a minor decrease in catalytic performance.

Keywords: aerobic oxidation; ruthenium; heterogeneous catalysis; lignin valorization; guaiacyl glycerol-β-guaiacyl ether

1. Introduction

Lignocellulosic biomass, predominantly comprised of cellulose, hemicellulose and lignin, is an abundant and renewable carbon-based alternative to fossil resources [1]. Several applications with nanocomposites of cellulose and hemicelluloses have been reported, for example water-purification [2], (bio)sensing [3] and anti-microbial treatment [4]. However, lately, the transformation of materials, as well as their monomeric C_6 and C_5 carbohydrates, to value-added chemicals and fuels have been studied extensively [5–15]. In comparison, lignin has received much less attention as feedstock, possibly due to its complex polymeric structure and lower reactivity, even though it is a major part of lignocellulosic biomass, typically 30% by weight and 40% by energy content. However, recent developments have demonstrated lignin to be a potentially important feedstock for producing chemicals, especially aromatic compounds [16–23]. This progress is important for the future of biorefineries as valorization of the entire biomass substrate improves economic viability.

The direct transformation of lignin usually requires mechanical pretreatment and harsh reaction conditions, due to its poor solubility and complex heterogeneous structure. Thus, in order to understand the reactivity of lignin, in general, various lignin model compounds containing different structural linkages, such as α -O-4 and β -O-4, have been widely used as substrates. Among the different linkages,



the most abundant structural unit in lignin is the β -O-4 (Figure 1), representing approximately 60% of hardwood and 45–50% of softwood [24].



Figure 1. Schematic representation of typical lignin fragments and the corresponding β -O-4 lignin model compound guaiacyl glycerol- β -guaiacyl ether (GGGE).

Several studies have converted lignin and simple aromatic model compounds by catalytic oxidation under typically harsh reaction conditions and afforded low yield and/or selectivity to the targeted products, whereas dimeric lignin model compounds containing β -O-4 linkages have only been scarcely studied [25,26]. In this context, the exploration of bulky β -O-4 lignin model compounds may provide valuable insight that can be transferred to the reactivity of the complex lignin molecule, especially on cleavage of β -O-4 linkages and further reactivity of the formed monomers [18].

Aerobic oxidation of the bulky lignin model compound guaiacyl glycerol-β-guaiacyl ether (GGGE) has primarily been examined with vanadium-based homogeneous catalyst systems. Hence, Son et al. reported a vanadium-based catalyst for the non-oxidative C-O bond cleavage of dimeric lignin model compounds with a conversion of 80% [27]. Furthermore, vanadium complexes showed promising catalytic activity for oxidative C-C bond cleavage of GGGE compounds, and promoted multistep reactions affording C–C and C–O cleavage products from alternative dimeric β-O-4 lignin model compounds [28–30]. Alternatively, Rahimi et al. introduced a two-step, metal-free organocatalytic method using first 4-acetamido-TEMPO as the catalyst for chemoselective aerobic oxidation of the secondary benzylic alcohols in GGGE followed by C-C cleavage using H₂O₂ [23]. In addition, Leitner et al. more recently introduced a highly active and selective ruthenium-complex catalyst system for C–C bond cleavage of β -O-4 lignin linkages involving a dehydrogenation-initiated retro-aldol reaction [31]. Despite these promising homogeneous catalyst systems for selective cleavage of C–C and C–O bonds, separation and recyclability of the catalysts remains cumbersome for such catalytic systems [30,32]. In contrast, solid catalysts with supported metals/metal oxides can easily be recovered from liquid reaction mixtures, and can often be recycled multiple times with preservation of the catalytic performance.

Supported ruthenium catalysts such as Ru/alumina, are an effective and reusable heterogeneous catalyst system for aerobic oxidation of both activated and non-activated alcohols in the presence of sulfur, nitrogen and carbon-carbon double bonds [33], and they are therefore interesting in the context of oxidative lignin valorization. We previously examined such catalysts for the aerobic oxidation of the lignin model compound veratryl alcohol to veratraldehyde in water and methanol with good results [34]. In the present study, analogous ruthenium supported catalysts with the different supports

 γ -alumina (Ru/Al₂O₃), silica (Ru/SiO₂), zirconia (Ru/ZrO₂), spinel (Ru/MgAl₂O₄) and USY zeolite (Ru/HY), which were prepared, characterized and applied for aerobic oxidative cleavage of GGGE in acetonitrile to produce guaiacol, vanillin and vanillic acid under mild reaction conditions (Scheme 1). Acetonitrile was preferred as the reaction solvent to ensure dissolution of GGGE and the products, and reaction parameters such as temperature and time were optimized for the promising catalyst Ru/Al₂O₃ to increase the selectivity for the desirable products, and the recyclability of the catalyst examined by performing consecutive reaction runs. For comparison, other alumina-supported metal catalysts M/Al₂O₃ (M = Mn, Ag, Cu and Fe) were prepared and evaluated.



Scheme 1. Catalytic aerobic oxidation of guaiacyl glycerol-β-guaiacyl ether (GGGE) to guaiacol, vanillin and vanillic acid with supported metal catalysts.

2. Results and Discussion

2.1. Catalyst Screening

Catalysts with 5 wt.% M/Al_2O_3 (M = Ru, Ag, Fe, Mn, Cu) were initially tested for the aerobic oxidation of GGGE into guaiacol, vanillin and vanillic acid in acetonitrile at 160 °C with 5 bar 20% oxygen in argon for 20 h. The results are presented in Table 1.

Table 1. Catalytic oxidation of guaiacyl glycerol- β -guaiacyl ether (GGGE) over different metal/alumina catalysts ^a.

Entry	Catalyst	BET Surface Area (m²/g)	GGGE Conv. (%)	Product Yield (%)			
				Guaiaco	l Vanillin	Vanillic Acid	
1	-	-	70	11	<1	<1	
2	Al ₂ O ₃	204	73	15	<1	<1	
3	5 wt.% Fe/Al ₂ O ₃	154	92	23	7	4	
4	5 wt.% Mn/Al ₂ O ₃	152	>99	21	8	9	
5	5 wt.% Cu/Al ₂ O ₃	158	>99	9	3	<1	
6	5 wt.% Ag/Al ₂ O ₃	164	>99	27	10	8	
7	5 wt.% Ru/Al ₂ O ₃ (1) ^b	148	>99	28	11	11	
8	5 wt.% Ru/Al ₂ O ₃ (1) _{b,c}	148	-	3	42	6	
9	3 wt.% Ru/Al ₂ O ₃ (1) ^b	160	>99	20	8	6	
10	$1 \text{ wt.}\% \text{ Ru/Al}_2 \text{O}_3 (1)^{\text{b}}$	157	>99	18	8	6	
11	$5 \text{ wt.}\% \text{ Ru/Al}_2 \text{O}_3 (2)^{\text{d}}$	152	>99	24	9	3	
12	5 wt.% Ru/Al ₂ O ₃ (3) ^e	166	>99	34	13	11	

^a Reaction conditions: 10 mL 0.017 M GGGE in acetonitrile, 40 mg catalyst, 160 °C, 5 bar (20% oxygen in argon), 20 h. ^b Catalyst prepared using ruthenium(III) chloride. ^c 100 mg vanillin used as a substrate in 10 mL acetonitrile. ^d Catalyst prepared using ruthenium(III) acetylacetonate. ^e Catalyst prepared using ruthenium(IV) oxide.

In blank experiments with alumina support alone or without the catalyst about 70% of GGGE was converted, however, as expected only low yields of the desired product guaiacol (<15%) and traces of vanillin and vanillic acid (<1%) were obtained, suggesting that GGGE was possibly transformed into (unidentified) byproducts, e.g., polymers (Table 1, entries 1 and 2). In contrast, when employing the Ru/Al₂O₃ and Ag/Al₂O₃ catalysts the yield of guaiacol improved to 28 and 27%, respectively, with

the former catalyst performing the best and providing the highest yields of both vanillin (11%) and vanillic acid (11%) (Table 1, entries 6 and 7). When applying the other 5 wt.% metal/alumina catalysts the GGGE conversion remained also close to quantitative, but lower yields of the targeted products were obtained (Table 1, entries 3–5). Notably, in the case of 5 wt.% Cu/Al₂O₃ the transformation of GGGE to (unidentified) byproducts was even promoted compared to the blank experiments. With the 5 wt.% Ru/Al₂O₃ (1) catalyst, an additional experiment was performed using vanillin as the starting substrate instead of GGGE (under similar reaction conditions) to examine whether guaiacol was partly formed from vanillin by consecutive decarbonylation of vanillin (Table 1, entry 8). The obtained results showed a poor yield of guaiacol (3%) and vanillic acid (6%) along with a moderate conversion of vanillin (58%), inferring that guaiacol predominantly formed from the cleaving of the β -O-4 linkage in GGGE and vanillic acid predominantly formed from oxidation of vanillin.

2.2. Effect of Ru Precursor, Ru Loading and Catalyst Support

For metal/metal oxide catalysts it is typically found that the metal loading, metal precursor and support material influence the catalytic performance through changes in the physical- and structural properties [35-39]. Accordingly, Ru/Al₂O₃ catalysts were prepared with different metal loadings and supports using ruthenium(III) chloride precursor and the resultant catalysts were tested for the GGGE oxidation. Similarly, catalysts with 5 wt.% Ru were prepared with the three different precursors ruthenium(III) chloride, ruthenium(III) acetylacetonate and ruthenium(IV) oxide (Ru/Al₂O₃ (1), Ru/Al₂O₃ (2) and Ru/Al₂O₃ (3), respectively) and the resultant catalysts were tested (Tables 1 and 2).

For the catalysts with 1 and 3 wt.% Ru loading, the yields of guaiacol (18–20%) as well as vanillin (8%) and vanillic acid (6%) were lower than for 5 wt.% Ru/Al_2O_3 (1), confirming that the catalytic activity was dependent on the amount of the metal inventory (Table 1, entries 9 and 10). TEM images of the catalysts further showed that the former catalysts possessed relatively large Ru-particles of sizes 80–100 nm, while the 5 wt.% catalyst had particles with sizes of 40–60 nm, implying that smaller particles improved the catalytic conversion of GGGE to guaiacol, vanillin and vanillic acid (Figure S1). With the preferred 5 wt.% Ru metal loading, the yields of guaiacol, vanillin and vanillic acid were lower when ruthenium(III) acetylacetonate (i.e. Ru/Al_2O_3 (2)) was used as the precursor instead of ruthenium(III) chloride (Table 1, entry 11). In contrast, a slightly improved catalytic activity in terms of vanillin (34%) and guaiacol yields (13%) was observed when employing ruthenium(IV) oxide precursor (i.e. Ru/Al₂O₃ (3)) compared to Ru/Al₂O₃ (1) (Table 1, entry 12), whereas the yield of vanillic acid remained unchanged (11%). TEM images revealed that the Ru-particle sizes of the catalysts decreased in the order Ru/Al_2O_3 (2) (100–200 nm) > Ru/Al_2O_3 (1) (40–60 nm) > Ru/Al_2O_3 (3) (10–40 nm) (Figure 2). This size order followed the order of catalytic performance toward formation of guaiacol, vanillin and vanillic acid, corroborating that the metal precursor influenced particle formation, and the corresponding catalytic performance, as also observed previously when catalysts were prepared with different metal precursors [38].

The BET surface areas of the Ru catalysts as well as the other metal-based catalysts (148–166 m²/g) were significantly lower than the alumina support alone (204 m²/g), indicating some pore blocking in the catalysts by metal oxide particles and therefore likely also some change in pore size distributions for the different catalysts. For the 5 wt.% Ru/Al₂O₃ (1) catalyst with the lowest surface area, the increased acidity of the ruthenium(III) chloride precursor solution may have also possibly contributed in part to lowering the surface area by alteration of the Al₂O₃ support surface. Notably, for analogous Ru/Al₂O₃ catalysts prepared by similar methods a comparable relative decrease (20–30%) in surface area has also been found [37].





Figure 2. High-resolution TEM images of 5 wt.% Ru/Al_2O_3 (1) (**a**), 5 wt.% Ru/Al_2O_3 (2) (**b**) and 5 wt.% Ru/Al_2O_3 (3) (**c**) catalysts.

The influence of the catalyst support was examined for catalysts containing 5 wt.% Ru prepared using ruthenium(III) chloride precursor and conventional supports such as SiO₂, MgAl₂O₄ (spinel), HY (Si/Al ~ 6) and ZrO₂ (Table 2). All the catalysts based on the alternative supports gave full GGGC conversion with product yields of guaiacol (15–22%), vanillin (7–12%) and vanillic acid (8–10%) (Table 2, entries 1–4), which were comparable to the analogous 5 wt.% Ru/Al₂O₃ (1) (Table 1, entry 7). This finding suggested that the characteristics of the support materials was of minor importance for the catalytic performance under the applied conditions.

Table 2.	Catalytic	oxidation of	GGGE	with a	lternative	Ru/suppor	rt catalysts ^a
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Entry	Catalyst	BET Surface Area ^b (m²/g)	GGGEconv. (%)	Product Yield (%)			
				Guaiacol	Vanillin	Vanillic Acid	
1	5 wt.% Ru/SiO ₂	278	>99	22	7	10	
2	5 wt.% Ru/spinel	63	>99	20	12	8	
3	5 wt.% Ru/HY(6) ^c	698	>99	15	8	9	
4	5 wt.% Ru/ZrO ₂	97	>99	20	9	8	

^a Reaction conditions: 10 ml 0.017 M GGGE in acetonitrile, 40 mg catalyst (prepared using ruthenium (III) chloride), 160 °C, 5 bar (20% oxygen in argon), 20 h. ^b BET surface areas of support materials. ^c The number in parenthesis corresponds to the Si/Al ratio.

2.3. Effect of Reaction Time, Reaction Temperature and Oxygen Pressure

In order to optimize the reaction towards formation of guaiacol/vanillin/vanillic acid, the influence of reaction temperature and reaction time were examined using the 5 wt.% Ru/Al_2O_3 (3) catalyst and the results are illustrated in Figures 3 and 4, respectively. When the aerobic oxidation of GGGE was performed for 20 h at a relatively low temperature (120 °C), a low yield of guaiacol (8%) was obtained along with 8% vanillin and <2% vanillic acid with 52% conversion (Figure 3). At 140 °C, GGGE conversion (85%) product yields improved slightly, while full substrate conversion (>99%) and maximum product yields were found at 160 °C (see also Table 1, entry 12). With reaction times of less than 20 h at 160 °C, the GGGE conversion as well as the product formation was significantly lower and vanillic acid formed only after 3 h of reaction (Figure 4). Similarly, at a prolonged reaction time of 30 h the product yields decreased noticeably (21% guaiacol, 11% vanillin and 7% vanillic acid), indicating the formation of byproducts both by side reactions as well as product degradation. At even higher reaction temperatures (180 and 200 °C) the quantitative conversion was maintained but the yield of the products decreased significantly. This was likely due to deactivation of the Ru/Al_2O_3 (3) catalyst by Ru particle aggregation and formation of byproducts (unidentified) by consecutive reactions of the products, thus confirming 160 °C and 20 h to be the optimal conditions for obtaining the highest product yields.



Figure 3. Temperature study for the GGGE oxidation with 5 wt.% Ru/Al₂O₃ (3) catalyst. Reaction conditions: 10 mL 0.017 M GGGE in acetonitrile, 40 mg catalyst, 20 h, 5 bar (20% oxygen in argon).



Figure 4. Time-course study for the GGGE oxidation with 5 wt.% Ru/Al_2O_3 (3) catalyst. Reaction conditions: 10 mL 0.017 M GGGE in acetonitrile, 40 mg catalyst, 160 °C, 5 bar (20% oxygen in argon). All data were obtained from individual experiments.

The importance of oxygen being present for the product formation was further evaluated by performing a catalytic reaction under optimized conditions (160 °C, 20 h) with pure argon atmosphere (20 bar). The GGGE was quantitatively converted (>99%) as was found previously using 5 bar of 20% oxygen in argon (see Table 1, entry 12). However, only a moderate yield of guaiacol (24%) and very poor yields of vanillin (3%) and vanillic acid (<1%) were formed under argon atmosphere, thus confirming that oxygen promoted guaiacol formation and was a prerequisite for the production of vanillin and vanillic acid, as was also expected. Notably, full GGGE conversion and very similar product yields (32% guaiacol, 11% vanillin, 11% vanillic acid) were obtained using 5 bar of air instead of 5 bar of 20% oxygen in argon as also anticipated since both had similar oxygen content (i.e., $P_{O2} \approx 1$ bar). In contrast, <1% yield of the desired oxidation products were obtained using water as the solvent under similar reaction conditions (results not shown), possibly due to low oxygen solubility at the reaction conditions.

High-resolution NMR analysis of the post-reaction mixture obtained at the optimal reaction conditions (160 °C and 20 h) was performed in order to validate the reaction products, and to obtain insight into byproduct formation with the aim of understanding the loss of carbon from the overall carbon balance of the process. Guaiacol, vanillin and vanillic acid were confirmed to be the predominant reaction products, while a variety of minor aromatic byproducts was formed (Figure 5). These byproducts included 2-methoxy-1,4-benzoquinone as the main aromatic byproduct (2.5% yield) and benzoic acid alongside its derivatives (2% yield), as well as a plethora of additional, unidentified aromatic byproducts contributing to the loss of carbon. The 2-methoxy-1,4-benzoquinone was identified using in situ spectroscopy on crude post-reaction material (Figure S2), and has previously been described as a degradation product in the manganese peroxidase-catalyzed oxidation of guaiacol [40]. Hence, its presence indicated that overoxidation of the main reaction products occured at reaction conditions that were more severe than the optimum conditions, thus rationalizing the decline especially in guaiacol and vanillin yields at longer times or higher temperatures (Figures 3 and 4).



Figure 5. ¹H-¹³C HSQC spectrum of post-reaction mixture displayed showing the main products guaiacol (G), vanillin (VL) and vanillinc acid (VA) alongside a variety of minor byproducts, including benzoic acid and 2-methoxy-1,4-benzoquinone.

2.4. Catalyst Reuse

To examine catalyst viability, the 5 wt.% Ru/Al₂O₃ (3) catalyst was finally subjected to reuse in five consecutive oxidation reactions of GGGE under optimized reaction conditions, i.e., 160 °C and 20 h (Figure 6). The results revealed that the catalyst was recyclable and maintained good catalytic performance with high GGGE conversion during the five reaction runs. However, some decrease in the yields of guaiacol (34 to 30%), vanillin (13 to 8%) and vanillic acid (11 to 6%) occurred over the five recycles. This decline suggested that part of the catalytically active metal sites of the Ru/Al₂O₃ (3) catalyst was gradually lost during the reaction sequence. In this connection, TEM analysis of the catalyst after the five-time use confirmed that the spent catalyst contained Ru-based nanoparticles that were more uniformly shaped and larger (30–100 nm) than the fresh catalyst (7–60 nm) (Figure S3). The larger particles most likely formed during the intermediate catalyst calcinations, as also previously observed for Ru supported catalysts [41–43], and were expected to contain less catalytically active sites and therefore be (comparably) less active than smaller-sized particles.



Figure 6. Reuse of 5 wt.% Ru/Al_2O_3 (3) catalyst in five consecutive GGGE oxidation reactions. Reaction conditions: GGGE to catalyst mass ratio = 1.30, 160 °C, 5 bar (20% oxygen in argon).

3. Materials and Methods

3.1. General

Guaiacyl glycerol- β -guaiacyl ether (>99%, GGGE) was prepared from acetovanillone through a multiple step synthesis route using a reported procedure [44]. Vanillin (99%), vanillic acid (99%) manganese(II) acetate tetrahydrate (>99%), copper(II) acetate monohydrate (p.a.), silver(I) nitrate (p.a.), iron(III) nitrate nonahydrate (p.a.), ruthenium(IV) oxide hydrate (>99.9%), ruthenium(III) acetylacetonate (>97%), ruthenium(III) chloride hydrate (>99%), zirconium(IV) oxide (99%), magnesium aluminate (spinel) (99%), silica gel 60 (high-purity grade) and acetonitrile (99.8%) were purchased from Sigma Aldrich. γ -Aluminium oxide (>99%) was provided by Saint Gobain. Compressed oxygen (>99.99%) and argon (>99.99%) were purchased from Air Liquide, Denmark. All chemicals and gases were used as received.

3.2. Catalyst Preparation

The supported catalysts were prepared by wet impregnation where the appropriate amount of the metal precursor (Ru, Mn, Fe, Cu or Ag) was dissolved in water, the corresponding support (alumina, silica, zirconia, spinel or HY zeolite) slowly added and the resulting suspension stirred for 3 h. Then the mixture was dried overnight at 80 °C followed by calcination at 450 °C for 6 h in static air to obtain the corresponding supported catalyst with a metal content of 1–5 wt.% corresponding to the amount of added metal precursor. All catalysts were stored in a desiccator and used without further activation.

3.3. Catalyst Characterization

TEM images of the Ru supported catalysts were recorded on a FEI Tecnai Transmission Electron Microscope at 200 kV with samples deposited on a carbon support. EDS analysis was performed with an Oxford INCA system. Surface areas of the supported catalysts were determined by nitrogen sorption measurements at liquid nitrogen temperature on a Micromeritics ASAP 2020. Samples were outgassed in a vacuum at 150 °C for 4 h prior to the measurements, and the total surface areas were calculated according to the BET method.

3.4. Catalytic Oxidation Reactions

Catalytic experiments were performed in an autoclave (Microclave 50 mL reactor, Autoclave Engineers) charged with an appropriate amount of guaiacyl glycerol- β -guaiacyl ether (GGGE), catalyst (40 mg) and acetonitrile (10 mL) as the solvent. The reactor was pressurized with 5 bar of 20% oxygen in argon, and heated to the desired reaction temperature. Mechanical stirring of the reactor (300 rpm) was started once a temperature of 20 °C below the set point was reached. After the reaction, the autoclave was quenched in cold water, the catalyst removed by filtration and the reaction mixture subjected to analysis.

In the catalyst recyclability study, the catalyst was recovered by filtration after each reaction run, thoroughly washed with acetonitrile, dried overnight at 60 °C and calcined at 450 °C for 6 h before being used in the next reaction run as described above.

3.5. Product Analysis

Aliquots of the reaction mixture were subjected to HPLC analysis (Agilent 1200 series instrument, Agilent C-18 column, 15 cm length) in order to quantify the yield and conversion. The eluent was in all cases 60 vol.% aqueous acetonitrile solution. The conversions of GGGE and yields of the products (guaiacol, vanillin, vanillic acid) were determined from individual standard solutions with products identified by GC-MS analysis.

3.6. NMR Spectroscopy

NMR analyses were conducted to validate the presence and amount of the main reaction products and to obtain insight into the nature of major byproducts. For NMR analyses, samples were condensed on a rotary evaporator at 40 °C and re-dissolved in deuterated acetonitrile (>99.8 atom% deuterium). NMR spectra were recorded on an 800 MHz Bruker Avance II spectrometer equipped with a 18.7 T magnet (Oxford, United Kingdom) and a TCI z-gradient cryoprobe (Bruker, Karlsruhe, Germany) at 25 °C. The 2D NMR spectra included TOCSY with a 10 kHz spin lock field that was applied for 60 ms (2048 × 256 complex data points with 640 ms and 80 ms acquisition times), a sensitivity enhanced ¹H-¹³C HSQC (1024 × 1024 complex points, sampling 128 ms and 73 ms acquisition times), ¹H-¹³C HMBC (2048 × 256 complex data points, sampling 213 and 11 ms acquisition times) and a ¹H-¹³C HSQC TOCSY (1024 × 512 complex points with 107 ms and 42 ms acquisition times). Identification of byproducts in reaction mixtures were done by comparison to pure reference standards (e.g., acetic and benzoic acid) or by de novo structure determination (e.g., 2-methoxy-1,4-benzoquinone). All spectra were acquired in Bruker Topspin and processed in the same software with extensive zero filling in all dimensions.

4. Conclusions

An optimized 5 wt.% Ru/Al₂O₃ catalyst prepared with ruthenium(IV) oxide hydrate precursor was found to give superior yield of the monomeric aromatics guaiacol (34%), vanillin (13%) and vanillic acid (11%) in the aerobic oxidation of the lignin-model compound GGGE in acetonitrile at 5 bar (20% oxygen in argon) under optimized reaction conditions (160 °C, 20 h). In comparison, Ru/Al₂O₃ catalysts prepared with other ruthenium precursors were found to give lower yields of the desired products, which could be correlated to the particle sizes of the Ru-species measured by TEM. Furthermore, catalysts containing other transition metals (Ag, Fe, Mn, Co and Cu) supported on alumina, and ruthenium catalysts based on alternative supports (silica, spinel, HY and zirconia) were also significantly less active compared to the Ru/Al₂O₃ catalysts proved robust for recycling in five consecutive reaction runs with only minor activity loss corresponding to thermal regeneration between the runs.

Improved performance of Ru/Al₂O₃ catalysts was obtained by the optimization of catalyst preparation and reaction conditions for the oxidation of a lignin-model compound to monomeric aromatics. However, the reactivity of lignin-model systems may not be directly transferable to a complex system with native lignin, where more stable catalysts displaying higher activity and selectivity may be required in order to extend the role of lignin applications in biorefineries.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/10/832/s1, Figure S1: High-resolution TEM images of (A) fresh 1 wt.% Ru/Al₂O₃ (1) catalyst, (B) used 1 wt.% Ru/Al₂O₃ (1) catalyst, (C) fresh 3 wt.% Ru/Al₂O₃ (1) catalyst, (D) used 3 wt.% Ru/Al₂O₃ (1) catalyst, (E) fresh 5 wt.% Ru/Al₂O₃ (1) catalyst, (D) used 3 wt.% Ru/Al₂O₃ (1) catalyst, (E) fresh 5 wt.% Ru/Al₂O₃ (1) catalyst, Figure S2: Overlay of ¹H-¹³C HSQC and ¹H-¹³C HMBC NMR spectra of post-reaction material displayed as contour plots, showing the single and multiple-bond correlations in 2-methoxy-1,4-benzoquinone, with the inset displaying the full chemical shift assignment of the compound. Figure S3: High-resolution TEM catalysts images of (left) fresh 5 wt.% Ru/Al₂O₃ (3) catalyst, and (right) 5 wt.% Ru/Al₂O₃ (3) catalyst after five reaction runs.

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