Selective Hydrodeoxygenation of Guaiacol to Cyclohexane over Ru-Catalysts Based on MFI Nanosheets

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Abstract: Bio-oils derived from the pyrolysis of lignin-based biomass often contain a variety of oxygenated compounds, which can compromise their usefulness as a fuel. To improve the quality of bio-oil, catalytic hydrodeoxygenation (HDO) is a crucial step that removes oxygen from the oil in the form of water. In this study, we showed that MFI nanosheets are excellent supports for Ru-catalysts. We synthesized highly crystalline MFI nanosheets using a simple hydrothermal seeding procedure; the final material was obtained in 56 h of crystallization. We investigated the activity of Ru supported on different materials. Our findings indicated that Ru supported on hierarchical MFI demonstrated excellent activity in HDO of guaiacol. Our results demonstrated that Ru/ZNS-56 achieved nearly 100% selectivity towards cyclohexane under mild conditions (200 °C, 50 bar H2, 1 h).

Keywords: bio-oil; micro-mesoporous materials; Ru catalysts; hydrodeoxygenation; guaiacol; zeolite nanosheets; biomass valorization

1. Introduction

Zeolites are commonly used as catalyst supports and adsorbents in the oil-refining industry [1–3]. While some types of zeolites occur naturally as minerals, most are synthesized for catalytic applications. The channels in zeolites are often much smaller than the thickness of the crystals themselves, leading to diffusion limitations that make zeolites impractical for the catalytic treatment of oil cuts [4–6]. To address this issue, hierarchical structures containing both mesopores and micropores have been developed, allowing for the diffusion into micropores through mesopores [7,8]. The design of such porous materials for the catalysis tasks requires a combination of pores on micro- and meso-levels in a specific ratio. Hierarchical materials have several advantages over zeolites and mesoporous materials, including higher stability, acidity, and lack of diffusion limitations [9].

Zeolite nanosheets, which have been extensively studied over the past decade, are the most promising micro-mesoporous materials, as a decrease in the thickness of the zeolite layer significantly enhances catalytic activity [10–20]. Despite the effectiveness of hydrothermal synthesis of zeolite nanosheets in creating hierarchical structure with improved catalytic properties, the mechanism of crystallization is not well understood, and further research is needed to improve these materials and develop promising new catalysts.

The MFI nanosheets exhibit remarkable thermal and hydrothermal stability, mechanical strength, and strong acidity [18,21]. Typically, it takes more than a week for that type of material with high Al content to crystallize, and during this time, the organic template with ammonium groups may decay by Hoffman elimination, resulting in the formation of bulk zeolite [22]. However, it is possible to reduce the crystallization time to just 2.5 days by seeding the multim ammonium surfactant-directed synthesis with bulk zeolite crystals, which...
is a simple and typical method for zeolite synthesis [21]. Earlier we showed the possibility to reduce the crystallization time using oxyanion and microwave irradiation [23].

These nanosheets demonstrate superior catalytic performance compared to conventional bulk ZSM-5 [23,24]. This enhanced catalytic activity is attributed to the large number of active sites on the external surface of the nanosheets and the short diffusion pathway [25]. The nanosheets also show improved time-on-stream stability and higher coke tolerance in the conversion of methanol-to-gasoline [26]. Furthermore, they demonstrate enhanced activity, stability, and selectivity in the gas-phase Beckmann rearrangement of cyclohexanone oxime to e-caprolactam [27]. In addition, the MFI nanosheets with the titanosilicate composition are suitable for the epoxidation of olefins. They exhibit enhanced catalytic activity in the epoxidation of bulky cyclic alkenes, such as cyclohexene and cyclooctene, compared to TS-1 [16]. Finally, the MFI nanosheets containing the template prior to calcination exhibit a positive charge, making them suitable as anion exchangers [28].

One of the most widely applied types of catalysts to improve the quality of biomass-derived fractions are supported noble metal catalysts [29]. Noble metals, such as Ru, Rh, Pd, and Pt, are common catalysts that are activated in hydrogenation and hydrodeoxygenation processes and are not deactivated by water [30–32]. However, Ru-contained catalysts in particular possess the highest water stability and high hydrogenation activity under the studied conditions [33–36]. Many studies have shown higher activity of Ru catalysts in the bifunctional catalysis during HDO of bio-oil fractions compared to Pt- or Pd-based catalysts [37,38]. The Ru-contained catalysts based on micro-mesoporous materials possess high water stability and hydrogenation activity [12,35,39–42]. It was shown that the highest selectivity towards hydrocarbons can be achieved using highly acidic supports [43–46]. While these previous works revealed the unique catalytic activity and stability of MFI nanosheets, the question of whether the Ru-contained catalysts can still exhibit bifunctional activity in the HDO process has not yet been clearly answered. In the present study, we investigated the seeding synthesis of MFI nanosheets and used them as the supports of Ru-contained catalysts to reveal the effects of the textural and acidic properties on the catalytic behavior.

2. Materials and Methods

2.1. Materials Synthesis

The di-ammonium surfactant \([\text{C}_{22}\text{H}_{45}\text{N}^{+}-(\text{CH}_{3})_{2}\text{C}_{6}\text{H}_{12}\text{N}^{+}-(\text{CH}_{3})_{2}\text{C}_{6}\text{H}_{13}]\text{Br}_{2}\) (C22-6-6Br2 for short) was synthesized using a synthesis procedure reported by Ryong [18]. All organic compounds during the synthetic protocols were identified by $^1$H NMR.

Fumed silica (SiO2, Aldrich, St. Louis, MO, USA), tetraethylorthosilicate ((EtO)4Si 95%, Aldrich), tetrapropylammonium hydroxide solution ((NPr4OH, 20 wt. %, Sigma Aldrich), aluminium sulphate (Al2(SO4)3·18H2O, 98%, Aldrich), sodium hydroxide (NaOH, 97%, Sigma-Aldrich), perchloric acid (HClO4, 60 wt. %, Reáchem, Chennai, India), sodium perchlorate (NaClO4, 98%, Reáchem), and ammonium nitrate (NH4NO3, 99%, Reáchem) were used as the initial chemicals. ZSM-5 commercial zeolite (Zeolyst, CBV 3024E) was turned into an H-form by calcination at 550 °C for 6 h. All the syntheses and procedures were conducted in polypropylene vessels. An autoclave with a Teflon liner was used for the thermal conditioning of the reaction mixtures.

Typical synthesis procedures of ZNS-N (N-crystallization time, hours) were as follows: A—Seeding gel preparation, B—Micellar gel preparation; HT—Crystallization under hydrothermal conditions.

A. 1. NaOH 0.69 g, TPAOH 5.9 g (1M), H2O—35.5 g, dissolve and mix thoroughly
   2. Fumed silica (SiO2) 6.9 g, add silica in portions under stirring
   3. Aged at 100 °C for 16 h
   B. 1. H2O—17.0 g, NaOH—0.75 g, C22-6-6Br2—1.6 g, dissolve and mix thoroughly
   2. H2O—17.6 g, Al2(SO4)3·18H2O—0.49 g, mixing until a clear solution was obtained. Then, the content of the Al-contained vessel was added to the vessel with surfactant
   3. +2 mL of seeding gel (A)
4. The mixture was magnetically stirred for 1 h
5. This solution was added with 6.3 g of TEOS
6. Shake for one hour
7. Aged at 100 °C for 16 h (in a Teflon-lined stainless steel autoclave)

The resultant powders were separated by centrifugation, repeatedly washed with distilled water, and dried in air at 95 °C overnight. Finally, the product was calcined at 550 °C for 6 h in air flow to remove the surfactant. The H-form of the samples was obtained by ammonium nitrate exchange at 90 °C for 4 h (3 times), followed by drying and calcination at 550 °C for 3 h.

2.2. Catalysts Preparation

A typical procedure for preparing Ru-based catalysts includes impregnation of the support with an aqueous solution of ruthenium chloride (Aurat, ω(Ru) = 47.6 wt. %), taken in an amount corresponding to the moisture capacity, followed by solvent removal on a water bath in an air stream. After that, the sample was dried under ambient conditions overnight, then dried at 60 °C for 24 h, and finally calcined at 400 °C for 3 h. After that, all samples were reduced in a flow reactor system in a hydrogen stream at 350 °C for 3 h. When preparing the metal salt solution, the RuCl₃ amount was calculated to ensure a 2 wt. % of ruthenium content of the catalyst.

2.3. Characterization

The textural properties of the porous materials and catalysts were carried out by nitrogen adsorption (77 K) using a Micromeritics ASAP 2020 instrument (Micromeritics Instrument Corp., Norcross, GA, USA).

The composition of the samples was done by atomic absorption spectrometry using a PerkinElmer AAnalyst instrument (PerkinElmer, Inc., Waltham, MA, USA).

X-ray powder diffraction analysis was determined by a Rigaku D/MAX 2500 diffractometer (Rigaku, Tokyo, Japan) (CuKa radiation) in the range of 3–60°, with a goniometer rotation speed of 1° min⁻¹ in the low-angle region, and 2° min⁻¹ in the wide-angle region.

The acidity of the samples by Fourier transform infrared (FTIR) spectra was carried out on The Nicolet iS10 spectrometer (ThermoFisher, Fitchburg, WI, USA). Prior to the measurements, the samples were pressed into tablets and activated in the infrared (IR) cell attached to a vacuum liner at 400 °C for 2 h. Adsorption of pyridine was performed at 150 °C for 20 min. Excess probe molecules were further evacuated at 150 °C for 20 min. The numbers of Brønsted and Lewis acid sites were measured from the intensities of the bands at ca. 1545 and 1455 cm⁻¹ of adsorbed pyridine, respectively, using the molar extinction coefficients given by Tamura et al. [38].

High resolution microphotographs were obtained using the transmission electron microscopy (TEM) JEOL JEM-2100, with an accelerating voltage of 200 kV.

The morphology of the samples was determined by a Scanning electron microscopy (SEM) using a Carl Zeiss NVision 40 microscope equipped with an Oxford Instruments (Abingdon, UK) X-Max analyzer (80 mm²).

Pulse chemisorption of carbon monoxide was done in a quartz reactor using an AutoChem 2950HP (Micromeritics Instrument Corp., Norcross, GA, USA). Samples were reduced with H₂ at 350 °C for 0.5 h, purged with He for 0.5 h, and cooled down to room temperature. A mixture of 3% CO + 97% He (vol. %) was applied, and the loop volume was 0.5 mL.

2.4. Hydrodeoxygenation Procedure

Hydrogenation of guaiacol was conducted in a steel autoclave equipped with a magnetic stirrer and a pressure gauge. The autoclave was charged with 0.050 g of the catalyst and 2.00 g of the substrate solution. In a typical experiment, a catalyst with guaiacol (10 wt. % in n-C₁₂H₂₄) was put in the autoclave with the inner volume of 10 mL. The
autoclave was charged with hydrogen to a pressure of 50 bar. The reaction was run at 150–300 °C with a stirrer speed of 700 rpm. After the reaction, the autoclave was cooled down to room temperature; after that, the pressure was decreased to the atmospheric. The error bars are based on triplicate experiments.

The qualitative composition of the liquid products after catalytic experiments was done by gas chromatography–mass spectrometry using a Finnigan MAT 95 XL instrument equipped with a Varian VF-5MS capillary column and helium as a carrier gas (1.5 cm³/min). Toluene was used as the internal standard. In all catalytic experiments, >95% mass balance and carbon balance were achieved. The remaining unaccounted mass was most likely minor gaseous products that were not detected as a result of the analytical technique employed. Guaiacol conversion and product selectivity were calculated using the following equations:

\[
\text{Conversion} = \frac{\sum S_i \cdot f_i}{\sum S_i \cdot f_i + S_{\text{gua}} \cdot f(\text{gua})} \times 100\%
\]

\[
\text{Selectivity} = \frac{S_i \cdot f_i}{\sum S_i \cdot f_i} \times 100\%
\]

\(S_i\)—peak area of a product (i), \(S_{\text{gua}}\)—peak area of guaiacol, \(f_i\)—response factor of a product (i).

3. Results and Discussion

Figure 1 shows the powder X-ray diffraction patterns, \(N_2\) adsorption–desorption isotherms, and pore size distribution of the micro-mesoporous materials. The isotherms of all calcined samples exhibit a type IV\textsuperscript{th} type with slight deviations. It should be noted that at low pressure (\(P/P_0 < 0.5\)), these isotherms correspond to the \(I\)\textsuperscript{st} type of isotherms. The adsorbed volume of \(N_2\) at a low pressure increases with hydrothermal synthesis time, indicating the growth of crystallinity. The high-pressure area of the isotherms showed a transformation in profile from ZNS-12 to ZNS-56, indicating the growth of crystallinity and a decrease in mesoporosity. The textural characteristics of the samples are presented in Table 1. According to these data, \(S_{\text{BET}}\) gradually decreased from ZNS-12 (754 m²/g) to ZNS-56 (470 m²/g), while \(S_{\text{micro}}\) increased simultaneously (from 30 m²/g to 160 m²/g). The pore size distribution data suggests the presence of ordered mesopores in all samples. It should be noted that pore ordering decreased with an increasing crystallization time. This phenomenon could be due to the phase transformation from MCM-41-like structure to the MFI nanosheets.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Si/Al a</th>
<th>(S_{\text{BET}}) b (m²/g)</th>
<th>(V_{\text{total}}) c (cm³/g)</th>
<th>(S_{\text{micro}}) d (m²/g)</th>
<th>(S_{\text{meso}}) e (m²/g)</th>
<th>Residual Na, wt. % a</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5 (CBV 3024E)</td>
<td>16</td>
<td>413</td>
<td>0.28</td>
<td>337</td>
<td>76</td>
<td>0</td>
</tr>
<tr>
<td>ZNS-12</td>
<td>20</td>
<td>754</td>
<td>0.69</td>
<td>30</td>
<td>724</td>
<td>1.5</td>
</tr>
<tr>
<td>ZNS-24</td>
<td>21</td>
<td>614</td>
<td>0.57</td>
<td>65</td>
<td>549</td>
<td>1.2</td>
</tr>
<tr>
<td>ZNS-56</td>
<td>21</td>
<td>470</td>
<td>0.25</td>
<td>160</td>
<td>310</td>
<td>0</td>
</tr>
</tbody>
</table>

\(a\) by ICP/OES analysis, \(b\) BET-specific surface area obtained from the adsorption isotherm in the relative pressure range 0.05–0.20, \(c\) total pore volume at the relative pressure 0.95, \(d\) microporous surface area obtained from the \(t\)-plot method, \(e\) mesoporous surface area calculated as \(S_{\text{BET}} - S_{\text{micro}}\).

The powder X-ray diffraction patterns showed that the samples possess a crystalline structure. However, ZNS-12 clearly had an amorphous halo in 15–40°. With the increase of crystallization time, the amorphous halo also gradually disappeared. This alteration is related to the crystallinity growth.
Table 1. Textural characteristics of calcined samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Si/Al</th>
<th>SBET (m²/g)</th>
<th>Vtotal (cm³/g)</th>
<th>Smicro (m²/g)</th>
<th>Smeso (m²/g)</th>
<th>Residual Na, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5 (CBV 3024E)</td>
<td>16</td>
<td>413</td>
<td>0.28</td>
<td>337</td>
<td>76</td>
<td>0</td>
</tr>
<tr>
<td>ZNS-12</td>
<td>20</td>
<td>754</td>
<td>0.69</td>
<td>30</td>
<td>724</td>
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<td>21</td>
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<td>549</td>
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</tr>
<tr>
<td>ZNS-56</td>
<td>21</td>
<td>470</td>
<td>0.25</td>
<td>160</td>
<td>310</td>
<td>0</td>
</tr>
</tbody>
</table>

a by ICP/OES analysis, b BET-specific surface area obtained from the adsorption isotherm in the relative pressure range 0.05–0.20, c total pore volume at the relative pressure 0.95, d microporous surface area obtained from the t-plot method, e mesoporous surface area calculated as SBET-Smicro.

Figure 1. (A) N₂ adsorption isotherms, (B) corresponding pore size distributions, (C) powder XRD patterns of micro-mesoporous materials.

The SEM and TEM microphotographs of the micro-mesoporous materials are presented in Figure 2. The structures of those materials support the physicochemical characteristics discussed above. ZNS-12 and ZNS-24 possessed the structure similar to the MCM-41-like. The difference between these two samples was the level of crystallinity. In the previous study, we showed that the MFI nanocrystals could be located near amorphous globules [20,39]. The ZNS-56 sample consisted of MFI nanosheets. Previous studies have reported the synthesis of MFI zeolite nanosheets exhibiting a nanosponge-like morphology, resulting in a narrow pore size distribution [40,41]. The morphology and characteristics of these MFI zeolite nanosheets were similar to the ZNS-56 sample studied in this work [21].

Figure 2. TEM (top) and SEM (bottom) images of micro-mesoporous materials.
The micro-mesoporous materials were used for the Ru-containing catalysts synthesis that were applied in the guaiacol hydrogenation in an organic solvent. The catalysts based on the synthesized micro-mesoporous materials demonstrated a high activity in the hydrogenation of guaiacol under the following conditions: 200 °C, 50 bar H₂, reaction time 0.25 ÷ 3 h. The results are presented in Table 2 and Figure 3. The kinetic curves are shown in Figure 3A. The conversion of guaiacol reached >90% after 1 hour in all experiments. After the one hour reaction time, the products’ distribution tended to the constant value. The difference of the samples activity was most noticeable at the beginning of the reaction (Table S1).

Table 2. The acidity of supports and Ru-catalysts determined by FTIR spectroscopy of adsorbed pyridine, µmole/g.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BAS</th>
<th>LAS</th>
<th>BAS/LAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5 (CBV 3024E)</td>
<td>256</td>
<td>44</td>
<td>5.82</td>
</tr>
<tr>
<td>ZNS-12</td>
<td>24</td>
<td>156</td>
<td>0.15</td>
</tr>
<tr>
<td>ZNS-24</td>
<td>31</td>
<td>145</td>
<td>0.21</td>
</tr>
<tr>
<td>ZNS-56</td>
<td>201</td>
<td>32</td>
<td>6.28</td>
</tr>
<tr>
<td>Ru/ZSM-5 (CBV 3024E)</td>
<td>250</td>
<td>35</td>
<td>7.14</td>
</tr>
<tr>
<td>Ru/ZNS-12</td>
<td>22</td>
<td>145</td>
<td>0.15</td>
</tr>
<tr>
<td>Ru/ZNS-24</td>
<td>31</td>
<td>134</td>
<td>0.23</td>
</tr>
<tr>
<td>Ru/ZNS-56</td>
<td>200</td>
<td>30</td>
<td>6.67</td>
</tr>
</tbody>
</table>

Figure 3. Comparison of Ru-catalysts activity during guaiacol hydrogenation in dodecane at 50 bar H₂: (A) kinetic curves at 200 °C and (B) effect of temperature during 1 h of reaction.

In order to study the reasons for the products diversity, the acidity of the catalysts was studied using FTIR spectroscopy of adsorbed pyridine. The results are presented in Table 2. The results showed that the Brønsted acidity increased with the crystallization time (from ZNS-12 to ZNS-56), indicating a correlation between the Brønsted acidity and crystallinity of the micro-mesoporous materials. Previous studies have revealed that the Brønsted acid sites are formed by bridging hydroxyl (OH) groups located within the channels of zeolite, whereas the Lewis acid sites are situated on the external surface [42]. We found that an enhancement in crystallinity lead to an increase in Brønsted acidity only, whereas Lewis acidity remained mostly unaffected. Ryoo’s research suggested that there is no noticeable disparity in the local concentration of acid sites between the external surfaces and internal micropores, and a significant increase in both types of acidity can be achieved by opening
internal surfaces during nanosheet formation [25]. Consequently, an increase in the overall acidity in the ZNS-56 sample was expected.

It was found out that the HDO activity (selectivity towards fully hydrogenated- and deoxygenated-product–cyclohexane) under these conditions increased with the support acidity. There are studies that demonstrated the synergetic interactions of metal clusters with acid sites [21,27]. Those clusters are in a close contact with the acidic centers—what causes the transfer of electrons from Ru(0) and leads to the development of electron-deficient metal species (Ru$^{5+}$)—that are responsible for the certain properties of Ru-catalysts. The results obtained by FTIR spectroscopy of adsorbed pyridine demonstrated that the main interactions centres were Lewis acid sites. The concentration of Brønsted acid sites in all materials remained almost constant after the introduction of Ru. Therefore, it can be concluded that the intact Brønsted acid sites can still be active in the HDO of guaiacol.

The particles’ size distribution was determined using CO pulse chemisorption. The results showed that the average particles size was 4.2 nm for Ru/ZNS-56, and 4.5 nm for Ru/ZNS-24 and Ru/ZNS-12. To observe the influence of temperature on the products selectivity, an additional series of experiments was carried out. The activity of Ru catalysts based on micro-mesoporous materials had been investigated in the temperature range of 150–300 °C (5 MPa pressure, 1 h). The selectivity towards fully HDO product–cyclohexane was significantly increased with the increase of temperature. At 200 °C, a fully hydrodeoxygenated product—cyclohexane was observed for Ru/ZNS-56 (Table S1). Further temperature increasing did not change the product’s distribution. It should be noted that the increase in HDO activity was observed for all catalysts. A fully hydrogenated product–2-methoxycyclohexanol was observed at the lowest reaction temperature; in general, the selectivity towards this product was inversely corresponded to the samples acidity.

The morphology of a used catalyst was studied using TEM. Figure 4 shows the difference in Ru-species after the guaiacol hydrogenation procedure. Ru nanoparticles underwent a slight growth, and CO chemisorption demonstrated that the average particle’s size increased from 4.5 to 4.8 nm.

The stability of Ru-containing catalysts was tested under the same conditions in four catalytic runs. After the reaction, the catalyst was washed with acetone in order to remove the products, dried at ambient temperature, and placed in the autoclave with the substrate. The reaction conditions were (T—200 °C, P—50 bar H$_2$, $\tau$—3 h).

Figure 5 shows that the activity of the catalyst decreased on subsequent uses. ICP analysis of the liquid products showed that leaching from the Ru-catalyst was absent
and, therefore, it could not be the cause of the loss of activity. It was suggested that the difference in the catalysts’ reuse activity was due to their morphology. The activity decrease in the case of catalyst with nanosheets morphology–Ru/ZNS-56 was minimum, whereas in the case of MCM-41-like structure–Ru/ZNS-12 and bulk zeolite, the decrease in activity was significant.

Figure 4. TEM images of ZNS-12 before (A) and after (B) catalytic reaction at 200 °C, 50 bar H2, 3 h.

The stability of Ru-containing catalysts was tested under the same conditions in four catalytic runs. After the reaction, the catalyst was washed with acetone in order to remove the products, dried at ambient temperature, and placed in the autoclave with the substrate. The reaction conditions were (T—200 °C, P—50 bar H2, τ—3 h).

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Figure 5. Ru-catalysts activity after subsequent uses. Reaction conditions: 200 °C, P—50 bar H2, τ—3 h.

4. Conclusions

High active Ru-catalysts based on micro-mesoporous materials were successfully synthesized. Catalytic hydrogenation was carried out on Ru-catalysts using guaiacol as the model bio-oil compound. It was possible to provide an accelerated method of MFI nanosheets synthesis using zeolite seeds. Owing to the Brønsted acid sites available for the oxygen-contained substances, the Ru-based catalyst with the MFI nanosheets exhibited a very high catalytic activity in guaiacol hydrogenation compared with a conventional ZSM-5 zeolite.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/micro3020042/s1. Table S1. Selectivity over different catalysts. Reaction conditions: 200 °C, 50 bar H2, catalysts mass 0.05 g, 2.00 g of substrate (10 wt. % of guaiacol in n-C12H34). Table S2. Selectivity over different catalysts. Reaction conditions: 50 bar H2, 1 hour, catalysts mass 0.05 g, 2.00 g of substrate (10 wt. % of guaiacol in n-C12H34).

Author Contributions: Conceptualization, E.N. and A.M.; methodology, V.R. and D.G.; validation, A.M. and E.N.; formal analysis, A.S.; investigation, D.R. and D.T.; resources, E.N.; data curation, K.W.; writing—original draft preparation, D.T.; writing—review and editing, E.N.; visualization, A.S.; supervision, A.M.; project administration, E.N.; funding acquisition, E.N. All authors have read and agreed to the published version of the manuscript.

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