



Article Catalytic Pyrolysis of Lignin Model Compounds (Pyrocatechol, Guaiacol, Vanillic and Ferulic Acids) over Nanoceria Catalyst for Biomass Conversion

Nataliia Nastasiienko ^{1,*}, Tetiana Kulik ^{1,*}, Borys Palianytsia ¹, Julia Laskin ², Tetiana Cherniavska ¹, Mykola Kartel ¹ and Mats Larsson ³

- ¹ Chuiko Institute of Surface Chemistry, NAS of Ukraine, 17 General Naumov Str., 03164 Kyiv, Ukraine; borbor@i.ua (B.P.); t-cherniavska@ukr.net (T.C.); nikar@kartel.kiev.ua (M.K.)
- ² Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA; jlaskin@purdue.edu
- ³ Department of Physics, AlbaNova University Center, Stockholm University, SE-106 91 Stockholm, Sweden; ml@fysik.su.se
- Correspondence: nastasienkon@ukr.net (N.N.); tanyakulyk.isc.ms@gmail.com (T.K.); Tel.: +38-044-422-9676 (N.N. & T.K.)

Abstract: Understanding the mechanisms of thermal transformations of model lignin compounds (MLC) over nanoscale catalysts is important for improving the technologic processes occurring in the pyrolytic conversion of lignocellulose biomass into biofuels and value-added chemicals. Herein, we investigate catalytic pyrolysis of MLC (pyrocatechol (P), guaiacol (G), ferulic (FA), and vanillic acids (VA)) over nanoceria using FT-IR spectroscopy, temperature-programmed desorption mass spectrometry (TPD MS), and thermogravimetric analysis (DTG/DTA/TG). FT-IR spectroscopic studies indicate that the active groups of aromatic rings of P, G, VA, and FA as well as carboxylate groups of VA and FA are involved in the interaction with nanoceria surface. We explore the general transformation mechanisms of different surface complexes and identify their decomposition products. We demonstrate that decomposition of carboxylate acid complexes occurs by decarboxylation. When FA is used as a precursor, this reaction generates 4-vinylguaiacol. Complexes of VA and FA formed through both active groups of the aromatic ring and decompose on the CeO₂ surface to generate hydroxybenzene. The formation of alkylated products accompanies catalytic pyrolysis of acids due to processes of transalkylation on the surface.

Keywords: kinetics and mechanisms; bio-oil upgrading; kinetic parameters; 4-vinylguaiacol; surface complex; FT-IR spectroscopy; temperature-programmed desorption mass spectrometry

1. Introduction

Lignocellulose feedstock is a major potential renewable source of bio-oils and a large number of valuable chemicals. A total of 10–25% of lignocellulosic raw material is lignin [1]. The exact structure of lignin is still unknown; however, it is believed that lignin is formed through biosynthesis of *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [2]. Lignin determines the strength of trunks and stems of plants [3]. Due to its rigid structure, this natural polymer is currently used mainly for heat and energy production [4–7]. However, the growing amount of research on the production of bio-oil and various chemicals from lignocellulosic raw materials motivates the search for effective ways to process lignin [4,5,7].

Due to its unique structure, lignin can be a source of a large number of aromatic compounds, both monomers and polymers [1,8,9]. Since the structure of this natural polymer is extremely complex, model compounds are often used to study its conversion to high value-added chemicals [8,10]. Ferulic and vanillic acids, as well as pyrocatechol and guaiacol are common products of lignin processing [1,8,11–13], and therefore are often used as model lignin compounds [4,8,11,14–17]. These compounds are lignin structural units of



Citation: Nastasiienko, N.; Kulik, T.; Palianytsia, B.; Laskin, J.; Cherniavska, T.; Kartel, M.; Larsson, M. Catalytic Pyrolysis of Lignin Model Compounds (Pyrocatechol, Guaiacol, Vanillic and Ferulic Acids) over Nanoceria Catalyst for Biomass Conversion. *Appl. Sci.* 2021, *11*, 7205. https://doi.org/10.3390/app11167205

Academic Editor: María Atienza-Martínez

Received: 1 July 2021 Accepted: 28 July 2021 Published: 5 August 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). various sizes and contain almost the entire list of functional groups present in the lignin macromolecule. Among these products, guaiacol is an ideal model compound for assessing the performance of various catalysts, as it is a typical component of pyrolysis oil and one of the most complex methoxyphenols for deoxygenation [18,19]. Pyrocatechol is often an intermediate in converting other model lignin compounds, for example, guaiacol [8,20]. Ferulic acid may be used for the production of valuable aromatic chemicals, in particular 4-vinylguaiacol [20–24], vanillin, and vanillic acid [24–26].

In addition to lignin, these compounds are found in large quantities in other polymers of vegetable raw materials and in the waste generated during their processing (winedistilleries, olive oil processing, table olive industries, pulp paper processing, etc.) [26–29]. Due to the high toxicity of phenol-containing compounds to microorganisms [29–31], special attention is directed to their utilization [24,32].

Pyrolysis is commonly used for lignin processing due to its ability to effectively separate this polymer's strong structure [8,11,33,34]. However, high-temperature conversion of these raw materials generates a large number of final pyrolysis products. Various catalytic systems are used to overcome these imperfections [34]. CeO₂ is often used as a catalyst in the catalytic conversions of lignocellulosic raw materials [35–40]. Its catalytic properties are attributed to the ease with which it alternates between the 3+ and 4+ oxidation states, depending on the environmental conditions. [35]. The corresponding number of oxygen vacancies compensates for the decrease in the positive charge of Ce³⁺. The concentration of defects, both Ce³⁺ ions and oxygen vacancies, on the oxide surface is higher than in the bulk [41]. Therefore, nanosized cerium oxide has higher concentrations of Ce³⁺ ions and, accordingly, redox activity compared to large particles, since the surface-to-volume ratio increases [42]).

In the conversion and valorization of lignocellulosic raw materials and model compounds of lignin, cerium oxide is combined with other catalysts, particularly metals [38,39] and zirconium oxide [16,35,43]. In the work of Deng and co-authors [32], CeO₂ oxide with platinum deposited on its surface was used for the oxidative conversion of lignin and 2-phenoxy-1-phenyl-ethanol, which contains β -O-4 bonds and C α -hydroxyl groups, in monomeric aromatic compounds (4-methoxy-phenol, acetophenone, methyl benzoate (82%, 38%, and 40%). Pt/CeO₂ catalysts have also been used to convert 4-propyl-phenol to propylcyclohexane. [37]. The yield of propyl-cyclohexane was 83%, and propyl-cyclohexanol was < 1%. In this case, the catalyst worked effectively both in the presence of water and in anhydrous conditions [37].

Catalytic systems composed of both CeO₂ and ZrO₂ have proven their effectiveness [16,35,38,43]. They have many advantages over the individual oxides [35]. In particular, the combination of CeO₂ and ZrO₂ promotes a decrease in the required surface temperature and reduction volume as well as an increase in the number of oxygen vacancies. Such catalytic systems dissociate hydrogen and create oxygen vacancies under mild conditions. The inclusion of zirconium ions in the cerium lattice leads to structural compression and promotes the formation of oxygen vacancies. In addition, the presence of zirconium partially suppresses crystallization during the synthesis of catalysts and leads to the formation of small and active crystallites [35].

Using a CeO_2/ZrO_2 catalyst for the hydrodeoxygenation of guaiacol [35], valuable products such as phenol, catechol, and benzene were obtained. In addition, the use of this catalytic system increased the conversion efficiency of guaiacol and eliminated the formation of the undesirable oligomeric products containing hydrogenated rings. Moreover, these catalysts showed no signs of deactivation after 72 h of flow [35].

The efficiency of CeO₂, CeO₂-ZrO₂, Ni/CeO₂, and Ni/CeO₂-ZrO₂ catalysts for hydrodeoxygenation of phenol at intermediate temperature and pressure (275 °C and 100 bar) in a batch reactor was tested in [43]. Oxide catalysts (CeO₂, CeO₂/ZrO₂) showed low activity on the hydrodeoxygenation of phenol under these conditions due to their inability to hydrogenate the phenolic ring [43]. Reduced metal catalysts for both noble and base metals were significantly more active. Hydrodeoxygenation of phenol proceeded through initial hydrogenation to cyclohexanone, which rapidly hydrogenates to cyclohexanol [43]. Ni/CeO₂ and Ni/CeO₂-ZrO₂ were the most active catalysts for the initial hydrogenation of phenol to cyclohexanol but were insufficiently active in the next stage of deoxygenation [43].

Catalysts CeO₂, ZrO₂, Al₂O₃, CeO₂-SiO₂, and CeO₂-ZrO₂ were used in the ketonization of valeric acid into 5-nonanone, [44–46] and various fatty acids (C₂-C₁₀, D₆CCOOH, and CH₃COOH) into symmetric ketones [46]. The majority of the studied acids [46], especially valeric, acetic, levulinic, furandicarboxylic, and other acids, can be obtained by converting lignocellulosic biomass [47]. Conversely, lignin is a source for a number of natural cinnamic acids [1,48].

In [38], the activity and surface properties based on oxides of CeO₂ and ZrO₂ coated with nickel (Ni/CeO₂-ZrO₂) were used in the thermochemical conversion of cellulose. The catalyst Ni/CeO₂-ZrO₂ was effective in producing hydrogen during the conversion of cellulose raw materials. The presence of cerium oxide in such catalytic systems contributed to a slower decrease in their activity versus Ni/ZrO₂. It has been shown [38] that the tested catalysts allow the efficient formation of a gaseous fraction [38]. At the same time, in studies [16], Ni/CeO₂-ZrO₂ catalytic systems were used for lignin conversion. The main phenolic compounds in the obtained lignin oil were: guaiacol, methylguaiacol, ethylguaiacol, vanillin, and homovanillic acid [16]. However, the exact mechanisms of the transformations that occurred remain unclear.

In this work, we examined thermal transformations of several aromatic model compounds of lignin (guaiacol, pyrocatechol, vanillic acid, and ferulic acid) over the nanoceria catalyst. The results reported in this study are important for establishing the catalytic transformation mechanisms of both lignin and its processing products and other phenolcontaining plant raw materials over the CeO₂-based catalytic systems.

2. Materials and Methods

The model compounds used in this work were pyrocatechol (99%, Changzhou Winsun Import & Export Co., Ltd, Changzhou, Jiangsu, China), guaiacol (\geq 98%, Alfa Aesar, Karlsruhe, Germany), vanillic acid (97%, Sigma-Aldrich, Buchs, Switzerland) and ferulic acid (98%, Alfa Aesar, Karlsruhe, Germany). No further purification of these compounds was conducted in this work. Nanosized cerium dioxide (99.5%, S_{Ar} = 71 m²/g, Alfa Aesar, Karlsruhe, Germany) was pre-calcined at 500 °C for 2 h to remove organic matter.

A series of samples, P/CeO₂, G/CeO₂, VA/CeO₂, and FA/CeO₂, with concentrations of phenolic compounds of 0.1, 0.3, 0.6, 0.9, and 1.2 mmol/g were prepared. The concentration range of 0.1–1.2 mmol/g was selected based on previous studies [49]. According to [49], the maximum adsorption values for cinnamic acid and its derivatives, including ferulic acid, are almost equal and amount to $\approx 2.9 \times 10^{-4}$ mol/g irrespective of the differences in the reaction sites of their molecules. The samples were prepared by impregnation of 100 mg of CeO₂ with 2 mL of P, G, VA, and FA solutions in ethanol. The suspensions were stirred for several minutes and then dried at room temperature in the air.

Infrared spectra were recorded on a Thermo Nicolet Nexus FT-IR instrument (Thermo Nicolet Corporation, Madison, WI, USA) within the range of 4000–400 cm⁻¹, working in diffuse reflection mode. The resolution was 4 cm⁻¹, scanning speed—0.5 cm/s, and number of scans—50. Before the FTIR studies, pure CeO₂ and samples P/CeO₂, G/CeO₂, VA/CeO₂, and FA/CeO₂ were mixed with KBr (\geq 99%, Alfarus, Kyiv, Ukraine) (1:10). KBr was pre-calcined for 2 h at 500 °C. Pure phenolic compounds were mixed with KBr in a ratio of 1:100.

The TPD MS-experiment was performed on an MX-7304 monopole mass spectrometer (Electron, Sumy, Ukraine) with electron ionization, re-equipped for thermal desorption measurements [45,46,50]. At the beginning of the experiment, a sample weighing 10–20 mg was placed in a quartz-molybdenum ampoule and pumped out at room temperature to a pressure of ~5 × 10⁻⁵ Pa. The rate of programmed linear heating was 0.17 °C/s. Heating was increased from room temperature to 750 °C. Volatile products of thermolysis entered the ionization chamber of the mass spectrometer and were ionized and fragmented under

the action of electrons. The range of the investigated masses was 1–210 a.m.u. The total number of mass spectra recorded during the experiment reached ~240. The slow heating of the sample and the high pumping rate of volatile thermolysis products made it possible to neglect diffusion effects. Under such conditions, the intensity of the ion current was proportional to the rate of desorption.

Kinetic parameters of the chemical reactions and processes of the lignin model compound on the nanoceria surface (temperature of the maximum desorption rate T_{max} , reaction order *n*, activation energy E^{\neq} , pre-exponential factor ν_0 , and change of activation entropy ΔS^{\neq}) were calculated from the TPD-MS data by an in-house computer program using the linear form of the Arrhenius equation [45,46,50].

Thermogravimetric analysis, differential thermogravimetric analysis (DTG), and differential thermal analysis (DTA) were performed using a TGA/DTA analyzer (Q-1500D, Hungary). Samples weighing 100 mg were heated from room temperature to 1000 °C. The heating rate was 10 °C/min in an air atmosphere.

3. Results and Discussion

3.1. FT-IR Spectroscopic Studies

3.1.1. Pyrocatechol

FTIR spectra of CeO₂, pure P, and samples P/CeO₂ are presented in Figure 1. Interpretation of the obtained results, performed on the basis of experimental data [51,52] and the results of quantum chemical calculations of the frequencies of normal vibrations of pyrocatechol in the crystalline and gaseous states [53], are presented in Table 1. The symbol ν is used to denote valence vibrations, β for out-of-plane deformation vibrations, and δ for non-planar deformation vibrations.



Figure 1. Fourier transform-infrared (FT-IR) spectra of pure CeO₂ (a), samples of P/CeO₂ with different contents of FA (0.1: b; 0.3: c; 0.6: d; 0.9: e; 1.2 mmol/g: f) and pure P (g).

	Frequen	Frequency (cm ⁻¹)			
Assignments	Р	P/CeO ₂	Kef.		
β(CH)	721	_	[53]		
β(CH)	937	_	[53]		
$\delta(OH) + \delta(CH))$	756	_	[53]		
$\nu(CC) + \nu(CO) + \beta(CCC))$	769	_	[53]		
$\nu(CO) + \nu(CC) + \beta(CCH)$	1167	-	[53]		
β (CCH) + ν (CC) + β (COH)	1188	1188	[51,53]		
β (CCH) + β (COH) + ν (CC)	1242	-	[53]		
β (CCH) + β (COH) + ν (CC)	1255	1261	[51,53]		
$\nu(CC) + \nu(CO) + \beta(CCC)$	1281	-	[51,53]		
β (CCH) + β (COH) + ν (CC)	1363	1361	[53]		
$\beta(COH) + \nu(CO)$	_	1273 *			
ν(CO) ⁻	_	1297			
β (CCH) + ν (CC) + β (COH) + β (CCO)	1440	1446	[53]		
$\nu(CC) + \beta(CH)$	1471	-	[53]		
$\nu(CC) + \beta(CH)$	-	1483			
$\nu(CC) + \beta(CH)$	1514	1514 *	[53]		
$\nu(CC) + \beta(CH)$	_	1576			
$\nu(CC) + \beta(CH)$	1603	1603 *	[53]		
$\nu(CC) + \beta(CH)$	1620	_	[53]		

Table 1. Assignments of infrared bands of pure P and of P/CeO ₂ (0.6)	umol/g)	;)
---	---------	----

* band appears for P concentrations > 0.6 mmol/g.

According to [53], most of the bands of this dihydroxybenzene have a mixed shape. Figure 1 shows significant changes in the P/CeO₂ spectra compared with pure P (Figure 1, Table 1), which is the result of the interaction of P molecules with oxide. The absorption bands at 721 and 937 cm⁻¹, which correspond to C–H stretching vibrations [53] of pure pyrocatechol molecules in the crystalline state, are a sign of association due to intermolecular hydrogen bonds [53]. The disappearance of these absorptions for P/CeO₂ indicates the destruction of this association structure of P due to interaction with the oxide surface.

The obtained spectra of the studied samples contain several other features indicating the interaction of OH groups of pyrocatechol with CeO₂. In particular, one of these signs is a significant decrease in the intensity of the bands 756 (δ (OH) + δ (CH)) and 769 cm⁻¹ (ν (CC) + ν (CO) + β (CCC)) [53].

There are bands 849 and 859 cm⁻¹ (Figure 1) for pyrocatechol in the region of 800–900 cm⁻¹, which according to [48,53], are mixed and associated with non-planar deformation vibrations of CH, deformation vibrations of CC, as well as vibrations of COH groups. For P/CeO_2 samples, changes in this region of the spectrum are observed due to the interaction of OH groups of P with the oxide surface. Absorption at 1041 cm⁻¹ for pyrocatechol is mainly due to the stretching vibrations of the CC, and 1095 cm⁻¹ is associated with vibrations of CC, CH, and COH groups. For P/CeO_2 samples, these bands are shifted toward lower frequencies, and their relative intensity decreases.

In addition, for P/CeO₂ samples, changes were found in the range $1150-1400 \text{ cm}^{-1}$. This region's absorption mainly corresponds to stretching and bending vibrations of COH [51,53].

Analysis of the IR spectra of pyrocatechol in the crystalline state and the gas phase [48] shows that the ultrathin structure of the bands in this region is associated with the formation of intermolecular and intramolecular bonds. From Figure 1, it is seen that the maximum of 1167 cm⁻¹, which is due mainly to v(CO) vibration [53], essentially disappears for all concentrations of P/CeO₂. At the same time, the intensity of the bands at 1188 and 1365 cm⁻¹, which partially corresponds to the β (COH) vibrations [51,53], decreases significantly. Instead of a wide band with three peaks at 1242, 1255 (β (COH) [51,53]), and 1281 cm⁻¹ (v(CO)) [51,53], for lower concentrations, one maximum was detected at 1261 cm⁻¹, and only when the concentration of P increases to 0.6 mmol/g, a peak appears at 1273 cm⁻¹.

At the same time, all P/CeO₂ spectra contained a new band at 1297 cm⁻¹, which may indicate the formation of a bond between pyrocatechol and CeO₂. It is known that the new bands found in this area by the interaction of phenol and phenolic compounds with metal surfaces, as well as surfaces of oxides and hydroxides of metals [54–58], were signs of the formation of new bonds.

The binding of P to the oxide surface significantly affected the absorption of its aromatic ring, which manifested in the displacement of the absorption bands of P and changes in their intensity. In particular, for pure P, the vibration band v (CC) was registered at 1471, 1514, 1603, and 1620 cm⁻¹ [53], while in the P/CeO₂ spectrum, the corresponding absorptions were registered at 1446, 1483, and 1576 cm⁻¹. Bands characteristic of pure P (1471, 1514, 1603, and 1620 cm⁻¹) also appeared in the spectra of P/CeO₂ samples with a P concentration above 0.6 mmol/g (Figure 1). This is probably because the amount of P exceeds the number of active centers of the CeO₂ surface. The obtained results indicate the formation of chemisorbed pyrocatechol complexes on the CeO₂ surface.

The P/CeO₂ spectrum (Figure 1) is similar to the IR spectra of pyrocatechol adsorbed on the nanosized TiO₂ surface [51,59–61]. According to the results of quantum chemical calculations [61] and experimental data [51,56,60,61], this type of spectra of P adsorbed on TiO₂, in which the bands 1250 cm⁻¹ and 1475 cm⁻¹ are the most intense, is more characteristic of complexes with a bidentate bridge structure. Since the most intense absorptions in the P/CeO₂ spectrum correspond to the bands 1263 and 1483 cm⁻¹ (Figure 1), it is probable that the P complexes on the CeO₂ surface also have a bidentate bridge structure (two oxide atoms of phenolic groups of P interact with two metal atoms).

3.1.2. Guaiacol

The FT-IR spectra obtained for pure G and immobilized on the surface of CeO₂ are shown in Figure 2. The absence for G/CeO₂ of the absorption band at 1364 cm⁻¹, which corresponds to β (OH) [62] (Table 2), as well as the decrease in the intensity of absorption at 1261 cm⁻¹ (v(CO) [62]), indicates the participation of the OH group of G in the interaction with CeO₂.



Figure 2. Fourier transform-infrared (FT-IR) spectra of pure CeO_2 (a), samples of G/CeO_2 with different contents of G (0.1: b; 0.3: c; 0.6: d; 0.9: e; 1.2 mmol/g: f) and pure G (g).

Accionmente	Frequen	$cy (cm^{-1})$	D .(
Assignments	G	G/CeO ₂	Ker.
v _s (COCH ₃)	1024	1018	[63]
$\nu_{as}(COCH_3)$	1225	1217	[63]
ν(COH)	1261	1261	[63]
ν(CO)⁻	-	1288	[63]
ν(CO)⁻	-	1323	[63]
β(COH)	1363	-	[63]
β(CH ₃)	1444	-	[63]
β(CH ₃)	1469	_	[63]
$\nu(CC) + \beta(CH_3)$	1458	1456	[63]
ν(CO)	1508	1498	[63]
$\nu(CC)$	1597	1595	[63]
v(CC)	1617	-	[63]

Table 2. Assignments of characteristic infrared bands of pure G and of G/CeO₂ (0.6 mmol/g).

At the same time, for these samples, the bands of symmetric (ν_s) and asymmetric (ν_{as}) valence vibrations of the C-O-CH₃ groups, which were registered for guaiacol at 1024 and 1225 cm⁻¹ [63], shifted to 1018 and 1217 cm⁻¹, respectively. In addition, absorption bands in the range 1444–1469 cm⁻¹, corresponding to the β (CH₃) vibrations [62,63], were transformed. In particular, the peaks at 1444 and 1469 cm⁻¹ disappeared, and the maximum at 1458 cm⁻¹ shifted to 1456 cm⁻¹. These changes indicate the interaction of the methoxyl groups of G with CeO₂.

The new bands at 1288 and 1323 cm⁻¹ in the spectra of G/CeO₂ samples were a sign of the formation of chemisorbed G complexes [62]. The absorptions for ν (CH₃) at 2843 cm⁻¹ partially remained in the spectra of G/CeO₂.Therefore, the interaction of the COCH₃ group with the oxide surface probably occurred through an oxygen atom without cleavage of CH₃. At the same time, it is possible that several methoxyl groups may have been freed.

Thus, the obtained data (Figure 2) indicate the formation of G complexes on the nanoceria CeO_2 bound to the oxide surface through the phenolic and methoxyl groups simultaneously, as well as separately through each of these groups.

In addition, the shift of the band of C = C vibrations may also indicate the interaction of the aromatic ring G with the oxide surface [62]. Figure 2 shows that the C = C band, which for pure G is about 1502 cm⁻¹, for the G/CeO₂ samples is shifted to 1498 cm⁻¹. According to [62], such a shift may be a sign of the presence on the CeO₂ surface of weakly bound G complexes, which occur due to the simultaneous formation of hydrogen bonds between the CH-group of the aromatic ring and the surface hydroxyl as well as OH group of G and the surface cerium atom.

3.1.3. Vanillic Acid

Figure 3 shows the spectra of pure VA immobilized on CeO₂. The presence of different COH groups in the VA molecule complicates the interpretation of the obtained spectra. Literature data [15,59,64,65] and our FT-IR spectroscopic studies of P, G, and carboxylic acids [22,45,50] were used to analyze the IR spectra of pure VA and VA/CeO₂. From the obtained spectra (Figure 3, Table 3), it was found that both the carboxyl group and the active groups of the aromatic ring of VA are involved in the interaction with CeO₂. In particular, for VA/CeO₂ samples, a decrease in the intensity of bands at 1030 cm⁻¹ ($\nu_{\rm s}$ (COCH₃)), 1240 cm⁻¹ ($\nu_{\rm \alpha s}$ (COCH₃)) [15,64] and at 1113, 1188, 1456, and 1473 cm⁻¹ (β (CH₃)) [15,65] was observed. This indicates the participation of the methoxyl group in the interaction with the oxide surface.



Figure 3. Fourier transform-infrared (FT-IR) spectra of pure CeO_2 (a), samples of VA/CeO₂ with different contents of VA (0.1: b; 0.3: c; 0.6: d; 0.9: e; 1.2 mmol/g: f) and pure VA (g).

Table 3. Assignments of characteristic infrared bands of pure VA and of VA/CeO₂ (0.6 mmol/g).

Assistments	Frequer	D (
Assignments	VA	VA/CeO ₂	Kef.
δ(COH)	920	_ *	[15]
$\nu_{s}(COCH_{3})$	1030	1018	[15]
β(CH ₃)	1113	1113	[61]
β(CH ₃)	1188	1188	[15,65]
$v_{as}(COCH_3)$	1240	1240	[15]
$\nu(CO_{ap})$	1284	1288	[15]
$\nu(COH) + \beta(OH)$	1299	-	[15]
ν(CO) ⁻	-	1275	
β(CH ₃)	1456	1456	[15,65]
β(CH ₃)	1473	1467	[15,65]
$\nu_{\rm s}({\rm COO^-})$	-	1410	
$\nu_{as}(COO^{-})$	-	1539	
$\nu(C = O)$	1686	_ *	[15]

* for VA concentrations 0.1–0.3 mmol/g.

A wide intense band, which in the spectra of pure acid has two maxima at 1284 cm⁻¹ and 1299 cm⁻¹, occurs mainly as a result of vibrations of carboxyl and aromatic COH groups ((COH)_{ar}) of acid [15,65]. In the spectra of the VA/CeO₂ samples, it undergoes significant transformations; instead of two maxima, a peak appears at 1288 cm⁻¹ and a shoulder in the 1275 cm⁻¹ region. From this, we can conclude that both the carboxyl and phenolic groups can be involved in binding to the surface of CeO₂.

According to studies of complexes of ferulic and caffeic acids with the metal ions $(Cu^{2+}, Al^{3+}, Na^+) CuCl_2$, $AlCl_3$, and Na [66], new absorption bands associated with the formation of bonds between aromatic ligands of these acids and metal ions can appear in the FT-IR spectra in the region from 1090 to 1300 cm⁻¹. Their position depends on the type of metal and the reagent ratio [66]. The high reactivity of phenolic OH groups of a number of carboxylic aromatic acids (vanillic, gallic, and caffeic) in interaction with cerium oxide was also recorded in [67] by UV-Vis spectroscopy.

A number of signs indicating the formation of carboxylate complexes were detected in the VA/CeO₂ spectra. In particular, the absorption at 1686 cm⁻¹ (ν (C = O)) and 920 cm⁻¹ (δ (COH)) [15]) disappeared for concentrations of 0.1–0.3 mmol/g, and for higher concentrations the intensity of these bands were smaller compared to pure VA. At the same time, the broad bands appeared at ~1410 cm⁻¹ (ν _s(COO⁻)) and 1539 cm⁻¹ (ν _{as}(COO⁻). The presence in this part of the spectrum of absorption bands ν (CC) (at 1523 cm⁻¹—for

pure VA) prevented an accurately identification of the bands at ~1510 cm⁻¹ for VA/CeO₂ samples. It may correspond to both $v_{as}(COO^-)$ and v(CC). The difference, $\Delta v = v_{as}(COO) - v_s(COO^-)$, was used as a criterion to establish the coordination of the COO⁻ group to the metal [68] and oxide surfaces [22,45,59,69–71]. The value of Δv for VA/CeO₂ was 129 cm⁻¹, which corresponded to the bidentate VA complexes with a bridge structure formed on the nanoceria surface.

3.1.4. Ferulic Acid

FA has a more complex structure compared to VA because it has a group C = C in the aliphatic part of the acid. This is manifested in its vibrational spectrum (Figure 4, Table 4). The interaction of FA with the oxide surface caused a number of changes in the spectra of FA/CeO₂ (Figure 4). Bands 1036 cm⁻¹ (v_s(C-O-CH₃)) and 1205 cm⁻¹ (v_{as}(C-O-CH₃)) [72,73] for FA/CeO₂ were shifted to 1034 cm⁻¹ and 1211 cm⁻¹, respectively. In addition, bands at 1115 and 1178 cm⁻¹ disappeared in the FA/CeO₂ spectra, which was most likely associated with β (CH₃) vibrations [72], and a new band appeared at 1124 cm⁻¹. The intensity of the band 1466 cm⁻¹ (β (CH₃)) [64,72] significantly decreased (Figure 4). This indicates the participation of the methoxyl group in the interaction with the nanoceria surface.



Figure 4. Fourier transform-infrared spectra of pure CeO₂ (a), samples of FA/CeO₂ with different contents of FA (0.1: b; 0.3: c; 0.6: d; 0.9: e; 1.2 mmol/g: f) and pure FA (g).

Assistments	Freque	ncy (cm ⁻¹)	D (
Assignments —	FA	FA/CeO ₂	Kef.
δ(COH)	920	-	[64,74]
$\nu_{s}(\text{COCH}_{3})$	1036	1034	[72,73]
β(CH ₃)	1115	1124	[73]
$\beta(OH)_{ap}$	1167	-	[73]
$\beta(OH)_{ap}$	1178	-	[73]
$v_{as}(COCH_3)$	1205	1211	[72,73]
$\nu(CO)_{ap}$	1290	-	[72,73]
$\nu(CO)_{ap}^{-}$	-	1296	
v(CO)	-	1405	
$\nu_{\rm s}({\rm COO^-})$		1450	
$\beta(CH_3)$	1466	1468	[64,72]
$v_{as}(COO^{-})$	-	1502	
$\nu(CC)_{ap}$	1601	1601	[72]
$v(C = \hat{O})$	-	1608	
v(C = C)	1620	1637	[72]
$\nu_{s}(COO^{-})$	1666	-	[72]
$\nu_{s}(COO^{-})$	1691	-	[72]

Table 4. Assignments of characteristic infrared bands of pure FA and of FA/CeO₂ (0.6 mmol/g).

The absorption ratios at 1115 cm⁻¹ for pure FA in the literature data differ between $(\beta(CH_3)-[72])$ and $(\beta(CH)-[74])$, as well as the absorption ratios of bands at 1113 cm⁻¹ for VA $(\beta(CH_3)-[65])$ and $(\beta(CH)-[15])$. However, these bands all corresponded to $(\beta(CH_3))$, while the new bands, which appeared at 1124 cm⁻¹ for FA/CeO₂ and 1130 cm⁻¹—for VA/CeO₂, corresponded to $\beta(CH_3)$ vibrations of methoxyl groups involved in the interaction with the surface.

The interaction of the aromatic OH group of FA with CeO₂ can be evidenced by the absence of bands in the spectra of the FA/CeO₂ samples at 1167 cm⁻¹ β (OH)_{ar} [72] and 1290 cm⁻¹ (ν (CO)_{ar}) [72], and the appearance of absorption at 1296 cm⁻¹ (0.1–0.6 mmol/g). Thus, we can discuss the interaction of FA with the surface of CeO₂ through both methoxyl and phenolic groups.

The formation of carboxylate complexes of FA on the cerium oxide surface was also detected by the FT-IR spectra of FA/CeO₂ samples (Figure 4). The appearance of bands at 1405 cm⁻¹ (CO) and 1608 cm⁻¹ (C = O) may be associated with the formation of monodentate carboxylate complexes ($\Delta v = v(C = O) - v(C-O) = 203 \text{ cm}^{-1}$). The band 1608 cm⁻¹ overlapped with the absorption of the aromatic ring vibration (1601 cm⁻¹). The new bands at 1450 cm⁻¹ (v_{as} (COO⁻)) and 1502 cm⁻¹ (v_{as} (COO⁻)) corresponded to the bidentate chelate complexes, since $\Delta v = 52 \text{ cm}^{-1}$.

The C = O vibrations at 1666 and 1691 cm⁻¹ as well as β (COH) at 1325 cm⁻¹ and δ (COH) at 949 cm⁻¹ ([64,74] in the spectra of FA/CeO₂ (0.1-0.6 mmol/g) disappeared. The appearance of these and other bands of pure acid in the FA/CeO₂ spectra (0.9–1.2 mmol/g) was due to the formation of intermolecular acid associates. This was confirmed by the presence of absorptions in the region of 2400 cm⁻¹, which correspond to v(OH) of dimers [64]. FA associates can form on the surface when the number of FA molecules exceeds the available active centers of the oxide surface.

A significant shift up to 1637 cm⁻¹ was observed for the absorption band ν (C = C) for the FA/CeO₂ samples. Such a type of shift was also found in the interaction of FA with metals [74,75].

3.2. *Thermal Transformations of Model Lignin Compounds on the Surface of CeO*₂ 3.2.1. Pyrocatechol

The study of thermal transformations of P/CeO₂ samples by the TPD MS method is presented in Figure 5. According to thermograms and the P/T-curve (Figure 5), the thermal decomposition of P/CeO₂ occurred in several stages at the range of 50–750 °C. At the same time, no desorption of pyrocatechol in molecular form (M.r. = 110 Da, m/z 110) was observed over the entire temperature range studied. This indicates that pyrocatechol binds to the surface of nanoceria, and its pyrolysis occurs due to the transformation of surface complexes. This is confirmed by the data of IR spectroscopy, according to which changes in the absorption of COH groups and the appearance of a new band at 1297 cm⁻¹ indicate chemisorption of pyrocatechol.

In this case, one feature was observed: the peaks at a temperature of about 120 °C on the TPD curves for aliphatic series ions m/z 99, 85, 71, 57, and 43. According to [76], such a set of ions is characteristic of aliphatic compounds, namely, alkyl derivatives, alicyclic alcohols (m/z 99 (C₆H₁₁O), m/z 85 (C₆H₁₂), m/z 71 (C₅H₁₁), m/z 57 (C₄H₉), and m/z 43 (C₃H₇)). The formation of aliphatic products can result from the decomposition of phenolate complexes of pyrocatechol. It is known that the Ar-OH bond is one of the strongest types of C-O bonds, for example, for guaiacol and other phenol derivatives [35]. It is believed that, before breaking, this bond must first be weakened by hydrogenating the aromatic ring [43,77,78]. According to [43], deoxygenation in the presence of the catalysts CeO₂ and CeO₂-ZrO₂ occurs more easily from the saturated cycle than from the unsaturated cycle. This is due to the dissociation energy of the CO bond in alcohols, which decreases in the following order: aromatic alcohol (469 kJ/mol), secondary alcohol (385 kJ/mol), primary alcohol (383 kJ/mol), tertiary alcohol (379 kJ/mol) [43]. We do not rule out the possibility of such a process on the surface of CeO₂, because during the study, we recorded

an intense signal of hydrogen evolution (m/z 3) (Figure 5B). The formation of aliphatic products was likely due to complex redox processes on the surface of nanoceria. However, the intensity of these processes was low. The main processes were of deep destruction of pyrocatechol. This conclusion can be made by comparing the intensities of TPD peaks of the aliphatic series with TPD peaks, which characterize the processes of dehydration (m/z18), decarboxylation (m/z 44), and desorption of CO and C₂H₄ (m/z 28) (Figure 5C,D). The strong influence of the interactions with catalyst surface on the structure of the pyrocatechol molecule was also indicated by the obtained IR spectra. Figure 1 shows that significant changes occurred not only in the absorption of COH groups, through which the interaction occurs, but also in the absorption of the aromatic ring. In particular, the absorption at 1471 cm⁻¹ shifted by 12 cm⁻¹ to the high-frequency region, and the absorption at 1603 and 1620 cm⁻¹ was almost invisible for small concentrations (0.1–0.3 mmol/g).



Figure 5. Thermal decomposition of P/CeO₂ (0.6 mmol/g); vapor pressure measured as a function of temperature for the FA/Al₂O₃ sample (**A**); mass spectra at 120 °C (**B**); TPD curves for ions with m/z 18, 28, and 44 (**C**); for ions with m/z 43, 57, 71, 85, and 99 (**D**).

Figure 6 and Table 5 show the results of a DTG/DTA/TG study of CeO₂ and P/CeO₂ samples. The main weight loss of the CeO₂ sample is recorded in the temperature range 20–200 °C, which was probably associated with the desorption of water from the oxide surface. The decomposition of the G/CeO₂ sample, according to the DTG curve (Figure 6A), proceeded in two stages: 100–150 °C and 150–430 °C. All stages were exothermic. The main weight loss occurred in the second stage.



Figure 6. Differential thermal analysis (DTA), differential thermogravimetric analysis (DTG), and thermogravimetric (TG) curves for CeO₂ (**A**) and P/CeO₂ (0.6 mmol/g) (**B**).

Sample	Stage	T _{max} (°C)	Volatiles (%)	Char (%)
P/CeO ₂	$I \\ II \\ \Sigma(I + II)$	85 224	8.4 72.3 80.7	19.3

Table 5. Pyrolysis yields for TGA pyrolysis of P/CeO2 (0.6 mmol/g).

3.2.2. Guaiacol

Pyrolysis of guaiacol on the surface of nanoceria proceeded similarly to pyrolysis of pyrocatechol (Figure 7). Namely, there was no desorption of guaiacol in molecular form (M.r. = 124 Da, m/z 124); the formation of aliphatic products (m/z 99, 85, 71, 57, 43) occurred in the same temperature range. Consequently, their formation was probably the result of transformations of similar surface complexes P and G on the nanoceria surface. It could also be phenolate complexes, which were confirmed above using IR spectroscopy.



Figure 7. Thermal decomposition of G/CeO₂ (0.6 mmol/g); mass spectra at 120 °C and vapor pressure measured as a function of temperature for the G/CeO₂ sample (**A**); TPD curves for ions with m/z 3, 18, 28, 31, and 44 (**B**); for ions with m/z 43, 57, 71, 85, and 99 (**C**); for ions with m/z 3, 12, 15, 31, 50, 78, and 94 (**D**).

The presence of peaks on the TPD curves for ions with m/z 31, 32 (CH₃OH) and m/z 94 (PhOH) indicates the presence of an additional stage of pyrolysis, probably as a result of thermal transformations of G-complexes bound to the surface through the methoxyl group, the formation of which was evidenced by a number of changes recorded in the absorption of the methoxyl group during the study of these samples by the FT-IR spectroscopy (Figure 2 and Table 2).

A peak at ~358 °C on the TPD curve for the ion with m/z 78 (benzene) was recorded as well as a minor release of the product with m/z 94 (hydroxybenzene). The intensity of the latter was low. These peaks could be associated with the decomposition of G-complexes, which were formed due to the interaction of both active groups of the aromatic ring with two active centers of the cerium oxide surface. The existence of bidentate structures on the oxide surface was evidenced by the disappearance of absorption at 1363 cm⁻¹ (β (COH)) and the appearance of new bands at 1288 and 1323 cm⁻¹ in the IR spectra of the G/CeO₂ samples (Figure 2). The work [35] confirms the possibility of forming such G-complexes on the CeO₂ surface. It was found that the hydrodeoxygenation of guaiacol over CeO₂-ZrO₂ catalysts required two oxygen vacancies [35].

Intense peaks on the TPD curves of ions with m/z 28 (C₂H₄), m/z 14 (CH₂), m/z 12 (C), and m/z 3 (H) at 225 °C were observed during thermal decomposition of the G/CeO₂ samples (Figure 7B). The presence of these peaks indicates intense desorption of ethylene

 $(C_2H_4, M.r. = 28, m/z 28, 14, 12)$, that can serve as confirmation of the alkylation processes of the nanoceria surface, which occurs during the pyrolysis of G. The data presented in [35] confirm the possibility of alkylation of the oxide surface during pyrolysis of G.

The DTG/DTA/TG study results of the G/CeO₂ pyrolysis are presented in Figure 8. The thermal decomposition of the sample occurred up to 400 °C. On the DTG curve, we can distinguish two stages of weight loss for the G/CeO₂ sample. The first stage corresponded to T_{max} ~100 °C, the second to T_{max} ~180 °C. All stages were exothermic. The maximum weight loss occurred in the second stage at ~180 °C (Table 6).



Figure 8. Differential thermal analysis (DTA), differential thermogravimetric analysis (DTG), and thermogravimetric (TG) curves for G/CeO₂ (0.6 mmol/g).

Sample	Stage	T _{max} (°C)	Volatiles (%)	Char (%)
G/CeO ₂		100 180	20.3 49.3	30.4
G/CeO ₂	$\Pi \Sigma(I + II)$	180	49.3 69.6	

Table 6. Pyrolysis yields for TGA pyrolysis of G/CeO₂ (0.6 mmol/g).

Analysis of TPD MS and DTG data of the G/CeO_2 samples (Table 6 and Figures 7 and 8) may indicate that the greatest weight loss occurs due to the decomposition of the G-complexes formed through the methoxyl group.

3.2.3. Vanillic Acid

The TPD MS study results of the VA/CeO₂ sample are presented in Figure 9. The decomposition interval of VA on the CeO₂ surface was 100–750 °C (Figure 9). According to thermograms and the P/T-curve (Figure 9C,D), the pyrolysis of VA on the CeO₂ surface occurred in several main stages: 130, 270, 370, 550, and 650 °C.



Figure 9. Thermal decomposition of VA/CeO₂ (0.6 mmol/g); mass spectra at 270 °C (**A**) and 410 °C (**B**); TPD-curves for ions with m/z 18, 24, 44, and vapor pressure measured as a function of temperature for the VA/CeO₂ sample (**C**); TPD-curves for ions with m/z 31, 94,109, 124, 151, and 182 and for ions with m/z 94, 108, and 124 (**D**).

The low-intense peak of decarboxylation (m/z 44, T_{max} ~130 °C) probably corresponds to the decomposition of associates of VA, which formed on the oxide surface, as was recorded during the pyrolysis of caffeic acid on CeO_2 [79] (Figure 9C). The formation of such associates in the VA/CeO_2 sample was confirmed by the presence in their IR spectra of bands at 1686 cm⁻¹ (ν (C = O)) and 920 cm⁻¹ (δ (COH)) (Figure 3) as well as in the region 2400–2700 cm⁻¹, which belongs to pure acid. Intense release of guaiacol (M.r. = 124 Da, m/z 124, $T_{max} \sim 270 \ ^{\circ}C$) can be a consequence of the decarboxylation of VA molecules bound to the oxide surface through the carboxyl group (Scheme 1), similar to the decomposition of the caffeic acid carboxylate complexes on the CeO₂ surface [79] and on the SiO_2 surface [80]. The involvement of the carboxyl group of VA in the interaction with the oxide was confirmed by the appearance of $v(COO^{-})$ bands (1410, 1539 cm⁻¹) in the IR spectra (Figure 3). The second low-intensity peak was observed for guaiacol (m/z 124) $(T_{max} \sim 330 \degree C, Figure 9D)$, which can be formed by pyrolysis of VA molecules bound to the oxide through OH_{ar}. The possibility of such a bond is indicated by the transformation of the 1284 cm⁻¹ band, which corresponds to the vibrations of the CO_{ap} group (Figure 3). Along with gualacol at about 330 °C, the release of a product with m/z 108 was recorded, which can be identified as anisole. It can also be a conversion product of a VA complex linked through OH_{ar}. However, since the C-OH bond was strong [14], and the probability of breaking this bond is small, a product with m/z 108 may correspond to cresol.



Scheme 1. The decarboxylation of VA molecules bound to the oxide surface through the carboxyl group.

It is known that phenol can be transalkylated to various cresol isomers [81]. This reaction requires Lewis acid sites, which promote the formation of a methyl cation as an

intermediate in the alkylation reaction [82]. In addition, it is known [81] that CeO₂ is a good catalyst for ortho-methylation of phenol with methanol. Therefore, it is likely that surface methoxy groups, which are formed by the decomposition of VA complexes associated with the methoxyl group, can react with oxygen vacancies, turning into surface methyl groups involved in the transalkylation reaction [35]. The presence of the methoxyl and methyl groups linked to the surface was confirmed by peaks on the TPD curves of the ions with m/z 32, 31, and 15. These peaks at $T_{max} \approx 294$ °C are probably related to desorption methanol (CH₃OH, M.r. = 32 Da, m/z 32, 31) [76] (Figure 9D).

In our opinion, the release of hydroxybenzene (T_{max} ~380 °C, Figure 9D) can also result from the transformation of the phenolic complex linked through both active groups of the aromatic ring (Scheme 2). Such a decomposition mechanism was observed for similar caffeic acid complexes on the surfaces of CeO₂ and SiO₂ [79,80].



Scheme 2. The decomposition of the phenolic complex of VA.

The ion with m/z 151 was observed in the mass spectra of the VA/CeO₂ sample in a wide temperature range (150–450 °C) (Figure 9A). T_{max} of TPD peak for this ion was located at ~ 380 °C (Figure 9D). The presence of this peak could be related to the formation of the vanillin (M.r. = 152 Da, m/z 151 (100%), m/z 152 (93%), m/z 81 (32%), m/z 109 (25%), and m/z 123 (18%) [83]). Vanillin can form due to the VA reduction processes on the nanoceria surface.

The DTG/DTA/TG data obtained during the pyrolysis of the VA/CeO₂ sample are shown in Figure 10. Thermal decomposition of the sample proceeded in three main stages and continued in the range from 100 to 500 $^{\circ}$ C. All stages were exothermic.



Figure 10. Differential thermal analysis (DTA), differential thermogravimetric analysis (DTG), and thermogravimetric (TG) curves for VA/CeO₂.

Analysis of the results of the TG/DTG and TPD MS studies shows that the greatest weight loss occurred during the decomposition of the carboxylate complexes with the release of guaiacol ($T_{max} = 265 \text{ °C}$) (Table 7).

Sample	Stage	T_{max} (°C)	Volatiles (%)	Char (%)	
VA/CeO ₂	Ι	115	4.3		
VA/CeO ₂	II	175	10.9	01.0	
VA/CeO ₂	III	265	63.0	21.8	
VA/CeO ₂	$\Sigma(I + II + III)$		78.2		

Table 7. Pyrolysis yields for TGA pyrolysis of VA/CeO₂ (0.6 mmol/g).

3.2.4. Ferulic Acid

The results of the TPD MS study of the FA/CeO₂ sample are presented in Figures 11 and 12. According to Figure 11, the main decomposition products were the 3-methoxy-4-vinyl phenol (MVPh) (M.r. = 150 Da, m/z 150, $T_{max} \approx 110$ and 220 °C), guaiacol (Mr = 124 Da, m/z 124, $T_{max} \approx 261$ °C), 4-Vinylmethylguaiacol (Mr = 164 Da, m/z 164, $T_{max} \approx 334$ °C) and hydroxybenzene (Mr = 94 Da, m/z 94, $T_{max} \approx 407$ °C). The decomposition of the sample occurred from 55 to 700 °C (Figure 12A,B).



Figure 11. Mass spectra obtained by decomposition of FA/CeO₂ at a temperature of 250 °C (**A**), 330 °C (**B**), and 400 °C (**C**).



Figure 12. Thermal decomposition of FA/CeO2 (0.6 mmol/g); vapor pressure measured as a function of temperature for the FA/CeO₂ sample (**A**); TPD curves for ions with m/z 18, 24, and 44 (**B**), for ions with m/z 77, 107, 135, and 150 (**C**) and for ions with m/z 94, 108, 124, 128, and 164 (**D**).

The MVPh was formed as a result of the decarboxylation of FA. The TPD curve of the MVPh molecular ion had two peaks at 110 and 220 °C (Figure 12C). During the decomposition of FA in the pristine state in the air atmosphere, the release of MVPh was registered at 280 °C [22]. Conversely, during the TPD MS study, its formation was observed at T_{max} 480 °C [23]. The temperature maximum rate of the MVF formation on the SiO₂ surface corresponded to 400 °C [50]. Thus, the interaction of FA with the CeO₂ surface led to a significant decrease in the temperature of the MVPh formation. The release of the MVPh at $T_{max} = 110$ °C may be associated with the decomposition of monodentate carboxylate complexes (Scheme 3) and the destruction of FA associates (Scheme 4), the presence of which was evidenced by the FT-IR spectra of FA/CeO₂.



Scheme 3. The decomposition of the monodentate carboxylate complexes of FA.



Scheme 4. The decomposition of FA associates.

The second peak (~ 220 °C) was formed due to the transformation of the bidentate carboxylate complexes (Scheme 5). The second peak (~ 220 °C) was formed due to the transformation of the bidentate carboxylate complexes (Scheme 5), which were detected in the IR spectroscopic study of FA/CeO₂ by the appearance of bands ν (COO⁻) at 1405, 1450, and 1502 cm⁻¹.



Scheme 5. The decomposition of the bidentate carboxylate complexes of FA.

Increasing the amount of FA on the oxide surface, the first TPD peak of the MVPh desorption increased compared to the second (Figure 13). In this case, the relative intensity of the absorption band (1608 cm⁻¹) corresponding to C = O vibrations of VA molecules, which form monodentate carboxylate complexes, also increased in the IR spectra of FA/CeO₂ (Figure 4). This indicated an increase in the relative amount of these complexes at higher acid concentrations.



Figure 13. TPD-curves for the ion with m/z 150 (3-methoxy-4-vinilphenol), obtained by thermal decomposition of samples of FA/CeO₂ (a: 0.6 mmol/g, b: 0.9 mmol/g, c: 1.2 mmol/g).

The destruction of FA complexes formed on the surface of CeO₂ with the participation of aromatic ligands was accompanied by the release of guaiacol (M.r. = 124 Da, m/z 124) (Scheme 6) and hydroxybenzene (M.r. = 94 Da, m/z 94) (Figure 12D). The participation in the interaction with the oxide of both active groups of the aromatic ring was confirmed by the obtained data of FTIR spectroscopy, presented in Figure 4. The thermal transformation of FA molecules bound to the oxide surface through the OCH₃ group occurred with the formation of guaiacol (M.r. = 124 Da, m/z 124, $T_{max} \approx 265$ °C).



Scheme 6. The guaiacol formation.

FA complexes formed due to the simultaneous interaction of OH and OCH₃ groups of the aromatic ring with the CeO₂ surface being destroyed at about 400 °C (Scheme 7). As a result, hydroxybenzene was formed (M.r. = 94 Da, m/z 94, $T_{max} \approx 407$ °C) (Figure 12D). In the same way, similar complexes of caffeic acid decomposed on the CeO₂ surface [79].



Scheme 7. The hydroxybenzene formation.

In addition, the presence of the TPD peak for the ions with m/z 164 and 178 may be due to the methylation processes of the aromatic ring, according to the Scheme 7, with the formation of methylated 4-vinylguaiacols (Figure 14, Scheme 8).



Figure 14. TPD-curves for the ion with m/z 93, 121, 147, 164, and 178, obtained by thermal decomposition of samples of FA/CeO₂.



Scheme 8. The methylated 4-vinylguaiacols formation.

At higher temperatures, desorption of aromatic products such as naphthalene (m/z 128, $T_{max} \approx 430$ °C) was detected (Figure 12D). However, the intensity of their release was low. The formation of polyaromatic products was also detected during the pyrolysis of caffeic and ferulic acids and a number of coumarins on the surfaces of nanoscale oxides [50, 80,84]. However, the decomposition of cinnamic acid on the SiO₂ surface did not reveal such products [85]. Therefore, their formation was seemingly due to the transformation of complexes bound to the oxide through the active groups of the aromatic ring.

In accordance with DTG/DTA/TG data obtained by pyrolysis of the FA/CeO₂ sample (Figure 15), the decomposition of FA occurred in the temperature range of 100 to 500 °C in four stages. All stages were exothermic. The maximum weight loss corresponded to the third stage (~259 °C) (Table 8).



Figure 15. Differential thermal analysis (DTA), differential thermogravimetric analysis (DTG), and thermogravimetric (TG) curves for FA/CeO₂.

Sample	Stage	T_{max} (°C)	Volatiles (%)	Char (%)
	Ι	120	7.7	
	II	158	11.5	
FA/CeO ₂	III	219	23.0	12.6
_	IV	259	45.2	
	Σ (I–IV)		87.4	

Table 8. Pyrolysis yields for TGA pyrolysis of FA/CeO₂ (0.6 mmol/g).

3.2.5. Kinetic Parameters of the Catalytic Reactions of Vanillic and Ferulic Acids during Pyrolysis over Nanoceria Catalyst

The kinetic parameters of the formation of the main products during VA and FA catalytic pyrolysis were calculated in this study (Table 9). Based on calculated negative values of activation entropy, the formation processes of phenol, guaiacol, cresol, and methylated 4-vinylguaiacols run through highly ordered cyclic transition states on the nanoceria surface.

Pyrolysis Product or Its Fragment Ion	Scheme	m/z^{1}	<i>I</i> , a.u.	T _{range} , C	T_{max} , °C	n	E [≠] , kJ/mol	$rac{{ u _{0, \prime }}}{{ m s}^{-1}}$	$\Delta S^{ eq}$, cal/(K $ imes$ mol)	<i>R</i> ²²
					FA					
Phenol	7	94	0.107	250 - 570	407	1	118	$5.013 imes 10^6$	-29	0.949
Guaiacol	6	124	0.139	150-375	260	1	78	$1.665 imes 10^5$	-36	0.957
4 37. 1 . 1	2	150	3.0	70–200	120	-	-	-	-	-
4-Vinylgualacol	3	150	2.2	100-400	220	-	-	-	-	-
4-Vinylmethylguaiacol	8	164	0.209	188–427	332	1	109	1.628×10^7	-27	0.984
4-Vinyldimethylguaiacol	8	178	0.047	237–432	318	1	114	$4.200 imes 10^7$	-25	0.951
Naphthalene	-	128	0.04	320-520	430	-	-	-	-	-
					VA					
Phenol	2	94	0.05	295–471	382	1	121	1.371×10^{7}	-27	0.965
Cresol	-	108	0.023	238–374	322	1	137	3.383×10^{9}	-16	0.944
		124	0.067	193–390	275	1	91	1.575×10^{6}	-31	0.938
Guaiacol	1	109	0.097	190-411	276	1	90	$1.124 imes10^6$	-32	0.905
		81	0.087	190–397	274	1	82	$1.743 imes 10^5$	-35	0.937
Vanillin	-	151	0.026	180-420	~271	-	-	-	-	-

Table 9. Kinetic parameters (temperature of the maximum desorption rate T_{max} , reaction order *n*, activation energy E^{\neq} , pre-exponential factor v_0 , and change of activation entropy ΔS^{\neq}), temperature range (T_{range}) of formation and peak intensities (I) of the catalytic reactions of vanillic and ferulic acids during pyrolysis over nanoceria catalyst.

¹ m/z: ratio of ion mass to ion charge.² R^2 : coefficient of determination.

The formation of phenol was characterized by similar kinetic parameters for both vanillic and ferulic acids. The value of the activation energy was ~120 kJ mol⁻¹, and the change in the entropy of activation is ~28–29 (cal K⁻¹ mol⁻¹). Close kinetic parameters were observed for the formation of guaiacol for both vanillic and ferulic acids. This indicates that FA and VA have common pyrolysis pathways, probably due to thermal transformations of the same types of surface complexes. The processes of the formation of methylated products such as cresol in the case of VA and methylated 4-vinylguaiacols in the case of FA are also characterized by close temperatures of the maximum desorption rate of ~318–332 °C (Table 8).

4. Conclusions

The interactions of model compounds of lignin (P, G, VA, and FA) with the nanoceria surface were investigated by FT-IR spectroscopy. It was found that active groups of the aromatic ring ($(-OH_{ar})$ and $(-OCH_3)_{ar}$) as well as carboxylate groups, in the case of VA and FA, were involved in the interaction with the oxide. According to the FT-IR spectra, VA formed carboxylate complexes with a bidentate structure on the CeO₂ surface. In contrast, for FA, in addition to bidentate complexes, the existence of monodentate complexes was confirmed.

Thermal decomposition of P and G bound to the nanoceria surface through the OH group was probably accompanied by hydrogenation of the aromatic ring and its opening. The intensity of these processes was low. As a result of the thermal destruction of G complexes formed through the methoxyl group, hydroxybenzene was released. The thermal decomposition of P and G revealed signs of alkylation of the oxide surface. Catalytic pyrolysis of guaiacol and pyrocatechol led to the deep destruction of these compounds. The decomposition of carboxylic acids was accompanied by active processes of dehydration, decarbonylation, and decarboxylation. The main pyrolysis products of VA on the nanoceria surface were guaiacol and hydroxybenzene. Guaiacol can be formed due to the destruction of carboxylate complexes and the complexes formed through OH- and CH₃O-groups of the aromatic ring. Destruction of FA carboxylate complexes led to the formation of 3-methoxy-4-vinylphenol. As a result of the transformation of the complexes formed through OHand CH₃O-groups of the aromatic ring, guaiacol, and hydroxybenzene were formed. The decomposition of carboxylate complexes occurred at lower temperatures than complexes formed through OH- and CH₃O-groups. Thermolysis of both acids was accompanied by alkylation of the oxide surface. Polycyclic aromatic hydrocarbons (naphthalene) were also registered during the FA catalytic pyrolysis.

The kinetic parameters of the formation of the main products' catalytic pyrolysis (phenol, guaiacol, cresol, and methylated 4-vinylguaiacols) were calculated. The catalytic pyrolysis processes of VA and FA occurred through highly ordered cyclic transition states on the nanoceria surface.

Author Contributions: Conceptualization, T.K., M.K. and M.L.; methodology, N.N., B.P. and T.K.; investigation, N.N., B.P., T.C. and T.K.; resources, T.K.; writing—original draft preparation, N.N. and T.K.; writing—review and editing, N.N., T.K., J.L. and M.L.; visualization, N.N., T.K., and B.P.; supervision, M.K., T.K., J.L. and M.L.; project administration, T.K. and J.L.; funding acquisition, T.K. and M.L. All authors have read and agreed to the published version of the manuscript.

Funding: This publication is based on work supported by grant FSA3-20-66700 from the United States Civilian Research & Development Foundation (CRDF Global) with funding from the United States Department of State, by the Swedish Research Council (VR) under contract 348-2014-4250, by STCU (grant P707), and by NAS of Ukraine (program "new functional substances and materials of chemical production").

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The study did not report any data.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Isikgor, F.H.; Becer, C.R. Lignocellulosic biomass: A sustainable platform for the production of bio-based chemicals and polymers. *Polym. Chem.* 2015, *6*, 4497–4559. [CrossRef]
- Van Wyk, J.P.H. Biotechnology and the utilization of biowaste as a resource for bioproduct development. *TRENDS Biotech.* 2001, 19, 172–177. [CrossRef]
- 3. Chakar, F.S.; Ragauskas, A.J. Review of current and future softwood kraft lignin process chemistry. *Ind. Crop. Prod.* 2004, 20, 131–141. [CrossRef]
- 4. Linger, J.G.; Vardon, D.R.; Guarnieri, M.T.; Karp, E.M.; Hunsinger, G.B.; Franden, M.A.; Beckham, G.T. Lignin valorization through integrated biological funneling and chemical catalysis. *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 12013–12018. [CrossRef]
- Ragauskas, A.J.; Beckham, G.T.; Biddy, M.J.; Chandra, R.; Chen, F.; Davis, M.F.; Davison, B.H.; Dixon, R.A.; Gilna, P.; Keller, M.; et al. Lignin valorization: Improving lignin processing in the biorefinery. *Science* 2014, 344, 1246843. [CrossRef]
- Tuck, C.O.; Pérez, E.; Horváth, I.T.; Sheldon, R.A.; Poliakoff, M. Valorization of biomass: Deriving more value from waste. *Science* 2012, 337, 695–699. [CrossRef] [PubMed]
- 7. Boerjan, W.; Ralph, J.; Baucher, M. Lignin biosynthesis. Annu. Rev. Plant Biol. 2003, 54, 519–546. [CrossRef]
- 8. Zakzeski, J.; Bruijnincx, P.C.; Jongerius, A.L.; Weckhuysen, B.M. The catalytic valorization of lignin for the production of renewable chemicals. *Chem. Rev.* 2010, *110*, 3552–3599. [CrossRef]
- 9. Mathers, R.T. How well can renewable resources mimic commodity monomers and polymers? *J. Polym. Sci. Part A Polym. Chem.* **2012**, *50*, 1–15. [CrossRef]
- Zhang, Z.; Song, J.; Han, B. Catalytic transformation of lignocellulose into chemicals and fuel products in ionic liquids. *Chem. Rev.* 2017, 117, 6834–6880. [CrossRef] [PubMed]
- 11. Li, G.; Luo, Z.; Wang, W.; Cen, J. A Study of the Mechanisms of Guaiacol Pyrolysis Based on Free Radicals Detection Technology. *Catalysts* **2020**, *10*, 295. [CrossRef]
- 12. Yefremova, S.; Zharmenov, A.; Sukharnikov, Y.; Bunchuk, L.; Kablanbekov, A.; Anarbekov, K.; Kulik, T.; Nikolaichuk, A.; Palianytsia, B. Rice husk hydrolytic lignin transformation in carbonization process. *Molecules* **2019**, *24*, 3075. [CrossRef]
- 13. Wang, H.; Tucker, M.; Ji, Y. Recent development in chemical depolymerization of lignin: A review. J. Appl. Chem. 2013, 2013, 838645. [CrossRef]
- Ormond, T.K.; Baraban, J.H.; Porterfield, J.P.; Scheer, A.M.; Hemberger, P.; Troy, T.P.; Ahmed, M.; Nimlos, M.R.; Robichaud, D.J.; Daily, J.W.; et al. Thermal decompositions of the lignin model compounds: Salicylaldehyde and catechol. *J. Phys. Chem. A* 2018, 122, 5911–5924. [CrossRef] [PubMed]
- 15. González-Baró, A.C.; Parajón-Costa, B.S.; Franca, C.A.; Pis-Diez, R. Theoretical and spectroscopic study of vanillic acid. *J. Mol. Struct.* **2008**, *889*, 204–210. [CrossRef]
- Totong, S.; Daorattanachai, P.; Laosiripojana, N.; Idem, R. Catalytic depolymerization of alkaline lignin to value-added phenolicbased compounds over Ni/CeO₂-ZrO₂ catalyst synthesized with a one-step chemical reduction of Ni species using NaBH4 as the reducing agent. *Fuel Process. Technol.* 2020, 198, 106248. [CrossRef]
- 17. Cheng, H.; Wu, S.; Huang, J.; Zhang, X. Direct evidence from in situ FTIR spectroscopy that o-quinonemethide is a key intermediate during the pyrolysis of guaiacol. *Anal. Bioanal. Chem.* **2017**, *409*, 2531–2537. [CrossRef]
- 18. Bertero, M.; Gorostegui, H.A.; Orrabalis, C.J.; Guzmán, C.A.; Calandri, E.L.; Sedran, U. Characterization of the liquid products in the pyrolysis of residual chañar and palm fruit biomasses. *Fuel* **2014**, *116*, 409–414. [CrossRef]
- 19. Furimsky, E. Catalytic hydrodeoxygenation. Appl Catal. A Gen. 2000, 199, 147-190. [CrossRef]
- Hemberger, P.; Custodis, V.B.; Bodi, A.; Gerber, T.; van Bokhoven, J.A. Understanding the mechanism of catalytic fast pyrolysis by unveiling reactive intermediates in heterogeneous catalysis. *Nature Commun.* 2017, *8*, 15946. [CrossRef]
- Mathew, S.; Abraham, T.E.; Sudheesh, S. Rapid conversion of ferulic acid to 4-vinyl guaiacol and vanillin metabolites by Debaryomyces hansenii. J. Mol. Catal. B Enzym. 2007, 44, 48–52. [CrossRef]
- 22. Fiddler, W.; Parker, W.E.; Wasserman, A.E.; Doerr, R.C. Thermal decomposition of ferulic acid. J. Agric. Food Chem. 1967, 15, 757–761. [CrossRef]
- 23. Kulik, T.V.; Barvinchenko, V.N.; Palyanytsya, B.B.; Lipkovska, N.A.; Dudik, O.O. Thermal transformations of biologically active derivatives of cinnamic acid by TPD MS investigation. *J. Anal. Appl. Pyrol.* **2011**, *90*, 219–223. [CrossRef]
- Zhang, P.H.; Yu, X.Y.; Weng, L.X.; Sun, L.L.; Mao, Z.C.; Zhang, Y.L. Degradation of Ferulic Acid by the Endophytic Fungus Colletotrichum gloeosporioides TMTM-13 Associated with Ostrya rehderiana Chun. ACS Omega 2019, 4, 21000–21004. [CrossRef] [PubMed]
- Lesage-Meessen, L.; Haon, M.; Delattre, M.; Thibault, J.F.; Ceccaldi, B.C.; Asther, M. An attempt to channel the transformation of vanillic acid into vanillin by controlling methoxyhydroquinone formation in *Pycnoporus cinnabarinus* with cellobiose. *Appl. Microbiol. Biotechnol.* 1997, 47, 393–397. [CrossRef]
- 26. Abdelkafi, S.; Sayadi, S.; Ali Gam, Z.B.; Casalot, L.; Labat, M. Bioconversion of ferulic acid to vanillic acid by *Halomonas elongata* isolated from table-olive fermentation. *FEMS Microbiol. Lett.* **2006**, *262*, 115–120. [CrossRef]
- 27. Ye, M.; Yue, T.; Yuan, Y. Evolution of polyphenols and organic acids during the fermentation of apple cider. *J. Sci. Food Agric.* **2014**, *94*, 2951–2957. [CrossRef]

- 28. De Heredia, J.B.; Torregrosa, J.; Dominguez, J.R.; Peres, J.A. Kinetic model for phenolic compound oxidation by Fenton's reagent. *Chemosphere* **2001**, 45, 85–90. [CrossRef]
- Fiorentino, A.; Gentili, A.; Isidori, M.; Monaco, P.; Nardelli, A.; Parrella, A.; Temussi, F. Environmental effects caused by olive mill wastewaters: Toxicity comparison of low-molecular-weight phenol components. J. Agric. Food Chem. 2003, 51, 1005–1009. [CrossRef]
- Sayadi, S.; Allouche, N.; Jaoua, M.; Aloui, F. Detrimental effects of high molecular-mass polyphenols on olive mill wastewater biotreatment. *Process Biochem.* 2000, 35, 725–735. [CrossRef]
- 31. Ramos-Cormenzana, A.; Juarez-Jimenez, B.; Garcia-Pareja, M.P. Antimicrobial activity of olive mill wastewaters (alpechin) and biotransformed olive oil mill wastewater. *Int. Biodeterior. Biodegrad.* **1996**, *38*, 283–290. [CrossRef]
- 32. Xie, X.G.; Dai, C.C. Degradation of a model pollutant ferulic acid by the endophytic fungus *Phomopsis liquidambari*. *Biores*. *Technol*. **2015**, *179*, 35–42. [CrossRef]
- Sudarsanam, P.; Peeters, E.; Makshina, E.V.; Parvulescu, V.I.; Sels, B.F. Advances in porous and nanoscale catalysts for viable biomass conversion. *Chem. Soc. Rev.* 2019, 48, 2366–2421. [CrossRef]
- 34. Kabakcı, S.B.; Hacıbektaşoğlu, Ş. Catalytic Pyrolysis of Biomass. Pyrolysis 2017, 7, 167–196. [CrossRef]
- Schimming, S.M.; LaMont, O.D.; König, M.; Rogers, A.K.; D'Amico, A.D.; Yung, M.M.; Sievers, C. Hydrodeoxygenation of guaiacol over ceria–zirconia catalysts. *ChemSusChem* 2015, *8*, 2073–2083. [CrossRef]
- 36. Deng, W.; Zhang, H.; Wu, X.; Li, R.; Zhang, Q.; Wang, Y. Oxidative conversion of lignin and lignin model compounds catalyzed by CeO₂-supported Pd nanoparticles. *Green Chem.* **2015**, *17*, 5009–5018. [CrossRef]
- Ohta, H.; Kobayashi, H.; Hara, K.; Fukuoka, A. Hydrodeoxygenation of phenols as lignin models under acid-free conditions with carbon-supported platinum catalysts. *Chem. Commun.* 2011, 47, 12209–12211. [CrossRef]
- Grams, J.; Niewiadomski, M.; Ryczkowski, R.; Ruppert, A.M.; Kwapiński, W. Activity and characterization of Ni catalyst supported on CeO₂–ZrO₂ for thermo-chemical conversion of cellulose. *Int. J. Hydrogen Energy* 2016, 41, 8679–8687. [CrossRef]
- Song, W.L.; Dong, Q.; Hong, L.; Tian, Z.Q.; Tang, L.N.; Hao, W.; Zhang, H. Activating molecular oxygen with Au/CeO2 for the conversion of lignin model compounds and organosolv lignin. *RSC Adv.* 2019, *9*, 31070–31077. [CrossRef]
- 40. Yoshikawa, T.; Shinohara, S.; Yagi, T.; Ryumon, N.; Nakasaka, Y.; Tago, T.; Masuda, T. Production of phenols from lignin-derived slurry liquid using iron oxide catalyst. *Appl. Catal. B Environ.* **2014**, *146*, 289–297. [CrossRef]
- 41. Fronzi, M.; Soon, A.; Delley, B.; Traversa, E.; Stampfl, C. Stability and morphology of cerium oxide surfaces in an oxidizing environment: A first-principles investigation. *J. Chem. Phys.* **2009**, *131*, 104701. [CrossRef]
- 42. Spanier, J.E.; Robinson, R.D.; Zhang, F.; Chan, S.W.; Herman, I.P. Size-dependent properties of CeO₂-y nanoparticles as studied by Raman scattering. *Phys. Rev. B* 2001, *64*, 245407. [CrossRef]
- Mortensen, P.M.; Grunwaldt, J.D.; Jensen, P.A.; Jensen, A.D. Screening of catalysts for hydrodeoxygenation of phenol as a model compound for bio-oil. ACS Catal. 2013, 3, 1774–1785. [CrossRef]
- Zaytseva, Y.A.; Panchenko, V.N.; Simonov, M.; Shutilov, A.; Zenkovets, G.; Renz, M.; Simakova, I. Effect of Gas Atmosphere on Catalytic Behaviour of Zirconia, Ceria and Ceria Zirconia Catalysts in Valeric Acid Ketonization. *Top. Catal.* 2013, *56*, 846–855. [CrossRef]
- Kulyk, K.; Palianytsia, B.; Alexander, J.; Azizova, L.; Borysenko, M.; Larsson, M.; Kartel, M.; Kulik, T. Kinetics of Valeric Acid Ketonization and Ketenization in Catalytic Pyrolisis on Nanosized SiO₂, γ-Al₂O₃ CeO₂/SiO₂, Al₂O₃/TiO₂ and TiO₂/Al₂O₃. *Chem. Phys. Chem.* 2017, *18*, 1943–1955. [CrossRef] [PubMed]
- 46. Kulik, T.; Palianytsia, B.; Larsson, M. Catalytic Pyrolysis of Aliphatic Carboxylic Acids into Symmetric Ketones over Ceria-Based Catalysts: Kinetics, Isotope Effect and Mechanism. *Catalysts* **2020**, *10*, 179. [CrossRef]
- 47. Lange, J.P.; Price, R.; Ayoub, P.M.; Louis, J.; Petrus, L.; Clarke, L.; Gosselink, H. Valeric biofuels: A platform of cellulosic transportation fuels. *Angew. Chem. Int. Ed.* **2010**, *49*, 4479–4483. [CrossRef] [PubMed]
- 48. Li, S.; Deng, W.; Wang, S.; Wang, P.; An, D.; Li, Y.; Zhang, Q.; Wang, Y. Catalytic transformation of cellulose and its derivatives into functionalized organic acids. *ChemSusChem* **2018**, *11*, 1995–2028. [CrossRef]
- 49. Barvinchenko, V.N.; Lipkovskaya, N.A.; Kulik, T.V. Adsorption of Natural 3-Phenylpropenic Acids on Cerium Dioxide Surface. *Colloid J.* **2019**, *81*, 1–7. [CrossRef]
- Kulik, T.V.; Lipkovska, N.A.; Barvinchenko, V.N.; Palyanytsya, B.B.; Kazakova, O.A.; Dovbiy, O.A.; Pogorelyi, V.K. Interactions between bioactive ferulic acid and fumed silica by UV–vis spectroscopy, FT–IR, TPD MS investigation and quantum chemical methods. J. Colloid Interface Sci. 2009, 339, 60–68. [CrossRef]
- Janković, I.A.; Šaponjić, Z.V.; Čomor, M.I.; Nedeljković, J.M. Surface modification of colloidal TiO2 nanoparticles with bidentate benzene derivatives. J. Phys. Chem. C 2009, 113, 12645–12652. [CrossRef]
- 52. Connor, P.A.; Dobson, K.D.; McQuillan, A.J. New sol-gel attenuated total reflection infrared spectroscopic method for analysis of adsorption at metal oxide surfaces in aqueous solutions. Chelation of TiO₂, ZrO₂, and Al₂O₃ surfaces by catechol, 8-quinolinol, and acetylacetone. *Langmuir* **1995**, *11*, 4193–4195. [CrossRef]
- Bobkova, E.Y.; Vasilyeva, V.S.; Ksenofontov, M.A.; Ostrovskaya, L.E.; Shundalov, M.B. Spectral and energy characteristics of dihydroxybenzenes in the crystalline state. *Bull. BSU Ser. Phys.* 2009, *3*, 7–13.
- 54. Nelson, N.C.; Manzano, J.S.; Sadow, A.D.; Overbury, S.H.; Slowing, I.I. Selective hydrogenation of phenol catalyzed by palladium on high-surface-area ceria at room temperature and ambient pressure. *ACS Catal.* **2015**, *5*, 2051–2061. [CrossRef]

- 55. Singh, V.; Naka, T.; Takami, S.; Sahraneshin, A.; Togashi, T.; Aoki, N.; Adschiri, T. Hydrothermal synthesis of inorganic–organic hybrid gadolinium hydroxide nanoclusters with controlled size and morphology. *Dalton Trans.* 2013, 42, 16176–16184. [CrossRef]
- Huang, W.; Jiang, P.; Wei, C.; Zhuang, D.; Shi, J. Low-temperature one-step synthesis of covalently chelated ZnO/dopamine hybrid nanoparticles and their optical properties. *J. Mater. Res.* 2008, 23, 1946–1952. [CrossRef]
- 57. Hachani, R.; Lowdell, M.; Birchall, M.; Hervault, A.; Mertz, D.; Begin-Colin, S.; Thanh, N.T.K. Polyol synthesis, functionalisation, and biocompatibility studies of superparamagnetic iron oxide nanoparticles as potential MRI contrast agents. *Nanoscale* **2016**, *8*, 3278–3287. [CrossRef] [PubMed]
- Togashi, T.; Naka, T.; Asahina, S.; Sato, K.; Takami, S.; Adschiri, T. Surfactant-assisted one-pot synthesis of superparamagnetic magnetite nanoparticle clusters with tunable cluster size and magnetic field sensitivity. *Dalton Trans.* 2011, 40, 1073–1078. [CrossRef]
- Dugandžić, I.M.; Jovanović, D.J.; Mančić, L.T.; Zheng, N.; Ahrenkiel, S.P.; Milošević, O.B.; Nedeljković, J.M. Surface modification of submicronic TiO2 particles prepared by ultrasonic spray pyrolysis for visible light absorption. *J. Nanopart. Res.* 2012, 14, 1157. [CrossRef]
- Janković, I.A.; Šaponjić, Z.V.; Džunuzović, E.S.; Nedeljković, J.M. New hybrid properties of TiO 2 nanoparticles surface modified with catecholate type ligands. *Nanoscale Res. Lett.* 2010, 5, 81–88. [CrossRef]
- 61. Savić, T.D.; Janković, I.A.; Šaponjić, Z.V.; Čomor, M.I.; Veljković, D.Ž.; Zarić, S.D.; Nedeljković, J.M. Surface modification of anatase nanoparticles with fused ring catecholate type ligands: A combined DFT and experimental study of optical properties. *Nanoscale* **2012**, *4*, 1612–1619. [CrossRef]
- 62. Wang, X.; Zhu, S.; Wang, S.; Wang, J.; Fan, W.; Lv, Y. Ni nanoparticles entrapped in nickel phyllosilicate for selective hydrogenation of guaiacol to 2-methoxycyclohexanol. *Appl. Catal. A Gen.* **2018**, *568*, 231–241. [CrossRef]
- 63. Wang, X.; Zhu, S.; Wang, S.; He, Y.; Liu, Y.; Wang, J.; Lv, Y. Low temperature hydrodeoxygenation of guaiacol into cyclohexane over Ni/SiO2 catalyst combined with Hβ zeolite. *RSC Adv.* **2019**, *9*, 3868–3876. [CrossRef]
- 64. Nakanishi, K. Infrared Adsorption Spectroscopy; Practical; Holden Day: San Francisco, CA, USA, 1962; p. 216.
- 65. Clavijo, E.; Menéndez, J.R.; Aroca, R. Vibrational and surface-enhanced Raman spectra of vanillic acid. J. Raman Spectrosc. Int. J. Orig. Work Asp. Raman Spectrosc. Incl. High. Order Process. Brillouin Rayleigh Scatt. 2008, 39, 1178–1182. [CrossRef]
- 66. Khvan, A.M.; Kristallovich, E.L.; Abduazimov, K.A. Complexation of caffeic and ferulic acids by transition-metal ions. *Chem. Nat. Comp.* **2001**, *37*, 72–75. [CrossRef]
- 67. Sharpe, E.; Frasco, T.; Andreescu, D.; Andreescu, S. Portable ceria nanoparticle-based assay for rapid detection of food antioxidants (NanoCerac). *Analyst* 2013, 138, 249–262. [CrossRef]
- 68. Palacios, E.G.; Juárez-López, G.; Monhemius, A.J. Infrared spectroscopy of metal carboxylates: II. Analysis of Fe (III), Ni and Zn carboxylate solutions. *Hydrometallurgy* **2004**, *72*, 139–148. [CrossRef]
- 69. Yost, E.C.; Tejedor-Tejedor, M.I.; Anderson, M.A. In situ CIR-FTIR characterization of salicylate complexes at the goethite/aqueous solution interface. *Environ. Sci. Technol.* **1990**, *24*, 822–828. [CrossRef]
- Tunesi, S.; Anderson, M.A. Surface effects in photochemistry: An in situ cylindrical internal reflection-Fourier transform infrared investigation of the effect of ring substituents on chemisorption onto titania ceramic membranes. *Langmuir* 1992, *8*, 487–495. [CrossRef]
- Parrino, F.; Augugliaro, V.; Camera-Roda, G.; Loddo, V.; López-Muñoz, M.J.; Márquez-Álvarez, C.; Palmisano, G.; Palmisano, L.; Puma, M.A. Visible-light-induced oxidation of trans-ferulic acid by TiO₂ photocatalysis. J. Catal. 2012, 295, 254–260. [CrossRef]
- 72. Sebastian, S.; Sundaraganesan, N.; Manoharan, S. Molecular structure, spectroscopic studies and first-order molecular hyperpolarizabilities of ferulic acid by density functional study. *Spectrochim. Acta A* 2009, 74, 312–323. [CrossRef]
- 73. Ferrer, E.G.; Salinas, M.V.; Correa, M.J.; Vrdoljak, F.; Williams, P.A.M. ALP Inhibitors: Vanadyl(IV) Complexes of Ferulic and Cinnamic Acid. *Z. Naturforsch* 2005, 305–311. [CrossRef]
- 74. Kalinowska, M.; Piekut, J.; Bruss, A.; Follet, C.; Sienkiewicz-Gromiuk, J.; Świsłocka, R.; Rzączyńska, Z.; Lewandowski, W. Spectroscopic (FT-IR, FT-Raman,1H,13C NMR, UV/VIS), thermogravimetric and antimicrobial studies of Ca(II), Mn(II),Cu(II), Zn(II) and Cd(II) complexes of ferulic acid. Spectrochim. Acta A Mol. Biomol. Spectrosc. 2014, 122, 631–638. [CrossRef] [PubMed]
- Świsłocka, R.; Regulska, E.; Samsonowicz, M.; Lewandowski, W. Experimental and theoretical study on benzoic acid derivatives. J. Molec. Struct. 2013, 1044, 181–187. [CrossRef]
- 76. Lebedev, A.T. Mass Spectrometry in Organic Chemistry; Binom: Moscow, Russia, 2003; p. 493.
- 77. Zhao, C.; He, J.; Lemonidou, A.A.; Li, X.; Lercher, J.A. Aqueous-phase hydrodeoxygenation of bio-derived phenols to cycloalkanes. *J. Catal.* **2011**, *280*, 8–16. [CrossRef]
- Sharma, R.K.; Bakhshi, N.N. Catalytic upgrading of biomass-derived oils to transportation fuels and chemicals. *Can. J. Chem. Eng.* 1991, 69, 1071–1081. [CrossRef]
- Nastasiienko, N.; Palianytsia, B.; Kartel, M.; Larsson, M.; Kulik, T. Thermal Transformation of Caffeic Acid on the Nanoceria Surface Studied by Temperature Programmed Desorption Mass-Spectrometry, Thermogravimetric Analysis and FT–IR Spectroscopy. Colloids Interfaces 2019, 3, 34. [CrossRef]
- Kulik, T.V.; Lipkovska, N.O.; Barvinchenko, V.M.; Palyanytsya, B.B.; Kazakova, O.A.; Dudik, O.O.; Menyhárd, A.; László, K. Thermal transformation of bioactive caffeic acid on fumed silica seen by UV–Vis spectroscopy, thermogravimetric analysis, temperature programmed desorption mass spectrometry and quantum chemical methods. *J. Colloid Interface Sci.* 2016, 470, 132–141. [CrossRef]

- Sato, S.; Koizumi, K.; Nozaki, F. Ortho-selective methylation of phenol over CeO₂ catalyst. *Appl. Catal. A Gen.* 1995, 133, L7–L10. [CrossRef]
- Wandas, R.; Surygala, J.; Śliwka, E. Conversion of cresols and naphthalene in the hydroprocessing of three-component model mixtures simulating fast pyrolysis tars. *Fuel* 1996, 75, 687–694. [CrossRef]
- 83. NIST Chemistry Web Book. NIST Standard Reference Database Number 69. Available online: https://webbook.nist.gov/ chemistry (accessed on 24 June 2021).
- Kulyk, K.; Ishchenko, V.; Palyanytsya, B.; Khylya, V.; Borysenko, M.; Kulyk, T. A TPD-MS study of the interaction of coumarins and their heterocyclic derivatives with a surface of fumed silica and nanosized oxides CeO₂/SiO₂, TiO₂/SiO₂, Al₂O₃/SiO₂. J. Mass Spectrom. 2010, 45, 750–761. [CrossRef] [PubMed]
- 85. Kulik, T.V.; Barvinchenko, V.N.; Palyanitsa, B.B.; Smirnova, O.V.; Pogorelyi, V.K.; Chuiko, A.A. A desorption mass spectrometry study of the interaction of cinnamic acid with a silica surface. *Russ. J. Phys. Chem.* **2007**, *8*, 83–90. [CrossRef]