

Article

CuTiO₃ Perovskite-Type as an Efficient Catalyst for Alkaline Lignin Depolymerization Towards Selective Vanillin Production

Ratheeshkumar Shanmugam ¹, Arul Chan Basha ¹, Vinod Kumar ^{2,3}, Saravanan Ramiah Shanmugam ⁴, Malinee Sriariyanun ⁵ and Ponnusami Venkatachalam ^{1,*}

¹ Biomass Conversion and Bioproducts Laboratory, Center for Bioenergy, School of Chemical & Biotechnology, SASTRA Deemed University, Thirumalaisamudram, Thanjavur 613 401, Tamil Nadu, India; ratheeshdeva9751@gmail.com (R.S.); arulace10@gmail.com (A.C.B.)

² Magan Centre for Applied Mycology, Faculty of Engineering and Applied Sciences, Cranfield University, Cranfield MK43 0AL, UK; vinod.kumar@cranfield.ac.uk

³ Department of Engineering Technology, Cullen College of Engineering, University of Houston, Sugarland, TX 77479, USA

⁴ Department of Biosystems Engineering, Auburn University, Auburn, AL 36849, USA; srs0065@auburn.edu

⁵ Biorefinery and Process Automation Engineering Center, Department of Chemical and Process Engineering, The Sirindhorn International Thai-German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand; macintous@gmail.com

* Correspondence: vponnu@chem.sastra.edu

Abstract

Lignin is one of the most abundant biopolymers in nature. The major challenge in lignin depolymerization lies in the formation of complex mixtures that require extensive downstream separation. Selective depolymerization strategies aim to overcome this limitation by promoting controlled bond cleavage while suppressing undesired secondary reactions. In this work, a series of rare-earth-free, perovskite-type mixed metal oxides with general compositions Zn_xNi_{1-x}TiO₃ and Cu_yNi_{1-y}TiO₃ were synthesized and evaluated as heterogeneous catalysts for the base-catalyzed depolymerization of lignin. Among the investigated materials, CuTiO₃ exhibited superior catalytic performance, enabling the formation of vanillin as the dominant monomer with high selectivity. The selected catalyst was further characterized using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) surface area analysis. The combined effects of key reaction parameters, including temperature, pressure, lignin-to-catalyst ratio, NaOH concentration, and reaction time, were systematically investigated using response surface methodology (RSM). Under the optimized conditions (154 °C, 0.3 MPa, lignin-to-catalyst ratio of 24.5:1, 10 mL of 0.5 M NaOH, and 12 h reaction time), a monomer yield of 11.5 ± 0.46% with ~81% GC-selectivity toward vanillin was achieved. These findings demonstrate that perovskite-type titanates can serve as robust and reusable catalysts.

Keywords: lignin; selective lignin depolymerization; perovskite-type metal catalyst; vanillin



Academic Editors: Pengcheng Dai and Xin Gu

Received: 21 April 2026

Revised: 18 May 2026

Accepted: 19 May 2026

Published: 1 June 2026

Copyright: © 2026 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 \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Lignocellulosic biomass (LCB) is one of the most abundant materials on Earth, serving as a renewable carbon resource with an anticipated yearly output above one billion metric tons [1]. LCB is primarily composed of cellulose (35–50%), a linear homopolysaccharide of β-D-glucose; hemicellulose (20–35%), a branched heterogeneous polysaccharide containing various C5 and C6 sugars; and lignin (15–30%), a complex three-dimensional aromatic polymer formed from phenylpropanoid units. Because of its richness in fermentable sugar,

the cellulose and hemicellulose have been widely used in the fermentation industry for synthesizing bioproducts via cell factories. In contrast, the lignin remains substantially underutilized or is burnt for low-energy purposes because of its heterogeneity, complex structure, and recalcitrant nature, which collectively hinder its controlled depolymerization into value-added products [2–4]. Lignin is a phenylpropanoid polymer composed of three primary structural units: *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), derived respectively from the monolignols *p*-coumaryl, coniferyl, and sinapyl alcohols. These units are interconnected through a variety of ether and carbon-carbon linkages, including β -O-4, α -O-4, 4-O-5, β -1, β -5, 5-5', and β - β bonds [5,6]. Among these, β -O-4 aryl ether linkages constitute approximately 35–60% of the linkages in softwood lignin and 60–70% in hardwood lignin, making them the primary targets for depolymerization strategies. However, the coexistence of multiple bond types leads to a complex mixture of products upon depolymerization, complicating downstream separation and limiting practical applications [7].

Scientists have explored various strategies, including reductive, oxidative, thermal, hydrolytic, and acid-base-catalyzed approaches to valorize lignin [8]. These methods yield a diverse mixture of compounds, aldehydes, ketones, acids, and hydrocarbons. Their effectiveness is often limited by poor product selectivity, extensive repolymerization, and secondary degradation reactions [9]. Oxidative depolymerization typically produces oxygenated aromatic monomers such as apocynin, vanillin, syringaldehyde, and vanillic acid [10], whereas reductive pathways generally yield complex mixtures of phenolic compounds and hydrocarbons [11]. The limited selectivity of these approaches reduces monomer yields and poses significant challenges for downstream processing, scalability, and economic viability [12]. Furthermore, structural heterogeneity arising from variations in syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) unit ratios influences depolymerization pathways and ultimately determines product selectivity [13]. Consequently, developing selective depolymerization strategies that suppress undesired side reactions while promoting targeted bond cleavage remains a challenge in this domain. Among the available routes, base-catalyzed depolymerization (BCD) has attracted attention due to its operation under relatively mild conditions, enhanced lignin solubility in alkaline media, and selectivity toward oxygenated products, although the overall monomer yield is often lower than that obtained from reductive depolymerization techniques. In alkaline environments, phenolic hydroxyl and ether functionalities in lignin are readily deprotonated, facilitating the cleavage of key linkages, particularly aryl ether bonds, via base-promoted pathways [14]. However, homogeneous alkaline medium depolymerization often suffers from extensive condensation reactions and char formation. Suitable heterogeneous catalysts can mitigate these limitations by stabilizing the reactive intermediate and promoting selective bond cleavage while suppressing undesired side reactions through tailored acid-base surface functionalities.

Perovskite metal oxides (PMOs), denoted by ABO_3 , possess great structural flexibility, tunable electrical properties, and excellent catalytic activity. Doping these materials with low-valence cations instead of A-site metal ions generates oxygen vacancies. These vacancies enhance catalytic efficiency by facilitating the easier movement of oxygen through vacancy or interstitial reactions [15]. The defect chemistry of perovskites enables them to effectively catalyze oxidation and hydrogenation reactions. This is useful for depolymerizing lignin under mild conditions. PMOs can degrade lignin by selectively oxidizing lignin linkages, thereby yielding valuable aromatic compounds, including vanillin and syringaldehyde [16]. Such compounds are of commercial significance in the fields of flavor, fragrance, and pharmaceuticals. Vanillin is a high-value product that can be produced by the selective depolymerization of lignin. It has been reported that the yield of vanillin

obtained varies between 4.3% and 13.39% (*w/w*), depending on the catalytic process and reaction system. For instance, nitrobenzene has been utilized as an oxidant to achieve vanillin yields of over 13.39% is the highest yield in the literature records [17]. The ability of metal-based catalysts to facilitate selective lignin depolymerization while remaining stable and reusable significantly enhances their industrial significance. Certain challenges, however, need to be addressed to improve lignin depolymerization. Challenges such as Catalyst deactivation, differences between lignin feedstocks, and the need for scalable and cost-effective processes are the biggest barriers to commercialization. The heterogeneity of structure arising from non-uniform syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) unit ratios is expressed in the product selectivity on depolymerization [13]. Thus, there is a need to study the properties of catalysts on the yield and selectivity of monomers to develop fruitful methods for lignin conversion.

PMOs offer several advantages in addressing these problems. Their thermal and hydrothermal stability ensures long-term catalytic activity, while redox and acid-base tunability allow for the strict control of reaction pathways [18]. The perovskite has a general formula of ABO_3 , where the A-site metal has a larger ionic radius than the B-site. PMOs can also stabilize oxygen vacancies, which enhances their catalytic activity for oxidative depolymerization [19]. This architecture allows independent tailoring of both A- and B-site compositions without destroying the overall framework, enabling precise control over electronic structure, oxygen vacancy concentration, redox behavior, and surface reactivity. Such characteristics make PMOs highly suitable for catalytic applications involving redox reactions, C–O bond cleavage, hydrogen transfer, and oxygen mobility key processes in lignin depolymerization. The previous studies show that most of the PMOs used for lignin degradation were La-based. The La-based PMOs, such as $LaMnO_3$, $LaFeO_3$, $LaCoO_3$, and $LaNiO_3$, have achieved a promising monomer yield from lignin (Table 1). The La^{3+} has a large ionic radius, which stabilizes the perovskite structure, promoting the surface oxygen vacancy formation and resisting leaching in alkaline media [20]. Despite these widespread applications of La, it entails several constraints. Rare earth metals are expensive, geographically limited, and associated with environmentally intensive extraction processes. From the perspective of large-scale biomass valorization, the reliance on earth metal-based catalysts constitutes a significant barrier to industrial application. Therefore, the development of cost-effective earth-abundant and environmentally benign alternatives to La-based PMOs is both scientifically and economically imperative. In this context, replacing the A-site with first-row (3d) transition metals represents a compelling and underexplored strategy. Transition metals such as copper, nickel, and zinc are abundant, inexpensive, and widely utilized. In contrast, the first-row transition metals in the perovskite lattice impart significant redox activity and promote lattice distortion, oxygen vacancy formation, and enhanced metal oxygen covalency. For instance, partial substitution of alkaline earth metals such as Ca^{2+} and Sr^{2+} for La at the A-site demonstrated improved oxygen mobility [21,22]. Although PMOs incorporating 3d transition metals at the A-site are generally more structurally distorted and somewhat less stable than their La-based counterparts, they offer superior catalytic activity for reactions involving C–O bond cleavage, hydrogenolysis, and oxidation. The utilization of PMO catalysts in lignin valorization aligns with the principles of sustainable biorefinery processing. These catalysts facilitate cost-effective conversion of lignin into renewable chemical building blocks, supporting a circular bioeconomy. Further work is needed to optimize PMO-based catalytic systems, explore novel doping methods, and enhance the material's stability and reusability.

Table 1. Comparison of previous reports on use of PMO catalyst for lignin depolymerization.

S No	Perovskite	Process	Reactant	Duration (mins)	Temperature (°C)	Pressure (MPa)	Atmosphere	Solvent	Reactant to Catalyst Ratio	Product	Yield (%)	Ref
1	La _{0.6} Ce _{0.4} CoO ₃		sodium ligno sulfonate	720	240	1.1	N ₂	Ethanol: Methanol (1:1)	2:1	Lignin oil	13.05	[23]
2	LaNiO ₃ /MCM-41	Ultrasonic-assisted catalytic depolymerization	Commercial lignin	360	250	-	-	Ethanol/water (1:1)	5:1	Lignin oil	11.46	[24]
3	LaCo _{0.8} Cu _{0.2} O ₃	Catalytic wet aerobic oxidation	Steam-exploded lignin from corn	50	120	2	O ₂ (0.5 MPa)	2 N NaOH	2:1	Vanillin	5.3	[25]
				40						Syringaldehyde	12.8	
				120						<i>p</i> -hydroxy benzaldehyde	2.88	
3	La _{0.8} Sr _{0.2} FeO ₃	Catalytic pyrolysis	bagasse lignin	120	600	-	N ₂ (0.1 L/min)	-	3:1	Liquid product	25.73	[26]
4	LaFe _{0.2} Cu _{0.8} O ₃	Catalytic Oxidation	dealkaline lignin	150	160	0.8	O ₂	1 N NaOH	20:1	Syringaldehyde	10	[27]
6	LaCoO ₃	Catalytic Wet Oxidation	Steam-exploded lignin from cornstalk	60	120	2	O ₂ (0.5 MPa)	2 N NaOH	20:1	Vanillin	4.55	[28]
				50						Syringaldehyde	9.99	
				120						<i>p</i> -hydroxy benzaldehyde	2.23	
7	Ni–LaCoO ₃	hydrogenation	Kraft lignin	240	280	0.5	H ₂	Ethanol	10:1	Lignin-oil	72.4	[29]
8	(CH ₃) ₂ CHPbCl ₃	Photocatalytic degradation	organosolv lignin	60	100	-	-	Dioxane	40:1	Lignin degradation	98	[30]
9	LaFe _{0.9} Ni _{0.1} O ₃ /peroxydisulfate	Photocatalytic degradation	Alkali lignin from bamboo chips	105	25	-	-	Alkaline solution at 10 pH	10:1	Lignin oil	0.3	[31]
10	LaCoO ₃	Hydrothermal liquefaction	Alkali lignin	60	180	-	N ₂	Methanol	20:1	Lignin oil	67.20	[32]
	LaFeO ₃				140						59.74	
	LaNiO ₃				140						56.69	
11	La _{0.8} Pr _{0.2} NiO ₃	Catalytic pyrolysis	organosolv lignin	180	600	-	N ₂ (0.1 L/min)	-	3:1	liquid-phase product	21.34	[33]
12	LaMnO ₃	Catalytic Wet Air Oxidation	Cornstalk	30	120	1.5–2	N ₂	2 M NaOH	20:1	Syringaldehyde	9.30	[34]
										Vanillin	4.32	
13	LaMn _{0.8} Cu _{0.2} O ₃	Catalytic Oxidation	high-S poplar	10	175	2	He/O ₂	2 M NaOH	50:1	Monomer yield	30	[14]

The use of rare earth metals raises significant environmental and economic concerns because of their limited global availability. In the context of large-scale biorefinery development, such dependence represents a major obstacle to commercialization and long-term sustainability. Therefore, the development of rare-earth-metal-free, transition-metal-based PMOs for the selective BCD of lignin is an underexplored but strategically important area of research. First-row transition metals, including copper, nickel, and zinc, are especially promising candidates owing to their low cost, natural abundance, and versatile coordination chemistry. When incorporated into perovskite-related oxide structures, these metals can enable tunable acid-base properties, influence the adsorption behaviour of reactants and intermediates, and regulate surface oxygen vacancy concentrations. Here, we report the synthesis of transition metal-based PMOs for selective BCD of lignin. Two series of mixed-metal oxides $\text{Zn}_x\text{Ni}_{1-x}\text{TiO}_3$ and $\text{Cu}_y\text{Ni}_{1-y}\text{TiO}_3$, were synthesized and systematically screened for catalytic activity in BCD. The phase structure of the synthesized catalysts was confirmed by X-ray diffraction (XRD). The finalized catalyst was further analyzed with X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and nitrogen physisorption (BET analysis). Response surface methodology (RSM) was employed to identify the combined effect of parameters such as temperature, pressure, lignin to catalyst ratio, concentration of alkali, and duration on monomer yield and product selectivity.

2. Results and Discussion

2.1. Catalyst Screening

Two compositional series of mixed-metal PMOs, $\text{Cu}_x\text{Ni}_{1-x}\text{TiO}_3$ and $\text{Zn}_y\text{Ni}_{1-y}\text{TiO}_3$, were rationally designed and synthesized with controlled variation of the A-site metal ratio. The Cu–Ni series consisted of $\text{Cu}_{0.8}\text{Ni}_{0.2}\text{TiO}_3$ (Cu0.8), $\text{Cu}_{0.6}\text{Ni}_{0.4}\text{TiO}_3$ (Cu0.6), $\text{Cu}_{0.4}\text{Ni}_{0.6}\text{TiO}_3$ (Cu0.4), and $\text{Cu}_{0.2}\text{Ni}_{0.8}\text{TiO}_3$ (Cu0.2), while the Zn–Ni series comprised $\text{Zn}_{0.2}\text{Ni}_{0.8}\text{TiO}_3$ (Zn0.2), $\text{Zn}_{0.4}\text{Ni}_{0.6}\text{TiO}_3$ (Zn0.4), $\text{Zn}_{0.6}\text{Ni}_{0.4}\text{TiO}_3$ (Zn0.6), and $\text{Zn}_{0.8}\text{Ni}_{0.2}\text{TiO}_3$ (Zn0.8). The catalytic performance of the synthesized perovskite-type mixed metal oxides was systematically evaluated for lignin depolymerization, with particular emphasis on total monomer yield and selectivity toward vanillin (Figure 1). A pronounced dependence of catalytic activity on the nature and composition of the incorporated transition metals was observed. A systematic catalyst screening study was conducted to evaluate the influence of the catalyst on BCD toward selective aromatic monomer production. The catalytic performance was assessed in terms of total monomer yield and selectivity toward Vanillin, Acetovanillone, and Guaiacol. Statistical evaluation was performed using one-way ANOVA followed by Tukey's Honestly Significant Difference test ($\alpha = 0.05$), confirming that variations in catalytic performance were statistically significant rather than arising from experimental variability (Figure S1).

In the case of vanillin selectivity, CuTiO_3 exhibited the highest selectivity. Importantly, Tukey analysis revealed that CuTiO_3 is not significantly different from its other catalysts (Figure S1A & Table S1). However, all catalytic systems showed a statistically significant improvement compared to the system without a catalyst. For instance, CuTiO_3 vs. no catalyst showed a mean difference of 28.83 ($p < 0.001$), while ZnTiO_3 vs. no catalyst showed a mean difference of 22.3 ($p < 0.001$). This clearly demonstrates that the presence of a metal catalyst is essential for promoting selective aldehyde formation under alkaline conditions. The absence of significant differences among CuTiO_3 , NiTiO_3 , and ZnTiO_3 systems suggests that under alkaline oxidative conditions, vanillin formation is not solely dictated by metal identity but rather by the general ability of the catalyst to facilitate $\beta\text{--O--4}$ bond cleavage and $\text{C}\alpha$ oxidation [35]. However, numerically higher selectivity observed for CuTiO_3 indicates a favorable redox environment for aldehyde stabilization.

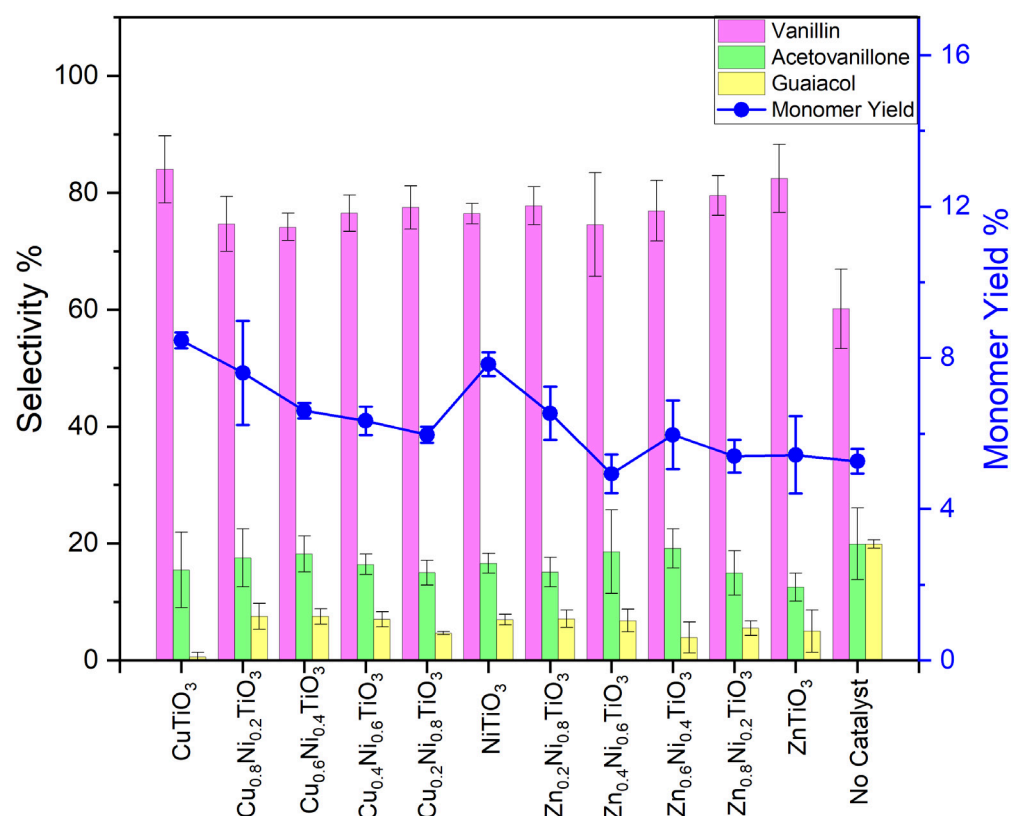


Figure 1. Screening of perovskite-type mixed metal oxides for the BCD of lignin. The stacked bars represent the product selectivity (%) toward vanillin, acetovanillone, and guaiacol, while the blue line corresponds to the total monomer yield (%). (Conditions: lignin: catalyst loading (25:1); 160 °C; 3 bar; 1 N NaOH; 8 h reaction time).

Tukey analysis reveal that catalysts do not alter the acetovanillone yield significantly (Figure S1B & Table S2). Mechanistically, this suggests that acetovanillone arises from secondary oxidation pathways intrinsic to alkaline depolymerization rather than being strongly catalytically mediated [35]. The statistical uniformity across systems supports the hypothesis that once lignin fragments are released, subsequent ketone formation proceeds via solution-phase oxidation rather than surface-controlled processes. In contrast, the analysis of Guaiacol revealed clear and statistically significant trends (Figure S1C & Table S3). The parent CuTiO₃ catalyst showed significantly lower guaiacol formation compared to Cu 0.8 ($p = 0.003$), Cu 0.6 ($p = 0.004$), Cu 0.4 ($p = 0.008$), NiTiO₃ ($p = 0.008$), and Zn 0.2/0.4 ($p < 0.01$). Furthermore, all catalytic systems produced dramatically lower guaiacol compared to the no-catalyst control ($p < 0.001$). These findings indicate that CuTiO₃ not only promotes vanillin formation but also effectively suppresses demethoxylation or deep aromatic degradation pathways leading to guaiacol. The statistically significant reduction in guaiacol relative to most other systems highlights CuTiO₃'s superior control over selective oxidative cleavage, minimizing undesirable side reactions. The big difference between catalytic and non-catalytic conditions (~97% of Guaiacol production was reduced with CuTiO₃ compared to no catalyst, $p < 0.001$) confirms that metal-mediated pathways play a crucial role in preventing uncontrolled lignin fragmentation.

Focusing on total aromatic monomer yield and product distribution among the single-metal titanates, CuTiO₃ exhibited the highest monomer yield (8.5%), followed by NiTiO₃ (7.8%) and ZnTiO₃ (5.4%), clearly demonstrating the superior depolymerization efficiency of the CuTiO₃ system. Statistical analysis confirmed that CuTiO₃ produced significantly higher yields compared to several mixed-metal and Zn-based catalysts, validating the

intrinsic activity of Cu sites in promoting lignin fragmentation (Figure S1D & Table S4). For the mixed-metal systems, monomer yield exhibited a clear composition-dependent trend. In the Cu–Ni–TiO₃ series, yields decreased progressively with increasing Ni substitution, from 7.6% for Cu 0.8 to 6.0% for Cu 0.2. This gradual decline suggests that dilution of Cu active sites reduces the density of catalytically competent redox centers responsible for β –O–4 bond cleavage. A similar trend was observed for the Zn–Ni–TiO₃ series, where Zn 0.2 yielded 7.6%, decreasing to 5.0–5.4% at higher Zn contents. However, the Zn-containing systems did not statistically outperform NiTiO₃, indicating that Zn substitution does not significantly enhance depolymerization efficiency under alkaline conditions.

Beyond total yield, catalyst composition strongly influenced product distribution. CuTiO₃ exhibited the highest selectivity toward Vanillin (~84%) (Figure S2), accompanied by pronounced suppression of guaiacol formation relative to both mixed-metal catalysts and the uncatalyzed reaction. In contrast, the reaction performed without a catalyst showed substantially lower vanillin selectivity (~60%) and markedly higher guaiacol formation. Tukey analysis suggests that all catalytic systems significantly improved vanillin selectivity compared to the no-catalyst case ($p < 0.001$), indicating the critical role of the solid catalyst in directing reaction pathways. The observed enhancement in vanillin selectivity over Cu-containing compositions is attributed to their ability to promote controlled fragmentation of lignin while stabilizing aldehyde-type intermediates and suppressing undesired condensation reactions. Under strongly alkaline conditions, lignin undergoes base-promoted cleavage of ether linkages, generating highly reactive phenolic and carbonyl-containing intermediates. Although the overall performance differences among the catalysts were not very large, CuTiO₃ was selected because it showed the highest suppression of guaiacol formation. While NiTiO₃ and Cu0.8 exhibited a yield comparable to that of CuTiO₃, only CuTiO₃ achieved 97% suppression of guaiacol production relative to the no-catalyst system. This indicates that the advantage of CuTiO₃ lies not only in its depolymerization activity, but also in its superior selectivity toward suppressing undesirable guaiacol formation. The CuTiO₃ surface likely provides a favorable adsorption environment that stabilizes such intermediates, thereby enhancing the probability of their desorption as low-molecular-weight monomers rather than undergoing secondary condensation [36]. Combining selectivity and yield results reveals a critical structure-activity relationship. Although multiple metals can promote vanillin formation, only Cu significantly enhances overall monomer production while simultaneously suppressing guaiacol formation. This dual functionality, efficient bond cleavage, and selective cleavage explain the statistically superior performance of the Cu-based system. Based on its consistently high performance across both yield and selectivity metrics, CuTiO₃ was identified as the optimal catalyst and was selected for further detailed characterization and reaction optimization studies.

2.2. Results of Catalyst Characterization

The XRD patterns of the synthesized perovskite-type mixed metal oxides are shown in Figure 2. The characteristic reflections corresponding to the perovskite-related phase were observed at 2θ values of 24–27°, 31–36°, 36–39°, ~41°, ~49°, ~54°, ~63°, and ~64°, which can be indexed to the (012), (104), (110), (113), (024), (116), (214), and (300) planes, respectively [36]. The detailed indexing of diffraction peaks for all compositions is summarized in Table S5.

The average crystallite sizes were estimated using the Debye–Scherrer equation (Equation (1)) (Table 2) and were found to be 40.32 nm (CuTiO₃), 80.43 nm (Cu0.8), 52.59 nm (Cu0.6), 65.04 nm (Cu0.4), 109.65 nm (Cu0.2), 56.71 nm (NiTiO₃), 77.76 nm (Zn0.2), 72.45 nm (Zn0.4), 88.48 nm (Zn0.6), 97.71 nm (Zn0.8), and 51.78 nm (ZnTiO₃). These values

fall within the nanocrystalline regime for all compositions, confirming the formation of nanostructured materials.

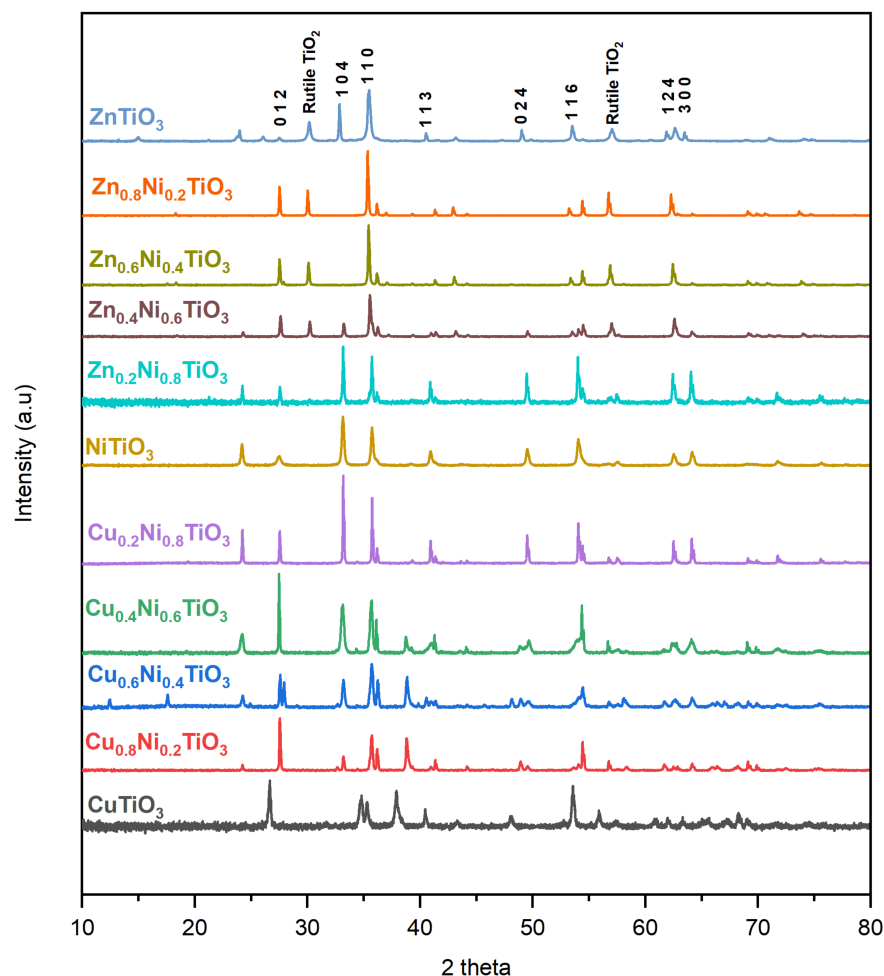


Figure 2. Powder XRD patterns of the synthesized perovskite-type and perovskite-type mixed metal oxides. Minor reflections associated with residual TiO_2 suggest imperfect phase transformation in some compositions.

Table 2. List of average crystalline size of the synthesized catalysts.

Catalyst	Average Crystallite Size (nm)
CuTiO_3	40.32
$\text{Cu}_{0.8}\text{Ni}_{0.2}\text{TiO}_3$	80.43
$\text{Cu}_{0.6}\text{Ni}_{0.4}\text{TiO}_3$	52.49
$\text{Cu}_{0.4}\text{Ni}_{0.6}\text{TiO}_3$	65.04
$\text{Cu}_{0.2}\text{Ni}_{0.8}\text{TiO}_3$	109.65
NiTiO_3	56.71
$\text{Zn}_{0.2}\text{Ni}_{0.8}\text{TiO}_3$	77.76
$\text{Zn}_{0.4}\text{Ni}_{0.6}\text{TiO}_3$	72.45
$\text{Zn}_{0.6}\text{Ni}_{0.4}\text{TiO}_3$	88.48
$\text{Zn}_{0.8}\text{Ni}_{0.2}\text{TiO}_3$	97.71
ZnTiO_3	51.78

A systematic shift in peak positions was observed with increasing Ni content in both the Cu–Ni– TiO_3 and Zn–Ni– TiO_3 series. In particular, slight shifts in the (012), (104), and

(110) reflections toward higher 2θ values were noted as the Ni concentration increased. This behavior can be attributed to the substitution of larger Cu^{2+} (0.73 Å) or Zn^{2+} ions by smaller Ni^{2+} ions (0.69 Å), leading to lattice contraction and reduced interplanar spacing [37–39]. Minor reflections corresponding to residual rutile TiO_2 were also detected, suggesting incomplete phase conversion during calcination.

The crystallite size was calculated using the Scherrer Equation (1)

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D is the crystallite size, K is the shape factor, λ is the X-ray wavelength, β is the full width at half maximum (FWHM), and θ is the Bragg angle.

XPS was employed to probe the surface chemical states of CuTiO_3 (Figure 3). The survey and high-resolution spectra confirmed the presence of Cu, Ti, and O species at the catalyst surface. The Cu 2p spectrum exhibited characteristic peaks at 932.5 eV ($\text{Cu } 2p_{3/2}$) and 951.4 eV ($\text{Cu } 2p_{1/2}$), accompanied by distinct shake-up satellite features at 941.0 and 961.7 eV, indicative of Cu^{2+} species. The Ti 2p region showed binding energies at 458.9 eV ($\text{Ti } 2p_{3/2}$) and 463.3 eV ($\text{Ti } 2p_{1/2}$), consistent with the presence of Ti^{4+} [40–44]. The residual standard deviation (STD) values obtained for Ti 2p, O 1s, and Cu 2p were 1.74, 1.84, and 1.26, respectively, indicating satisfactory fitting quality.

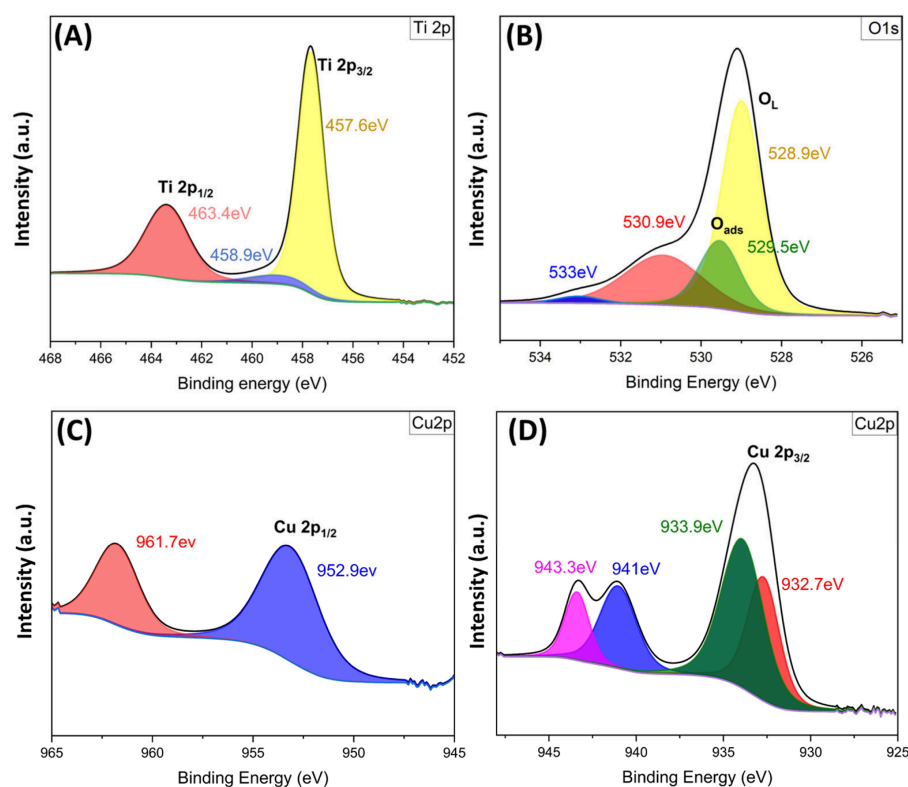


Figure 3. High-resolution XPS spectra of CuTiO_3 : (A) Cu 2p region, (B) deconvoluted Cu $2p_{3/2}$ region highlighting the main Cu^{2+} component and associated satellite features, (C) Ti 2p region confirming the presence of Ti^{4+} species, and (D) O 1s region showing contributions from lattice oxygen (O_L), surface-adsorbed oxygen species (O_{ads}), and defect-associated oxygen environments. These surface features reflect variations in local coordination and defect chemistry, which influence adsorption behavior and stabilization of lignin-derived intermediates.

The O 1s spectrum was deconvoluted into multiple components corresponding to lattice oxygen (O_L), surface-adsorbed oxygen species (O_{ads}), and defect-associated oxygen environments. The oxygen vacancies correspond to the non-lattice oxygen components. The

surface oxygen vacancy was calculated by the $O_{\text{ads}}/O_{\text{L}}$ ratio, which is found to be 0.46. The calculated oxygen vacancies on the surface were moderate compared to the literature [45,46]. These surface features are commonly associated with under-coordinated metal centers and structural distortions in PMOs. Rather than acting as active oxidizing agents, such surface defects can influence adsorption strength, surface basicity, and the stabilization of reactive lignin-derived intermediates. The relative abundance of these surface oxygen environments suggests the presence of coordinatively unsaturated sites that may play an important role in modulating adsorption–desorption equilibria during depolymerization.

Nitrogen physisorption measurements of CuTiO_3 were conducted at 77 K, and the corresponding adsorption–desorption isotherms are shown in Figure 4, with textural parameters summarized in Table S6. The BET surface area was determined to be $4.62 \text{ m}^2 \text{ g}^{-1}$, indicating a low-to-moderate surface area. The t-plot method revealed a microporous surface area of $2.86 \text{ m}^2 \text{ g}^{-1}$ and an external surface area of $1.76 \text{ m}^2 \text{ g}^{-1}$, suggesting that approximately 62% of the total surface area arises from micropores (<2 nm). The total pore volume, calculated at a relative pressure of 0.995, was $0.0425 \text{ cm}^3 \text{ g}^{-1}$, while the micropore volume was $0.00151 \text{ cm}^3 \text{ g}^{-1}$, confirming that the dominant porosity lies in the mesoporous regime [47]. BJH and Dollimore–Heal (D–H) analyses yielded cumulative pore volumes in the range of $0.041\text{--}0.045 \text{ cm}^3 \text{ g}^{-1}$. The presence of a hysteresis loop indicates an ink-bottle-type pore geometry, which is commonly associated with agglomerated particles [48]. The average pore diameter ranged from 32 to 72 nm, placing the material primarily within the mesoporous regime, with a minor contribution from microporosity likely arising from intragranular voids. The DFT pore size distribution revealed that the total pore volume for pores smaller than 233.9 nm was $0.0426 \text{ cm}^3 \text{ g}^{-1}$, whereas the volume of ultra micropores was only $0.00075 \text{ cm}^3 \text{ g}^{-1}$, further confirming the predominance of mesoporosity. The average particle size estimated from BET data was approximately $1.3 \text{ }\mu\text{m}$, indicating the formation of microscale agglomerates composed of nanocrystalline domains.

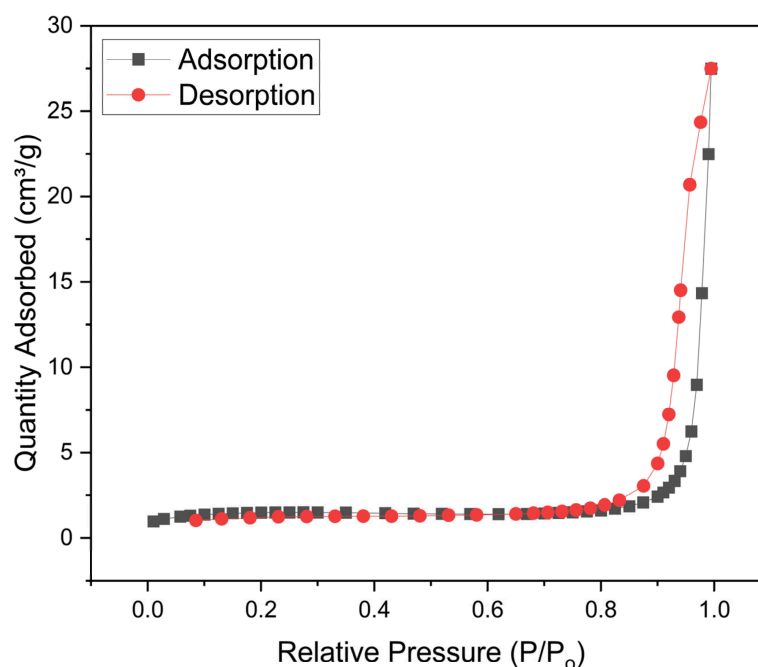


Figure 4. Nitrogen adsorption–desorption isotherms of CuTiO_3 measured at 77 K. The hysteresis loop indicates the presence of mesoporous textural features associated with interparticle voids and agglomerated nanocrystallites. The relatively low surface area and broad pore size distribution suggest that catalytic performance is primarily governed by surface chemical properties rather than purely by surface area.

SEM images of CuTiO_3 are shown in Figure 5. The micrographs reveal irregularly shaped particles with a heterogeneous size distribution and morphologies ranging from nearly spherical to polyhedral. Pronounced agglomeration was observed, likely arising from sintering effects during high-temperature calcination, which is consistent with the relatively low BET surface area [49]. The particle sizes extracted from the SEM images ranged from approximately 147 to 466 nm, indicating the formation of submicron crystallites. These values are consistent with the larger agglomerate size ($\sim 1.3 \mu\text{m}$) inferred from BET measurements.

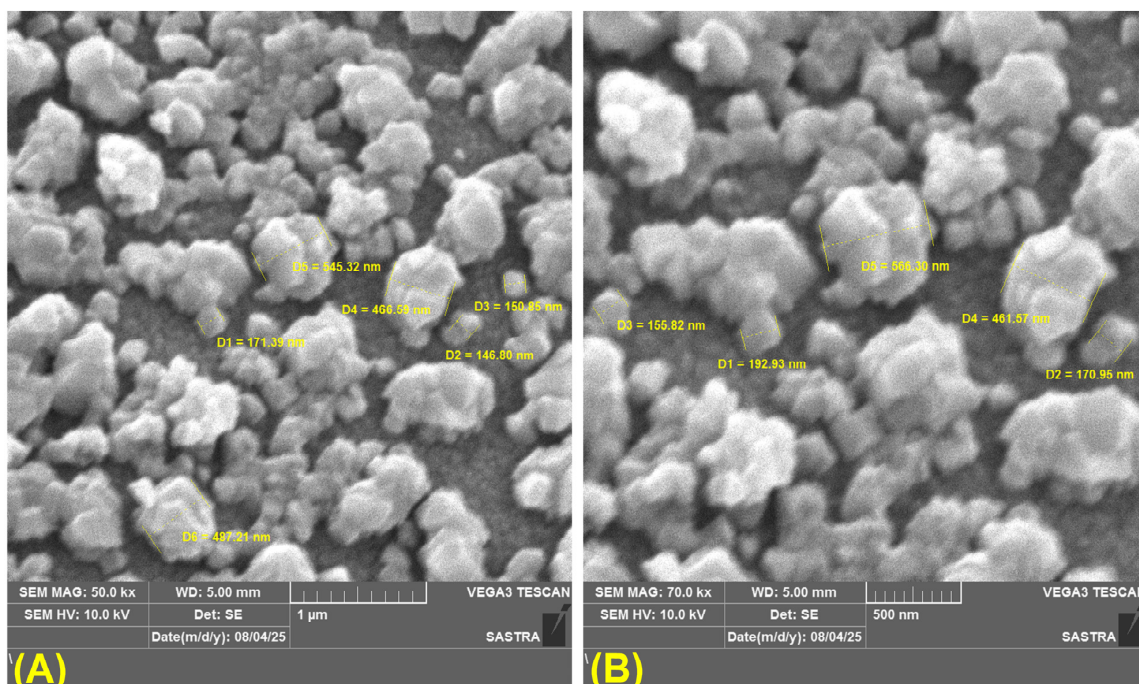


Figure 5. SEM images of CuTiO_3 recorded at (A) 50,000 $\times$ and (B) 70,000 $\times$ magnification. The micrographs reveal irregularly shaped particles with heterogeneous size distribution and pronounced agglomeration, likely arising from sintering during high-temperature calcination. The observed submicron crystallites form larger agglomerates, consistent with the textural properties derived from nitrogen physisorption measurements.

2.3. Response Surface Methodology of Lignin Depolymerization

A total of 50 experimental runs, including 8 center points, were conducted according to a central composite design (CCD), as summarized in Table 3 and the results are listed in Table 4. The experimental design, statistical analysis, and numerical optimization were performed using Design-Expert software (Version 12). A five-factor CCD was employed to develop a second-order quadratic polynomial model describing the relationship between the process variables and the monomer yield obtained from the BCD of lignin [50,51].

Table 3. The coded and actual levels of the factors used in the RSM study.

Code	Factor	Low Level (−1)	Medium Level (0)	High Level (+1)
A	Temperature $^{\circ}\text{C}$	100	145	190
B	Lignin to catalyst ratio	50:1	27.5:1	5:1
C	Pressure (Bar)	1	3	5
D	Time (Hours)	1	6.5	12
E	NaOH (M)	0.5	2.25	4

Table 4. The set and results of the experiments (Coded).

Run	Temperature	Catalyst Ratio	Pressure	Time	Solvent Conc	Monomer Yield (w/w)%
1	−1	1	−1	−1	−1	4.52
2	0	0	0	0	0	11.01
3	−1	−1	1	1	−1	6.72
4	0	0	0	0	0	11.98
5	1	1	−1	−1	1	8.41
6	1	−1	1	1	1	6.29
7	−1	1	−1	1	−1	8.76
8	1	−1	1	−1	1	8.63
9	1	−1	−1	−1	1	8.76
10	1	0	0	0	0	10.68
11	1	1	−1	1	1	8.26
12	0	0	0	−1	0	9.91
13	1	1	1	−1	1	8.65
14	1	1	1	1	1	7.37
15	1	−1	1	−1	−1	8.21
16	1	1	−1	1	−1	9.40
17	0	0	−1	0	0	9.32
18	1	−1	1	1	−1	8.82
19	0	0	0	0	0	11.85
20	−1	1	−1	−1	1	4.79
21	0	0	0	1	0	10.55
22	1	−1	−1	1	−1	9.20
23	0	0	0	0	−1	10.52
24	−1	1	1	−1	1	5.07
25	0	0	1	0	0	10.00
26	0	0	0	0	0	12.17
27	−1	−1	−1	1	1	7.77
28	0	0	0	0	0	11.38
29	0	0	0	0	0	10.96
30	0	1	0	0	0	9.31
31	−1	−1	1	−1	−1	4.17
32	−1	−1	−1	−1	−1	4.04
33	0	0	0	0	0	11.23
34	1	−1	−1	−1	−1	8.59
35	0	0	0	0	0	11.29
36	−1	1	1	1	−1	8.88
37	1	1	1	1	−1	9.72
38	−1	1	−1	1	1	8.52
39	1	1	1	−1	−1	9.17
40	−1	0	0	0	0	9.44
41	0	0	0	0	1	9.78
42	1	−1	−1	1	1	8.64
43	1	1	−1	−1	−1	7.72
44	−1	−1	1	−1	1	4.22
45	−1	1	1	1	1	7.38

Table 4. Cont.

Run	Temperature	Catalyst Ratio	Pressure	Time	Solvent Conc	Monomer Yield (w/w)%
46	−1	−1	−1	−1	1	5.05
47	−1	−1	1	1	1	5.34
48	−1	1	1	−1	−1	5.05
49	−1	−1	−1	1	−1	7.90
50	0	−1	0	0	0	8.87

The investigated independent variables were reaction temperature (A), lignin-to-catalyst ratio (B), pressure (C), reaction time (D), and NaOH concentration (E), each varied at three coded levels (−1, 0, and +1). The experimental response, defined as the monomer yield (Y, wt%), was fitted to the following quadratic polynomial Equation (2):

$$Y = \beta_0 + \sum_{i=1}^5 \beta_i X_i + \sum_{i < j} \beta_{ij} X_i X_j + \sum_{i=1}^5 \beta_{ii} X_i^2 \quad (2)$$

where Y is the predicted response (monomer yield), (X_i) represents the coded independent variables (A–E), (β_0) is the intercept, (β_i) are the linear coefficients, (β_{ij}) are the interaction coefficients, and (β_{ii}) are the quadratic coefficients describing curvature effects.

The fitted regression model for monomer yield is expressed as Equation (3):

$$Y = 10.999 + 1.144A + 0.287B - 0.176C + 0.722D - 0.250E - 0.195AB - 0.775AD + 0.264BC + 0.184BD - 0.289CD - 0.245CE - 0.372DE - 0.775A^2 - 1.746B^2 - 1.175C^2 \quad (3)$$

The intercept term ($\beta_0 = 10.999$) represents the predicted monomer yield at the center point of the experimental domain, where all variables are set at their coded zero levels. This relatively high baseline value indicates that the catalytic system exhibits appreciable activity even under moderate conditions. Among the linear terms, temperature (A) exhibited the strongest positive effect on monomer yield, followed by reaction time (D), suggesting that thermal activation and sufficient contact time are essential for effective lignin fragmentation under alkaline conditions. In contrast, pressure (C) and NaOH concentration (E) displayed weak negative linear contributions within the studied range, indicating that excessive severity may promote secondary reactions or reduce the stability of reactive intermediates. Several interaction terms were found to be significant, with the A–D interaction exhibiting the largest negative coefficient. This implies that simultaneous increases in temperature and reaction time beyond optimal values can be detrimental, likely due to enhanced secondary condensation or degradation pathways. The pronounced negative quadratic term for the lignin-to-catalyst ratio (B^2) indicates strong curvature, highlighting the existence of an optimal catalyst loading beyond which monomer yield decreases. This behavior underscores the importance of balancing lignin activation with the stabilization of depolymerization fragments.

Overall, the presence of significant quadratic and interaction terms confirms that the response surface is highly non-linear, characterized by a well-defined optimum region. Such curvature cannot be adequately captured by linear models, thereby justifying the use of RSM for process optimization. The model predicts that maximum monomer yield is achieved at moderate-to-high values of temperature and reaction time, while maintaining the other variables near their central levels to avoid excessive degradation or condensation. The statistical significance of the developed quadratic model and the interaction effects among the process variables were evaluated by analysis of variance (ANOVA), as summarized in Table 5. The model exhibited a high F-value (42.99) and a very low p -value (<0.0001), indicating that the regression is statistically significant and that the fitted

polynomial adequately captures the relationship between the independent variables and the monomer yield (Figure 6). This confirms the suitability of the quadratic model for describing the system within the investigated experimental domain.

Table 5. Statistical parameters for 2^5 designs.

Source	Sum of Squares	df	Mean Square	F-Value	<i>p</i> -Value
Model	234.12	20	11.71	42.99	<0.0001
A-Temperature	44.46	1	44.46	163.29	<0.0001
B-Catalyst Ratio	2.80	1	2.80	10.26	0.00329
C-Pressure	1.05	1	1.05	3.86	0.05901
D-Time	17.75	1	17.75	65.17	<0.0001
E-Solvent	2.12	1	2.12	7.80	0.00916
AB	1.21	1	1.21	4.46	0.04346
AC	0.18	1	0.18	0.66	0.42197
AD	19.21	1	19.21	70.55	<0.0001
AE	0.48	1	0.48	1.76	0.19500
BC	2.23	1	2.23	8.19	0.00775
BD	1.08	1	1.08	3.98	0.05566
BE	0.10	1	0.10	0.38	0.54098
CD	2.67	1	2.67	9.79	0.00397
CE	1.92	1	1.92	7.05	0.01276
DE	4.44	1	4.44	16.30	0.00036
A ²	0.69	1	0.69	2.54	0.12200
B ²	5.56	1	5.56	20.43	0.00010
C ²	2.13	1	2.13	7.84	0.00901
D ²	0.31	1	0.31	1.15	0.29315
E ²	0.48	1	0.48	1.75	0.19581
Residual	7.90	29	0.27		
Lack of Fit	6.44	22	0.29	1.41	0.33649
Pure Error	1.46	7	0.21		
Cor Total	242.02	49			

Among the linear terms, all variables except pressure (C) showed statistically significant effects on monomer yield ($p < 0.05$). The comparatively higher p -value for pressure ($p = 0.059$) suggests that its influence is weaker relative to the other parameters under the studied conditions. This indicates that pressure plays a secondary role in governing lignin depolymerization in the present alkaline system, compared to temperature, catalyst loading, reaction time, and base concentration. Several two-factor interaction terms, including AB, AD, BC, CD, CE, and DE, were statistically significant ($p < 0.05$), demonstrating that the combined influence of these variables cannot be interpreted independently. These interaction effects reflect the complex interdependence between thermal activation, catalyst availability, reaction duration, and alkaline strength, all of which collectively govern the stability and transformation of lignin-derived intermediates. The quadratic terms B² and C² were also statistically significant, confirming the presence of curvature in the response surface. This behavior indicates that both catalyst loading and pressure exhibit well-defined optimal values, beyond which the monomer yield decreases. In contrast, the quadratic

terms A^2 , D^2 , and E^2 were not significant within the explored ranges, suggesting that these variables exert nearly linear effects under the selected experimental conditions.

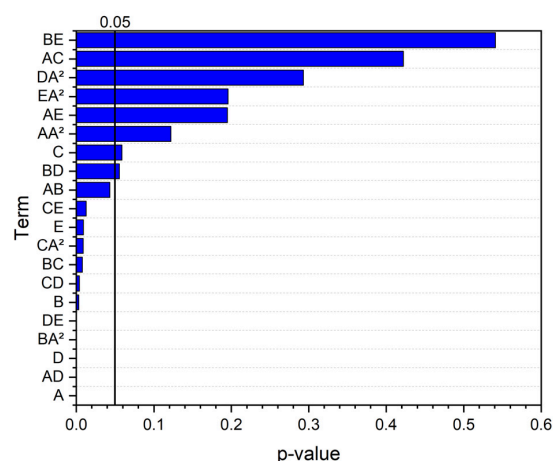


Figure 6. Pareto chart of standardized effects showing the significance of model terms on monomer yield obtained from RSM. The vertical reference line at $p = 0.05$ indicates the threshold for statistical significance.

The lack-of-fit test was not significant ($F = 1.41$, $p = 0.336$), indicating that the model adequately represents the experimental data and that no systematic deviation exists between the predicted and observed values. Furthermore, the residuals and pure error were within acceptable limits, confirming the robustness and predictive reliability of the developed model. As shown in Figure 7A, the normal probability plot of the residuals exhibits an approximately linear distribution, indicating that the residuals follow a near-normal distribution. Minor deviations observed at the extremes are typical of experimental systems and do not significantly affect the validity of the model. The absence of pronounced outliers further confirms the reliability of the experimental data and the suitability of the quadratic model for describing the system behavior. The residuals versus predicted values plot (Figure 7B) shows a random and uniform scatter of data points around the zero line, with no discernible trend or systematic pattern. This randomness indicates homoscedasticity, i.e., constant variance of residuals across the range of predicted responses, and confirms that no hidden variables or systematic errors are influencing the model. The lack of funnel-shaped or curved patterns further suggests that the selected quadratic model is adequate and that the inclusion of higher-order terms is unnecessary.

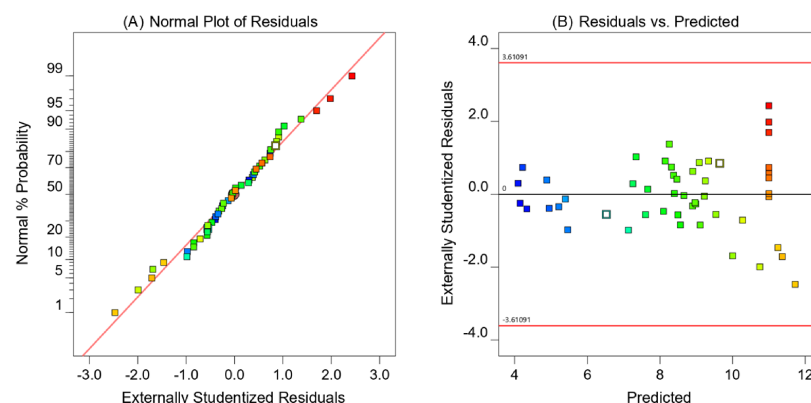


Figure 7. (A) Normal probability of residual values for lignin monomer yield vs. expected values, (B) Percentage monomer yield predicted vs. residual.

2.4. Effect of Process Parameters on Monomer Yield

Among the investigated variables, temperature exerted the most pronounced influence on monomer yield, as evidenced by its lowest p -value (<0.0001). The monomer yield increased markedly with increasing temperature up to an optimum, beyond which a slight decline was observed. At lower temperatures (100–120 °C), the yield remained relatively low (4–6%), reflecting insufficient thermal energy for effective lignin bond activation and fragmentation. As the temperature approached the center point of the experimental domain (≈ 145 °C), the yield increased substantially (10–11%), indicating more efficient depolymerization under these conditions. The optimal temperature was identified as approximately 155 °C, which provided sufficient activation energy for bond cleavage while limiting secondary degradation and condensation reactions. A decrease in product selectivity at elevated temperatures was also observed (Figure 8), suggesting that excessive thermal severity promotes side reactions, including repolymerization and further degradation of reactive intermediates [52]. This behavior highlights the importance of operating within a narrow temperature window that balances depolymerization efficiency and product stability. The interaction between temperature and lignin-to-catalyst ratio ($A \times B$) was among the most significant effects. While increasing temperature accelerates bond scission, its effectiveness is strongly modulated by catalyst loading. At low catalyst dosages, increasing temperature alone resulted in only modest improvements in yield, likely due to insufficient stabilization of reactive fragments at the catalyst surface. At excessively high temperatures (≈ 190 °C), a marginal decline in yield was observed, which may be attributed to enhanced secondary reactions, including condensation and irreversible degradation.

The lignin-to-catalyst ratio exhibited both a significant linear effect ($p = 0.0033$) and a strong quadratic effect (B^2 , $p = 0.0001$), indicating the presence of a well-defined optimum. At high lignin-to-catalyst ratios (50:1), monomer yield was relatively low, likely due to limited availability of active surface sites. Increasing the catalyst loading to an intermediate level (27.5:1) improved yield, reflecting enhanced substrate–surface interactions and stabilization of depolymerization fragments. Further increases in catalyst loading (5:1) resulted in a slight decline in yield, possibly due to excessive adsorption strength, restricted mass transfer, or promotion of secondary surface-mediated reactions [53].

Reaction time also played a critical role, exhibiting a significant positive linear effect ($p < 0.0001$). Longer reaction durations increased monomer yield, primarily by providing sufficient time for lignin fragmentation and desorption of stabilized products. However, the interaction between catalyst loading and time ($B \times D$) suggests that prolonged reaction times are only beneficial when sufficient catalytic sites are available. At low catalyst loadings, extending reaction time had minimal impact, whereas excessive residence times at high catalyst loadings promoted secondary condensation reactions.

The NaOH concentration primarily influenced lignin solubility, ionization of phenolic groups, and mass transfer to the catalyst surface. Under alkaline conditions, phenolic hydroxyl groups become deprotonated, increasing lignin solubility and susceptibility to nucleophilic cleavage. However, the model indicates that lower NaOH concentrations favored higher monomer yields. Excessively strong alkaline environments likely accelerate undesired side reactions, including condensation and over-fragmentation, thereby reducing monomer recovery. Pressure exerted a comparatively weaker linear effect ($p = 0.059$) but displayed a significant quadratic contribution (C^2 , $p = 0.009$), indicating a non-linear influence. Moderate pressure (≈ 3 bar) was associated with improved monomer yield, likely due to enhanced solvation and stabilization of reactive intermediates. At both lower and higher pressures, yield decreased, suggesting that pressure primarily modulates physical properties such as solvent density and volatility rather than directly influencing chemical transformation pathways.

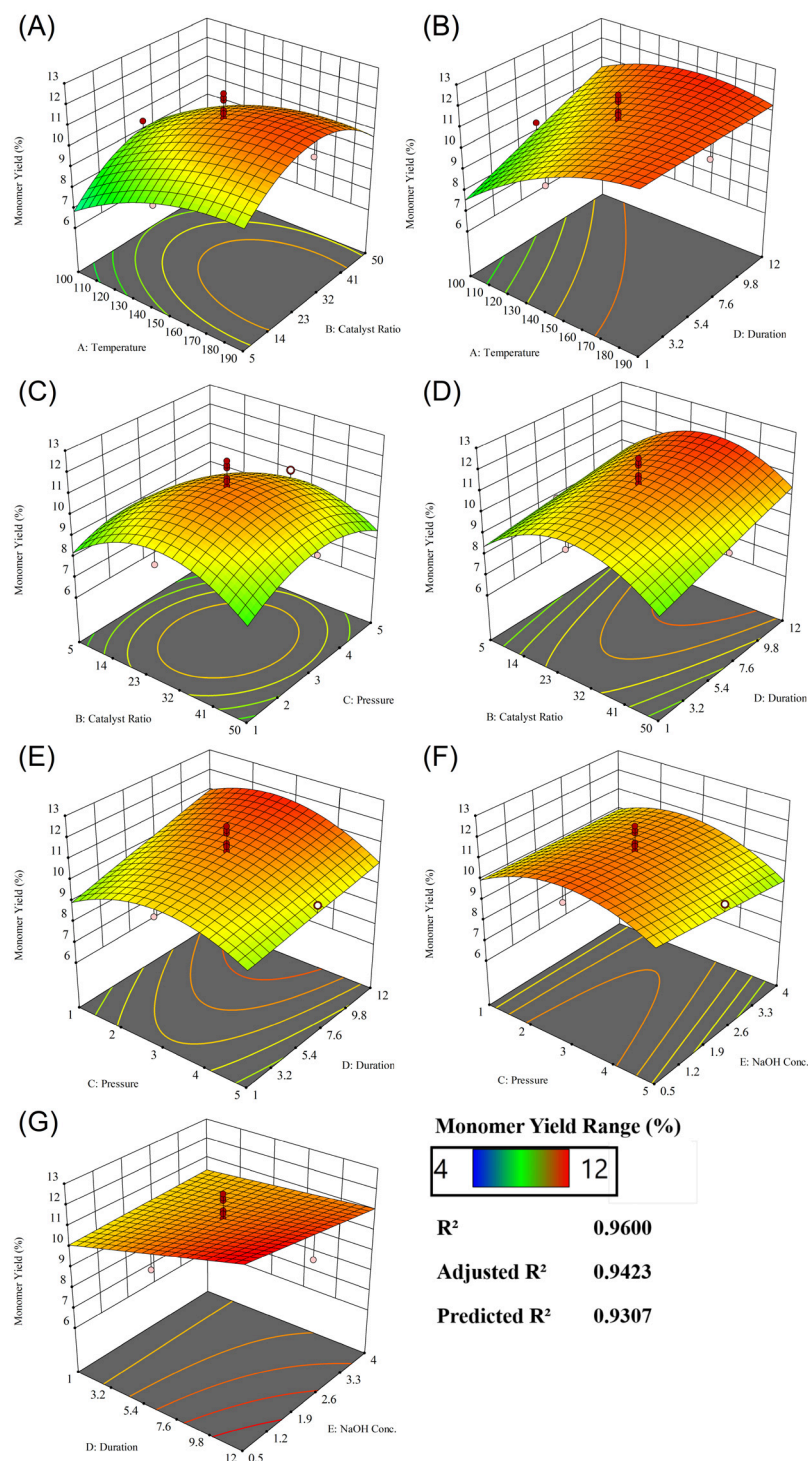


Figure 8. RSM plots illustration (A) temperature vs. catalyst ratio; (B) temperature vs. duration; (C) catalyst ratio vs. pressure; (D) duration vs. catalyst ratio; (E) pressure vs. duration; (F) solvent concentration vs. pressure; (G) solvent concentration vs. duration.

Based on the developed model, the predicted optimal conditions for maximum monomer yield were a temperature of 154 °C, lignin-to-catalyst ratio of 24.5:1, pressure of 3 bar, reaction time of 12 h, and NaOH concentration of 0.5 M. Under these conditions, the model predicted a yield of 12.4%, while the experimentally obtained yield was 11.5%, demonstrating good agreement between predicted and observed values. The optimized conditions reflect a balance between sufficient thermal activation, adequate catalyst surface availability, controlled alkaline strength, and appropriate residence time. Together, these

factors promote effective lignin fragmentation while suppressing undesired secondary reactions, leading to enhanced monomer recovery.

2.5. Reusability and Structural Stability of the Catalyst

The reusability of the synthesized PMOs catalyst was evaluated over five consecutive reaction cycles to assess its stability and sustained catalytic performance (Figure 9). A control experiment performed in the absence of the catalyst (0th cycle) yielded a monomer yield of 5.8%, representing the baseline contribution of the alkaline medium alone. Upon introduction of the catalyst, the monomer yield increased markedly to 10.62% in the first cycle, confirming the beneficial role of the solid catalyst in enhancing lignin depolymerization beyond homogeneous base-catalyzed hydrolysis.

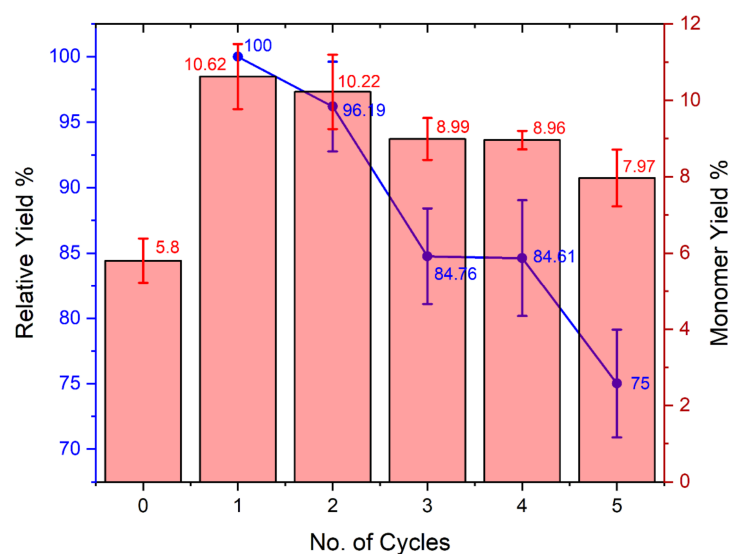


Figure 9. Reusability of Catalyst (Conditions: lignin: catalyst loading (25:1); 154 °C; 3 bars; 0.5 N NaOH; 12 h reaction time).

To quantify catalyst durability, the monomer yield obtained in the first cycle was taken as 100% relative activity. In the second cycle, the catalyst retained 96.19% of its initial activity, indicating minimal deactivation. By the fourth cycle, the relative activity decreased to approximately 84%, corresponding to a monomer yield of 8.9%, and further declined to 75% (7.97% yield) after the fifth cycle. Despite this gradual decrease, the catalyst preserved a substantial fraction of its original activity, demonstrating good operational stability. Compared with previously reported La-based perovskite catalysts, which retained 87–96.5% efficiency after 3–5 catalytic cycles, the present catalyst maintained 85% efficiency up to the fourth cycle, which further decreased to 75% after the fifth cycle. Nevertheless, considering its lower cost, the proposed catalyst may still represent an economically viable alternative [23,27–29,33,34]. The observed decline in performance can be attributed to several factors, including partial surface fouling by oligomeric or carbonaceous deposits, minor structural reorganization, and unavoidable physical losses during recovery and washing. In strongly alkaline environments, slow leaching of surface species and modification of surface coordination environments may also contribute to gradual deactivation. Importantly, no abrupt loss of activity was observed, suggesting that the bulk crystal structure remains largely intact during repeated use.

To further assess structural stability, the spent CuTiO_3 catalyst after multiple cycles was analyzed by XRD (Figure 10). The recycled catalyst exhibited sharper and more defined diffraction peaks compared to the fresh sample, indicating increased crystallinity. The average crystallite size increased from 40.32 nm for the fresh catalyst to 71.16 nm after reuse.

This growth is attributed to thermally driven crystallite coarsening, where smaller crystallites dissolve and redeposit onto larger ones a process commonly described as Ostwald ripening [54,55]. Although such coarsening can reduce surface area, it does not necessarily compromise catalytic functionality when surface chemistry rather than surface area dominates reactivity. Overall, the reusability results demonstrate that CuTiO_3 maintains substantial catalytic activity and structural integrity over multiple cycles, underscoring its potential for practical lignin valorization. The observed stability further supports the role of this material as a robust heterogeneous platform that promotes controlled depolymerization while suppressing extensive secondary condensation.

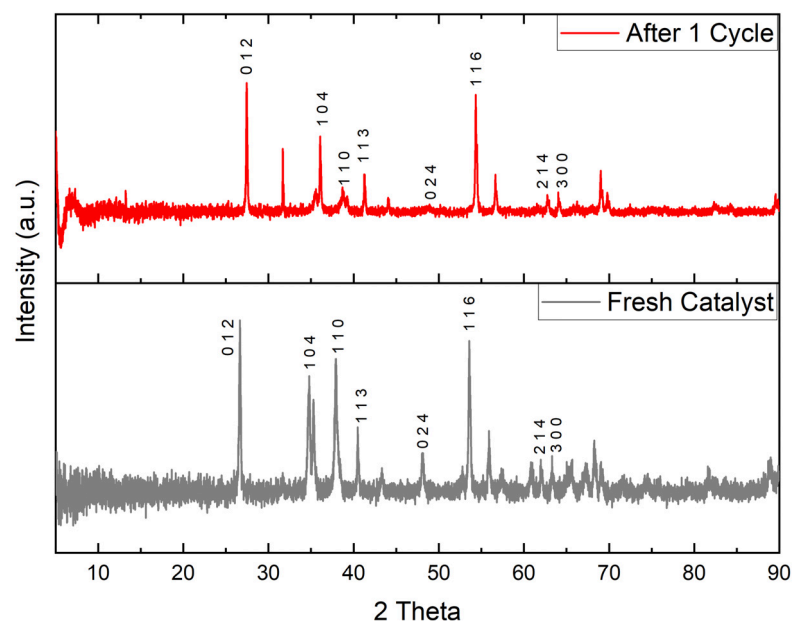


Figure 10. XRD pattern of the CuTiO_3 fresh and recycled catalyst.

2.6. Gel Permeation Chromatography Analysis

GPC was employed to assess the molecular weight distribution of lignin before and after depolymerization (Figure 11). Native commercial lignin exhibited poor solubility in tetrahydrofuran (THF); therefore, acetylation was performed prior to analysis to enhance its solubility [56]. In contrast, the lignin recovered from the depolymerization reaction (RL) was directly soluble in THF without any derivatization, indicating a substantial alteration in its molecular structure and polarity.

The acetylated lignin (AL) displayed a number-average molecular weight of approximately 1857 g mol^{-1} , whereas the depolymerized RL fraction exhibited a reduced molecular weight of approximately 1379 g mol^{-1} (Table S7). This clear downward shift in molecular weight distribution confirms that the lignin polymer backbone underwent effective fragmentation during the reaction. Importantly, the ability of RL to dissolve in THF without chemical modification further suggests a decrease in molecular complexity and intermolecular association, consistent with the formation of lower-molecular-weight fragments. This observation supports the monomer formation detected by GC-MS and confirms that depolymerization proceeded through controlled bond cleavage rather than extensive random degradation. The GPC results thus corroborate the catalytic screening and product analysis, demonstrating that the PMOs promotes effective lignin depolymerization while limiting extensive repolymerization or condensation. This behavior is consistent with a mechanism in which the catalyst stabilizes reactive intermediates and facilitates their desorption as smaller aromatic fragments rather than allowing them to recombine into higher-molecular-weight species.

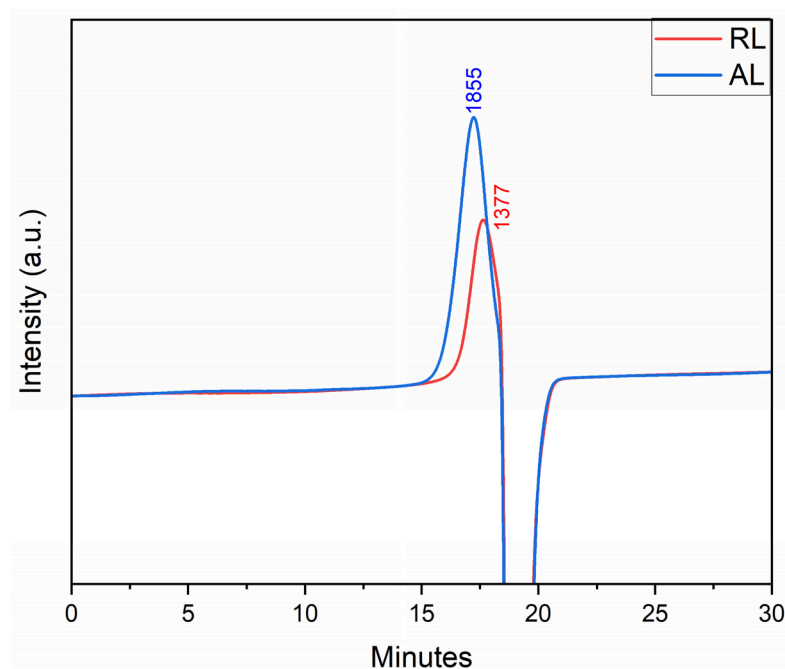


Figure 11. GPC analysis of Acetylated lignin (AL) & residual lignin (RL) after reaction.

3. Materials and Methods

3.1. Experimental Materials

Commercial dealkaline lignin was purchased from Tokyo Chemical Industry Co., Ltd. Tokyo, Japan. Titanium isopropoxide, sodium hydroxide, zinc acetate dihydrate, copper acetate monohydrate, and nickel acetate tetrahydrate were purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. HPLC-grade tetrahydrofuran (THF), vanillin, guaiacol, and acetovanillone were also procured from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. HPLC-grade dichloromethane (DCM) was obtained from Merck Life Science Pvt. Ltd., Mumbai, India. Nylon membrane syringe filters (0.2 μm pore size), (procured from Axiva SicheM Pvt. Ltd., Sonipat, India) were used for sample filtration prior to chromatographic analysis. All chemicals were of analytical grade and used as received without further purification. The depolymerization reactions were carried out using an Amar Eco-Catalyst Screening System equipped with seven parallel stainless steel batch reactors (25 mL each) purchased from Amar Equipment Pvt. Ltd., Mumbai, India.

3.2. Catalyst Preparation

PMOs with the general formula MTiO_3 ($\text{M} = \text{Cu}, \text{Ni}, \text{Zn}$) were synthesized using a sol-gel method. In a typical synthesis, 0.01 mol of the respective metal acetate, 0.01 mol of titanium isopropoxide, and 0.06 mol of citric acid were dissolved in 100 mL of ethanol under continuous stirring. The resulting solution was stirred for 1 h to ensure complete homogenization and subsequently heated at 70 $^{\circ}\text{C}$ for 48 h to promote gel formation. The obtained viscous gel was dried overnight and then calcined in a muffle furnace at 800 $^{\circ}\text{C}$ for 8 h with a heating rate of 5 $^{\circ}\text{C min}^{-1}$, following previously reported procedures [36,57]. The calcined powders were finely ground and stored in airtight containers for further use.

3.3. Catalyst Characterization

The phase composition and crystallographic structure of the synthesized catalysts were analyzed using powder XRD on a Bruker D8 Advance diffractometer (Bruker, Billerica, MA, USA) equipped with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), operated at 40 kV and 30 mA [58]. The diffraction patterns were recorded over a 2θ range of 10–80 $^{\circ}$. XPS measurements were

carried out using a Thermo Scientific K-Alpha spectrometer, Waltham, MA, USA with monochromatized Al K α radiation. XPS was employed to examine the surface elemental composition and oxidation states of the constituent elements. The acquired spectra were analyzed using CasaXPS software (version 2.5), Casa Software Ltd., Teignmouth Devon, UK. High-resolution Ti 2p, Cu 2p, and O 1s spectra were deconvoluted after Shirley background subtraction using mixed Gaussian-Lorentzian line shapes [59]. The specific surface area (SSA), pore volume, and pore size distribution of the catalysts were determined by nitrogen adsorption–desorption measurements at 77 K using a Micromeritics ASAP 2020 surface area analyzer, Malvern, Panalytical, Norcross, GA, USA. Prior to analysis, the samples were degassed under vacuum at 180 °C for 8 h. The SSA was calculated using the BET method, while the pore size distribution was derived using the Barrett–Joyner–Halenda (BJH) model [59]. The surface morphology of the catalysts was examined using an SEM (VEGA3, TESCAN, Warrendale, PA, USA). Prior to imaging, the samples were sputter-coated with a thin layer of gold to improve conductivity [60].

3.4. Base-Catalyzed Depolymerization of Lignin

In a typical depolymerization experiment, 25 mg of dealkaline lignin and the required amount of catalyst were added to 10 mL of aqueous NaOH solution in a 25 mL stainless steel batch reactor (Amar Eco-Catalyst Screening System, Amar Equipment, Mumbai, India, 25 mL). The reactor was sealed, purged with nitrogen to remove residual air, and then pressurized to the desired pressure. The reactor was heated to the target temperature (100–190 °C) and maintained for the specified reaction time (1–12 h) under continuous stirring. After completion of the reaction, the reactor was allowed to cool naturally to room temperature. The reaction mixture was transferred to a clean beaker, and the reactor was rinsed with distilled water. The washings were combined with the reaction mixture. The solid catalyst was separated from the liquid phase by centrifugation, for reuse in subsequent cycles.

The liquid phase was acidified with dilute HCl to precipitate unreacted lignin. The precipitated lignin was separated by filtration and used for subsequent molecular weight analysis by gel permeation chromatography (GPC). A 5 mL aliquot of the acidified filtrate was subjected to liquid–liquid extraction using HPLC-grade dichloromethane (DCM) (4 × 5 mL). The combined organic layers were concentrated to approximately 3 mL and filtered through a 0.2 μ m nylon syringe filter prior to GC-MS analysis.

Quantification of monomeric products was carried out using external calibration with authentic phenolic standards (vanillin, apocynin, and guaiacol) through a seven-point calibration in the concentration range of 1–500 ppm.

3.5. Yield and Selectivity

To ensure consistency and clarity in data interpretation, the performance of the catalytic system was evaluated in terms of monomer yield and product selectivity as defined below.

3.5.1. Monomer Yield

The monomer yield (Y, wt%) was defined as the mass of GC-MS-quantifiable aromatic monomers formed relative to the initial mass of lignin charged into the reactor. The yield was calculated using the following Equation (4):

$$\text{Monomer yield (wt\%)} = \left(\frac{C \times V_{\text{DCM}}}{V_{\text{sample}}} \times \frac{V_{\text{total}}}{W_{\text{lignin}}} \right) \times 100 \quad (4)$$

where:

C is the concentration of the monomer determined by GC-MS calibration (mg mL^{-1}),
 V_{DCM} is the volume of the concentrated dichloromethane extract (mL),
 V_{sample} is the volume of the acidified aqueous phase used for extraction (mL),
 V_{total} is the total volume of the acidified reaction mixture (mL),
 W_{lignin} is the initial mass of lignin used in the reaction (mg).

The reported monomer yield corresponds to the sum of the GC-MS-quantifiable phenolic products, primarily vanillin, guaiacol, and apocynin, and therefore represents an apparent monomer yield based on detectable low-molecular-weight aromatic compounds.

3.5.2. Product Selectivity

Product selectivity (S , %) toward a specific monomer (e.g., vanillin) was defined as the fraction of that monomer relative to the total amount of quantified monomers formed:

$$\text{Selectivity}_i(\%) = \frac{\text{Mass}_{\text{monomer}}}{\text{Mass}_{\text{total monomer}}} \times 100 \quad (5)$$

where:

$\text{Mass}_{\text{monomer}}$ is the mass of specific monomer quantified,

$\text{Mass}_{\text{total monomer}}$ is the mass of all quantified monomeric products.

Selectivity values were calculated based on GC-MS quantification using external calibration curves of authentic standards.

All reported yield and selectivity values represent mean values obtained from duplicate experiments, with deviations within $\pm 5\%$.

3.6. Response Surface Methodology (RSM)

The RSM was employed to systematically investigate the combined effects of key process variables on the monomer yield obtained from the BCD of lignin. The experimental design, statistical analysis, and model fitting were performed using Design-Expert software (Version 12), Stat-Ease Inc., Minneapolis, MN, USA.

Preliminary screening of influential parameters was conducted using a one-variable-at-a-time approach to identify the most significant factors affecting monomer formation [50]. Based on this preliminary analysis, five independent variables were selected for further optimization: reaction temperature (A), lignin-to-catalyst ratio (B), pressure (C), reaction time (D), and NaOH concentration (E). The selected ranges of these variables were chosen to encompass both kinetically controlled and mass-transfer-limited regimes while avoiding excessive degradation or condensation reactions. A central composite design (CCD) was employed to evaluate the individual and interactive effects of these parameters and to develop a second-order polynomial model describing the monomer yield as a function of the selected variables.

The experimental data were fitted to a quadratic polynomial model, and the adequacy of the model was assessed using analysis of variance (ANOVA). The statistical significance of the linear, interaction, and quadratic terms was evaluated based on the corresponding p -values, while the quality of the model fit was determined by the coefficient of determination (R^2), adjusted R^2 , predicted R^2 , and lack-of-fit tests. Three-dimensional response surface plots and contour plots were generated to visualize the effects of the independent variables and their interactions on the monomer yield. Numerical optimization was subsequently performed to identify the optimal reaction conditions that maximize monomer yield while maintaining high product selectivity.

3.7. Gel Permeation Chromatography (GPC) Analysis

The molecular weight distribution of lignin before and after depolymerization was analyzed using GPC. The measurements were performed on a Shimadzu LC-20AD UFLC system equipped with a SIL-20A autosampler and a RID-20A refractive index detector. The UFLC system along with the autosampler and detector was purchased from Shimadzu, Nakagyo, Kyoto, Japan. A WATERS Styragel® HR 4 THF column (Waters India Pvt Ltd., Bangalore, India) (7.8×300 mm) was used for all analyses.

Polystyrene standards with molecular weights ranging from 1.39×10^3 to 2.7×10^6 g mol⁻¹ (Shodex Pvt. Ltd., Hyderabad, India) were used for column calibration (Figures S3 and S4) [61]. HPLC-grade tetrahydrofuran (THF) was employed as the mobile phase at a constant flow rate of 0.6 mL min⁻¹. The detector temperature was maintained at 30 °C, while the column temperature was set at 35 °C.

As the commercial lignin used in this study was not soluble in THF, acetylation was performed prior to GPC analysis to improve its solubility. The detailed acetylation procedure is provided in the Supplementary Materials [56]. The residue lignin (RL) recovered after depolymerization exhibited sufficient solubility in THF and was analyzed directly without further derivatization.

3.8. Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

Qualitative and quantitative analysis of monomeric products obtained from lignin depolymerization was performed using a Shimadzu QP 2010 SE gas chromatograph coupled with a mass spectrometer. The system was supplied by Shimadzu, Geneo, Singapore. The instrument was equipped with an SH-I-5Sil MS capillary column (Shimadzu, Geneo, Singapore) (5% diphenyl/95% dimethylpolysiloxane, 30 m length, 0.25 mm internal diameter, and 0.25 µm film thickness). Helium was used as the carrier gas. The column flow rate was maintained at 1 mL min⁻¹, with a purge flow of 3 mL min⁻¹ and a linear velocity of 36.1 cm s⁻¹. The total flow rate was 9 mL min⁻¹, and the inlet pressure was set at 49.7 kPa. The injector temperature was maintained at 250 °C, and samples were injected in split mode with a split ratio of 5:1. The oven temperature program was as follows: initial temperature of 40 °C held for 1 min, ramped to 100 °C at 5 °C min⁻¹ and held for 3 min, followed by a second ramp to 260 °C at 4 °C min⁻¹ and held for 5 min. The total run time was 61 min. The ion source and interface temperatures were set at 230 °C and 270 °C, respectively. A solvent delay of 4 min was applied. Preliminary GC-MS screening revealed that the major monomeric products formed under the investigated reaction conditions were vanillin, apocynin, and guaiacol. Accordingly, external calibration was performed for these three compounds using seven-point calibration curves in the concentration range of 1–500 ppm.

3.9. Catalyst Reusability and Stability Tests

The reusability and operational stability of the selected catalyst were evaluated through consecutive depolymerization cycles under the optimized reaction conditions obtained from the RSM study (154 °C, 0.3 MPa, lignin-to-catalyst ratio of 24.5:1, 0.5 M NaOH, and 12 h reaction time). After the reaction completion, the solid catalyst was separated from the reaction mixture by centrifugation, followed by thorough washing with distilled water to remove any adsorbed organic species or residual alkali. The recovered catalyst was directly reused without any additional regeneration or thermal treatment. This procedure was repeated for five consecutive cycles to assess the retention of catalytic activity and selectivity. After each cycle, the liquid phase was processed following the standard workup protocol described in Section 2.4, and the monomer yield and selectivity toward vanillin were quantified using GC-MS. The catalytic activity in each cycle was expressed

relative to the initial activity in the first catalytic run, which was taken as 100%. Any loss in activity was attributed to possible surface fouling by oligomeric species, partial blockage of active sites, minor catalyst loss during recovery, or gradual structural changes under hydrothermal alkaline conditions. The recyclability performance was evaluated based on the retention of monomer yield and vanillin selectivity across repeated cycles.

4. Conclusions

This study demonstrates that rare-earth-free, transition-metal-based PMOs are effective heterogeneous catalysts for the selective BCD of lignin into value-added aromatic monomers, with CuTiO₃ exhibiting the highest monomer yield, the strongest selectivity toward vanillin, and ~97% suppression of guaiacol production compared to the no-catalyst system among the investigated catalysts. RSM optimization established the optimal reaction conditions as 154 °C, 24.5:1 lignin-to-catalyst ratio, 3 bar pressure, 12 h reaction time, and 0.5 M NaOH concentration. Under these conditions, the model predicted a monomer yield of 12.4%, while the experimental yield of 11.5% confirmed the reliability of the quadratic model. Reusability studies showed that CuTiO₃ retained approximately 75% of its initial activity after five consecutive cycles, with only gradual deactivation due to minor surface restructuring, fouling, and catalyst loss during recovery. Overall, the study identifies CuTiO₃ as a promising, earth-abundant, and reusable catalyst for lignin valorization and provides useful insights into composition-structure-performance relationships for the development of scalable and sustainable catalytic systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16060510/s1>, Figure S1: Comparative Statistical Evaluation of Monomer Yield and Product Selectivity over Perovskite Mixed-Metal Oxides via Tukey's Post Hoc Analysis (Means that do not share a letter are significantly different); Table S1: Tukey's Post Hoc multiple comparison analysis of vanillin selectivity over single- and mixed-metal perovskite catalysts. Mean differences, 95% confidence intervals (CI), and adjusted *p*-values are reported following one-way ANOVA ($\alpha = 0.05$). Significance levels are indicated as * $p < 0.03$, ** $p < 0.02$, *** $p < 0.01$, and ns (not significant); Table S2: Tukey's post hoc multiple comparison analysis of acetovanillone selectivity over single- and mixed-metal perovskite catalysts. Mean differences, 95% confidence intervals (CI), and adjusted *p*-values are reported following one-way ANOVA ($\alpha = 0.05$). Significance levels are indicated as * $p < 0.03$, ** $p < 0.02$, *** $p < 0.01$, and ns (not significant); Table S3: Tukey's post hoc multiple comparison analysis of guaiacol selectivity over single- and mixed-metal perovskite catalysts. Mean differences, 95% confidence intervals (CI), and adjusted *p*-values are reported following one-way ANOVA ($\alpha = 0.05$). Significance levels are indicated as * $p < 0.03$, ** $p < 0.02$, *** $p < 0.01$, and ns (not significant); Table S4: Tukey's post hoc multiple comparison analysis of monomer yield over single- and mixed-metal perovskite catalysts. Mean differences, 95% confidence intervals (CI), and adjusted *p*-values are reported following one-way ANOVA ($\alpha = 0.05$). Significance levels are indicated as * $p < 0.03$, ** $p < 0.02$, *** $p < 0.01$, and ns (not significant); Figure S2: GC-MS Chromatogram of CuTiO₃-catalysed lignin depolymerization; Table S5: The characteristic reflection peaks of the synthesized PMOs; Table S6: Summary of Textural Properties of CuTiO₃ Catalyst Obtained from N₂ Adsorption–Desorption (BET) Analysis; Table S7: Molecular weight and retention time of GPC standards and lignin samples; Figure S3: GPC analysis of Polystyrene standards; Figure S4 Calibration Curve for Log₁₀(Mw) vs. Retention Time of poly styrene standards ($R^2 = 0.9888$, Equation $y = -0.3187(RT) + 8.7616$); Reference no. [56,61] was cited in the Supplementary Material.

Author Contributions: Conceptualization, R.S. and P.V.; Methodology, R.S., V.K. and P.V.; Validation, V.K. and P.V.; Formal analysis, S.R.S. and P.V.; Investigation, R.S. and A.C.B.; Resources, M.S. and P.V.; Data curation, A.C.B.; Writing—original draft, R.S. and A.C.B.; Writing—review & editing, V.K., S.R.S., M.S. and P.V.; Visualization, S.R.S.; Supervision, M.S. and P.V. All authors have read and agreed to the published version of the manuscript.

Funding: P.V. would like to thank the Department of Science & Technology, India and SASTRA Deemed University for their support vide DST SR/FST/ET-I/2020/614(C). M.S. was supported by Thailand Science Research and Innovation (TSRI), and National Science Research and Innovation Fund (NSRF), King Mongkut's University of Technology North Bangkok (Project No. KMUTNB-FF-69-B-03).

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

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

Abbreviations

THF	Tetrahydrofuran
XPS	X-ray photoelectron spectroscopy
SEM	Scanning electron microscopy
XRD	X-Ray Diffraction
BET	Brunauer–Emmett–Teller
RSM	Response surface methodology
LCB	Lignocellulosic Biomass
BCD	Base catalyst Depolymerization
PMO	Perovskite Metal Oxide
DCM	Dichloromethane
BJH	Barrett–Joyner–Halenda
GPC	Gel Permeation Chromatography
CCD	Central composite design
ANOVA	Analysis of variance
AL	Acetylated Lignin
RL	Residue lignin

References

1. Trezza, A.; Mahboob, L.; Visibelli, A.; Geminiani, M.; Santucci, A. Lignin Waste Valorization in the Bioeconomy Era: Toward Sustainable Innovation and Climate Resilience. *Appl. Sci.* **2025**, *15*, 8038. [\[CrossRef\]](#)
2. Hasan, M.S.; Sardar, M.R.; Shafin, A.; Rahman, M.S.; Mahmud, M.; Hossen, M.M. A Brief Review on Applications of Lignin. *J. Chem. Rev.* **2023**, *5*, 56–82. [\[CrossRef\]](#)
3. Ali, S.; Rani, A.; Dar, M.; Qaisrani, M.; Noman, M.; Yoganathan, K.; Asad, M.; Berhanu, A.; Barwant, M.; Zhu, D. Recent Advances in Characterization and Valorization of Lignin and Its Value-Added Products: Challenges and Future Perspectives. *Biomass* **2024**, *4*, 947–977. [\[CrossRef\]](#)
4. Shanmugam, R.; Basha, A.C.; Kumar, V.; Shanmugam, S.R.; Sriariyanun, M.; Venkatachalam, P. Selective catalytic depolymerization of lignin for Biorenewable fuels and Chemicals: Opportunities and challenges. *Fuel* **2026**, *412*, 138111. [\[CrossRef\]](#)
5. Rashid, T.; Sher, F.; Rasheed, T.; Zafar, F.; Zhang, S.; Murugesan, T. Evaluation of current and future solvents for selective lignin dissolution—A review. *J. Mol. Liq.* **2021**, *321*, 114577. [\[CrossRef\]](#)
6. Zhou, N.; Thilakarathna, W.P.D.W.; He, Q.S.; Rupasinghe, H.P.V. A Review: Depolymerization of Lignin to Generate High-Value Bio-Products: Opportunities, Challenges, and Prospects. *Front. Energy Res.* **2022**, *9*, 758744. [\[CrossRef\]](#)
7. Ramzan, H.; Usman, M.; Nadeem, F.; Shahzaib, M.; Ur Rahman, M.; Singhania, R.R.; Jabeen, F.; Patel, A.K.; Qing, C.; Liu, S.; et al. Depolymerization of lignin: Recent progress towards value-added chemicals and biohydrogen production. *Bioresour. Technol.* **2023**, *386*, 129492. [\[CrossRef\]](#)
8. Roy, R.; Rahman, M.S.; Amit, T.A.; Jadhav, B. Recent Advances in Lignin Depolymerization Techniques: A Comparative Overview of Traditional and Greener Approaches. *Biomass* **2022**, *2*, 130–154. [\[CrossRef\]](#)
9. Wu, Z.; Jiang, Y.; Wang, X.; Xu, J.; Hu, L. A review on the separation of lignin depolymerized products. *Biomass Convers. Biorefin.* **2023**, *13*, 16667–16683. [\[CrossRef\]](#)
10. Kumaravel, S.; Thiruvengadam, P.; Karthick, K.; Sankar, S.S.; Karmakar, A.; Kundu, S. Green and sustainable route for oxidative depolymerization of lignin: New platform for fine chemicals and fuels. *Biotechnol. Prog.* **2021**, *37*, e3111. [\[CrossRef\]](#)
11. Yu, Z.; Kong, W.; Liang, W.; Guo, Y.; Cui, J.; Hu, Y.; Sun, Z.; Elangovan, S.; Xu, F. Heterogeneously Catalyzed Reductive Depolymerization of Lignin to Value-Added Chemicals. *ChemSusChem* **2025**, *18*, e202401399. [\[CrossRef\]](#)

12. Tian, Q.; Xu, P.; Huang, D.; Wang, H.; Wang, Z.; Qin, H.; He, Y.; Li, R.; Yin, L.; Chen, S.; et al. The driving force of biomass value-addition: Selective catalytic depolymerization of lignin to high-value chemicals. *J. Environ. Chem. Eng.* **2023**, *11*, 109719. [\[CrossRef\]](#)
13. Daelemans, B.; Sridharan, B.; Jusner, P.; Mukherjee, A.; Chen, J.; Kenny, J.K.; Dael, M.V.; Vanbroekhoven, K.; Deuss, P.J.; Stone, M.L.; et al. From lignin to market: A technical and economic perspective of reductive depolymerization approaches. *Green Chem.* **2025**, *27*, 13160–13178. [\[CrossRef\]](#)
14. Schutyser, W.; Kruger, J.S.; Robinson, A.M.; Katahira, R.; Brandner, D.G.; Cleveland, N.S.; Mittal, A.; Peterson, D.J.; Meilan, R.; Román-Leshkov, Y.; et al. Revisiting alkaline aerobic lignin oxidation. *Green Chem.* **2018**, *20*, 3828–3844. [\[CrossRef\]](#)
15. Wang, K.; Han, C.; Shao, Z.; Qiu, J.; Wang, S.; Liu, S. Perovskite Oxide Catalysts for Advanced Oxidation Reactions. *Adv. Funct. Mater.* **2021**, *31*, 2102089. [\[CrossRef\]](#)
16. Arandiyán, H.; Sudarsanam, P.; Bhargava, S.K.; Lee, A.F.; Wilson, K. Perovskite Catalysts for Biomass Valorization. *ACS Catal.* **2023**, *13*, 7879–7916. [\[CrossRef\]](#)
17. Wang, Y.; Sun, S.; Li, F.; Cao, X.; Sun, R. Production of vanillin from lignin: The relationship between β -O-4 linkages and vanillin yield. *Ind. Crops Prod.* **2018**, *116*, 116–121. [\[CrossRef\]](#)
18. Christy, M.; Choi, S.; Kwon, J.; Jeong, J.; Paik, U.; Song, T. The Perfect Imperfections of Perovskite Oxide Catalysts in the Aspect of Defect Equilibria. *Small Sci.* **2025**, *5*, 2400386. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Cho, J.; Kim, M.; Jung, J.C. A review on surface oxygen species in perovskite oxide catalysts for oxidation reactions: Toward rational catalyst design. *J. Environ. Chem. Eng.* **2025**, *13*, 119349. [\[CrossRef\]](#)
20. Labhasetwar, N.; Saravanan, G.; Kumar Megarajan, S.; Manwar, N.; Khobragade, R.; Doggali, P.; Grasset, F. Perovskite-type catalytic materials for environmental applications. *Sci. Technol. Adv. Mater.* **2015**, *16*, 036002. [\[CrossRef\]](#)
21. Zhu, H.; Zhang, P.; Dai, S. Recent Advances of Lanthanum-Based Perovskite Oxides for Catalysis. *ACS Catal.* **2015**, *5*, 6370–6385. [\[CrossRef\]](#)
22. Jiang, Y.; Li, Z.; Zhu, T.; Li, D.; Wang, H.; Zhu, X. Oxygen Storage Characteristics and Redox Behaviors of Lanthanum Perovskite Oxides with Transition Metals in the B-Sites. *Energy Fuels* **2023**, *37*, 9419–9433. [\[CrossRef\]](#)
23. Zhu, T.; Wang, Y.; Chang, M.; Xu, J.; Hao, X. Application of perovskite type oxide $\text{La}_x\text{Ce}_{1-x}\text{CoO}_3$ in lignin depolymerization and mono-phenol preparation. *RSC Adv.* **2025**, *15*, 1625–1640. [\[CrossRef\]](#)
24. Xu, J.; Yang, Y.; Liu, B.; Kong, Y.; Du, B.; Guo, Y.; Zhou, J.; Wang, X. Ultrasonic assisted enhanced catalytic effect of perovskite to promote depolymerization of lignin. *Int. J. Biol. Macromol.* **2022**, *218*, 431–438. [\[CrossRef\]](#)
25. Deng, H.; Lin, L.; Liu, S. Catalysis of Cu-Doped Co-Based Perovskite-Type Oxide in Wet Oxidation of Lignin To Produce Aromatic Aldehydes. *Energy Fuels* **2010**, *24*, 4797–4802. [\[CrossRef\]](#)
26. Wang, H.; Han, H.; Sun, E.; Zhang, Y.; Li, J.; Chen, Y.; Song, H.; Zhao, H.; Kang, Y. Production of aryl oxygen-containing compounds via catalytic pyrolysis of bagasse lignin over $\text{La}_{0.8}\text{M}_{0.2}\text{FeO}_3$ (M = La, Ca, Sr, Ba). *J. Anal. Appl. Pyrolysis* **2019**, *142*, 104624. [\[CrossRef\]](#)
27. Li, Y.; Zhu, J.; Zhang, Z.; Qu, Y.-S. Preparation of Syringaldehyde from Lignin by Catalytic Oxidation of Perovskite-Type Oxides. *ACS Omega* **2020**, *5*, 2107–2113. [\[CrossRef\]](#)
28. Deng, H.; Lin, L.; Sun, Y.; Pang, C.; Zhuang, J.; Ouyang, P.; Li, J.; Liu, S. Activity and Stability of Perovskite-Type Oxide LaCoO_3 Catalyst in Lignin Catalytic Wet Oxidation to Aromatic Aldehydes Process. *Energy Fuels* **2009**, *23*, 19–24. [\[CrossRef\]](#)
29. Zhu, Y.; Jiang, X.; Jin, X.; Song, W.; Zhao, Y. Catalytic depolymerization of lignin for hydrocarbon rich bio-oil production: Influence of Ni doped on LaCoO_3 catalysts and hydrogen sources. *J. Energy Inst.* **2025**, *118*, 101869. [\[CrossRef\]](#)
30. Kausar, S.; Altaf, A.A. Alkylammonium lead chloride perovskites: Synthesis, characterization and catalytic activity for conversion of lignin into value added products. *Mater. Chem. Phys.* **2023**, *310*, 128490. [\[CrossRef\]](#)
31. Liu, Y.; Xu, Z.; He, Y.; Liu, M.; Lin, C.; Lv, Y. Synergistic activation of persulfate by Fe-based perovskite photocatalysis for alkali lignin degradation in pulp and paper wastewater. *Environ. Sci. Pollut. Res.* **2024**, *31*, 57822–57831. [\[CrossRef\]](#)
32. Lou, J.; Liao, W.; Wang, Z.; Li, L.; Li, Y.; Xie, X. Hydrothermal liquefaction of lignin to aromatics over the perovskite catalysts. *J. Fuel Chem. Technol.* **2022**, *50*, 984–992. [\[CrossRef\]](#)
33. Han, H.; Yu, H.; Zhang, L.; Gao, J.; Zhang, Y.; Tian, Y.; Zhang, Y.; Wang, H.; Chen, Y. Phenolics production via the catalytic pyrolysis of organosolv lignin over praseodymium doped lanthanum nickelate. *Results Eng.* **2024**, *22*, 102189. [\[CrossRef\]](#)
34. Deng, H.; Lin, L.; Sun, Y.; Pang, C.; Zhuang, J.; Ouyang, P.; Li, Z.; Liu, S. Perovskite-type oxide LaMnO_3 : An efficient and recyclable heterogeneous catalyst for the wet aerobic oxidation of lignin to aromatic aldehydes. *Catal. Lett.* **2008**, *126*, 106–111. [\[CrossRef\]](#)
35. Mathieu, Y.; Vidal, J.D.; Arribas Martínez, L.; Abad Fernández, N.; Iborra, S.; Corma, A. Molecular Oxygen Lignin Depolymerization: An Insight into the Stability of Phenolic Monomers. *ChemSusChem* **2020**, *13*, 4743–4758. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Safari, S.; Seyed Ahmadian, S.M.; Amani-Ghadim, A.R. Visible light photocatalytic activity enhancing of MTiO_3 perovskites by M cation (M = Co, Cu, and Ni) substitution and Gadolinium doping. *J. Photochem. Photobiol. Chem.* **2020**, *394*, 112461. [\[CrossRef\]](#)

37. Deng, J.; Cui, Y.; Jiang, Z.; Du, R.; Yang, L.; Zhang, X.; He, R.; Zhang, J. Transition metal(II) ion doping of CsPb₂Br₅/CsPbBr₃ perovskite nanocrystals enables high luminescence efficiency and stability. *J. Mater. Chem. C* **2022**, *10*, 18336–18342. [\[CrossRef\]](#)
38. Dhiman, M.; Tripathi, M.; Singhal, S. Structural, optical and photocatalytic properties of different metal ions (Cr³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺) substituted quaternary perovskites. *Mater. Chem. Phys.* **2017**, *202*, 40–49. [\[CrossRef\]](#)
39. Gabal, M.A.; Al-luhaibi, R.S.; Al Angari, Y.M.; Awad, A.; Al-Juaid, A.A.; Saeed, A. Understanding the structural, magnetic, and electrical properties of MFe₂O₄ (M = Mg²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺) nanocrystalline ferrites. A comparative study. *Appl. Phys. A* **2025**, *131*, 116. [\[CrossRef\]](#)
40. Torres-Ochoa, J.A.; Cabrera-German, D.; Cortazar-Martinez, O.; Bravo-Sanchez, M.; Gomez-Sosa, G.; Herrera-Gomez, A. Peak-fitting of Cu 2p photoemission spectra in Cu⁰, Cu¹⁺, and Cu²⁺ oxides: A method for discriminating Cu⁰ from Cu¹⁺. *Appl. Surf. Sci.* **2023**, *622*, 156960. [\[CrossRef\]](#)
41. Sakamoto, K.; Hayashi, F.; Sato, K.; Hirano, M.; Ohtsu, N. XPS spectral analysis for a multiple oxide comprising NiO, TiO₂, and NiTiO₃. *Appl. Surf. Sci.* **2020**, *526*, 146729. [\[CrossRef\]](#)
42. Phani, A.R.; Santucci, S. Structural characterization of iron titanium oxide synthesized by sol–gel spin-coating technique. *Mater. Lett.* **2001**, *50*, 240–245. [\[CrossRef\]](#)
43. Subramaniam, T.; Mani, K.; Devaraj, S. Conversion of spent activated carbon into a value-added product, MnO₂/C nanocomposite, a bi-functional electrocatalyst for oxygen reaction and an electrode material for supercapacitors. *Electrochim. Acta* **2025**, *519*, 145828. [\[CrossRef\]](#)
44. Yao, C.; Zhang, Q.; Lu, H.; Zhang, X.; Fan, Y.; Luo, J.; Fang, R.; Liu, H.; Lyu, J.; Feng, F.; et al. Deep Learning Guided Exploration of Transition Metal Oxide Catalysts in Acetylene Selective Hydrogenation. *J. Am. Chem. Soc.* **2026**, *148*, 790–800. [\[CrossRef\]](#)
45. Nayak, B.B.; Hota, I.; Soren, S.; Parhi, P. Sm_{1–x}Sr_xMnO₃ (X = 0.1, 0.2, 0.3, and 0.4) perovskite (SSM) with a-site doping optimized as oxygen reduction reaction (ORR) electrocatalyst. *Electrochim. Acta* **2025**, *515*, 145609. [\[CrossRef\]](#)
46. Subramaniam, T.; Krishnaveni, B.S.; Devaraj, S. Tuning the surface oxygen vacancies of α-MnO₂ to enhance the kinetics of ORR and OER. *J. Mater. Sci. Mater. Electron.* **2024**, *35*, 1184. [\[CrossRef\]](#)
47. Buttersack, C.; Möllmer, J.; Hofmann, J.; Gläser, R. Determination of micropore volume and external surface of zeolites. *Microporous Mesoporous Mater.* **2016**, *236*, 63–70. [\[CrossRef\]](#)
48. Sotomayor, F.; Cychosz, K.; Thommes, M. Characterization of Micro/Mesoporous Materials by Physisorption: Concepts and Case Studies. *Acc. Mater. Surf. Res.* **2018**, *3*, 34–50.
49. Hou, Z.; Yang, W.; Zhan, Y.; Zhang, X.; Zhang, J. Effect of Calcination Temperature on the Microstructure, Composition and Properties of Agglomerated Nanometer CeO₂-Y₂O₃-ZrO₂ Powders for Plasma Spray–Physical Vapor Deposition (PS-PVD) and Coatings Thereof. *Nanomaterials* **2024**, *14*, 995. [\[CrossRef\]](#)
50. Rahman, S.S.A.; Pasupathi, S.; Karuppiyah, S. Statistical optimization, kinetic modeling, and techno-economic analysis for the production of high molecular mass dextran using sugarcane industrial waste-molasses. *Bioresour. Technol. Rep.* **2024**, *27*, 101902. [\[CrossRef\]](#)
51. Ponnusami, V.; Krithika, V.; Madhuran, R.; Srivastava, S.N. Biosorption of reactive dye using acid-treated rice husk: Factorial design analysis. *J. Hazard. Mater.* **2007**, *142*, 397–403. [\[CrossRef\]](#)
52. Dolan, D.; Brucato, R.; Reid, C.; Lee, A.F.; Wilson, K.; Voutchkova-Kostal, A.M. Selective lignin depolymerization via transfer hydrogenolysis using Pd/hydrotalcite catalysts: Model compounds to whole biomass. *Chem. Sci.* **2024**, *15*, 20223–20239. [\[CrossRef\]](#)
53. Kouris, P.D.; Brini, A.; Schepers, E.; Boot, M.D.; Van Den Heuvel, E.R.; Hensen, E.J.M. Optimizing Catalytic Depolymerization of Lignin in Ethanol with a Day-Clustered Box–Behnken Design. *Ind. Eng. Chem. Res.* **2023**, *62*, 6874–6885. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Kucharczyk, B.; Winiarski, J.; Szczygieł, I.; Adamska, K. Physicochemical Properties of LaFeO₃ Perovskite Prepared by Various Methods and Its Activity in the Oxidation of Hydrocarbons. *Ind. Eng. Chem. Res.* **2020**, *59*, 16603–16613. [\[CrossRef\]](#)
55. Cao, X.; Zhi, L.; Li, Y.; Fang, F.; Cui, X.; Ci, L.; Ding, K.; Wei, J. Fabrication of Perovskite Films with Large Columnar Grains via Solvent-Mediated Ostwald Ripening for Efficient Inverted Perovskite Solar Cells. *ACS Appl. Energy Mater.* **2018**, *1*, 868–875. [\[CrossRef\]](#)
56. Hazwan Hussin, M.; Aziz, A.A.; Iqbal, A.; Ibrahim, M.N.M.; Latif, N.H.A. Development and characterization novel bio-adhesive for wood using kenaf core (*Hibiscus cannabinus*) lignin and glyoxal. *Int. J. Biol. Macromol.* **2019**, *122*, 713–722. [\[CrossRef\]](#)
57. Zhang, H.; Shi, H.; You, H.; Su, M.; Huang, L.; Zhou, Z.; Zhang, C.; Zuo, J.; Yan, J.; Xiao, T.; et al. Cu-doped CaFeO₃ perovskite oxide as oxygen reduction catalyst in air cathode microbial fuel cells. *Environ. Res.* **2022**, *214*, 113968. [\[CrossRef\]](#)
58. Jasmin, J.; Anilkumar, P.; Deepak, S. Synthesis, analysis and characterization of surfactant-assisted TiO₂ nanoparticles for ammonia gas sensor applications. *Ceram. Int.* **2024**, *50*, 52262–52269. [\[CrossRef\]](#)
59. Sivaraman, S.; Shanmugam, S.R.; Venkatachalam, P.; Shanmugam, R.; Chan Basha, A.; Saady, N.M.C. Effect of pretreatment type on the physico-chemical properties of activated carbons derived from an invasive weed *Prosopis juliflora*: Potential applications. *Mater. Res. Express* **2025**, *12*, 015601. [\[CrossRef\]](#)

60. Krishnan, S.; Sivaraman, S.; Jothipandiyan, S.; Venkatachalam, P.; Ramiah Shanmugam, S.; Paramasivam, N. Bioprospecting of aqueous phase from pyrolysis of plant waste residues to disrupt MRSA biofilms. *Biofouling* **2023**, *39*, 231–243. [[CrossRef](#)]
61. Gaugler, E.C.; Radke, W.; Vogt, A.P.; Smith, D.A. Molar mass determination of lignins and characterization of their polymeric structures by multi-detector gel permeation chromatography. *J. Anal. Sci. Technol.* **2021**, *12*, 30. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.



DSPACE

<https://dspace.org/>

CuTiO₃ perovskite-type as an efficient catalyst for alkaline lignin depolymerization towards selective vanillin production

Shanmugam, Ratheeshkumar; Chan Basha, Arul; Kumar, Vinod; Shanmugam, Saravanan Ramiah; Sriariyanun, Malinee ...

2026-06

MDPI

<https://doi.org/10.3390/catal16060510>

Shanmugam R, Chan Basha A, Kumar V, et al., (2026) CuTiO₃ perovskite-type as an efficient catalyst for alkaline lignin depolymerization towards selective vanillin production. Catalysts, Volume 16, Issue 6, June 2026, Article number 510