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Co- and Ca-phosphate-based catalysts for the depolymerization of organosolv eucalyptus lignin

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Abstract

Depolymerization of purified organosolv eucalyptus wood lignin by the heterogeneous catalysts, cobalt polyphosphate (CoP_2O_6) and calcium phosphate ($\beta\text{-CaP}_2\text{O}_6$) was investigated. A total syringol yield of 16.7% was achieved with $\beta\text{-CaP}_2\text{O}_6$ in a methanol/water (50/50, wt/wt) solvent system after depolymerization at 300 °C for 1 h, showing selectivity of the catalyst.

Value-adding of lignin by conversion to phenol and phenol derivatives has attracted great interest because they are valuable products and can be used as feedstocks for the production of industrial mono-aromatic compounds (*e.g.*, benzene, xylene), liquid fuels and polymers. As summarized in a recent review paper, various lignins (*e.g.*, Kraft, organosolv, soda etc.) in different solvent systems (water, alcohol, organic acids, ionic liquids, etc.), catalyst types (acid, alkaline, heterogeneous, etc.) and reaction modes (direct depolymerization, hydrogenolysis, etc.) have been studied for the conversion of lignins to chemicals.¹ However, lignin conversion to useful products remains challenging, and product yields are low due to its highly recalcitrant and complex structure linked together by various types of ether, aryl and carbon-carbon bonds consisting of mainly $\beta\text{-O-4}$, 5–5 and 4–O–5 bonds. Depolymerization of lignin with heterogeneous catalysts has received increasing research interests because of the significant advantages including high reaction activity, high selectivity and the ability to readily recover the catalyst. In our previous work,² depolymerization of organosolv eucalyptus wood lignin with mesostructured silica catalyst, SBA-15 in a methanol/water (50/50, wt/wt) reaction system resulted in a total syringol yield of 23.0% after depolymerization for 1 h at a reaction temperature of 300 °C. This was the first reported study on lignin that gave such a high syringol yield. However, the production cost of mesostructured silica catalysts are high due to the use of expensive starting materials.

Therefore, low cost and effective heterogeneous catalysts are preferred for syringol production from lignin.

Metal phosphates are relatively low cost heterogeneous catalysts, and are well known for their catalytic performance to convert sugars, sugar alcohols and cyclic alcohols to other value-added chemicals such as 5-hydroxymethyl furfural (HMF) and isosorbide.³⁻⁵ We have previously reported the synthesis of phosphates of alkaline earth metals (Ca and Sr) and their applications in conversion of fructose, glucose, and cellulose to HMF⁶, and the effect of calcination temperature on catalytic performance of these catalysts.⁷ In the present study, we report the use of the phosphates of Co and Ca as solid catalysts for the depolymerization of treated (*i.e.*, purified) organosolv lignin (TOL) from woody eucalyptus to phenols. To the best of our knowledge, it is the first time that phosphate-based heterogeneous catalysts have been used to produce syringol by depolymerization of lignin.

Lignin and the phosphate solid catalysts were prepared and characterized according to previous publications.^{2,7} Phosphate solid catalysts were prepared using conventional precipitation in acetone-water mixture and calcined at 900 °C, which led to the formation of β -CaP₂O₆⁷ and CoP₂O₆ (Supplementary Figure 1) with confirmation by x-ray powder diffraction analysis (PDF no. 00-027-1120 for CoP₂O₆). The depolymerization of the treated and purified organosolv lignin (TOL) firstly was carried out in a stainless steel tubular reactor (3/8 inch O.D. and 12 cm, length) in which 35 mg of TOL was mixed with 2 mL water with and without catalyst (35 mg) and reacted at 250 °C for 1 h with a solution initial pH of 7. The pressure of the reactor rose from atmosphere to ~4.0 mPa during the depolymerization reaction. Commercial sulfided NiMo/Al₂O₃ catalyst was used for comparison. After depolymerization, the products were fractionated (Supplementary Figure 2) and characterized using the methods described in a previous publication.² The total mass of the isolated three

fractions (aqueous, residual lignin, and solid residue) was not dissimilar in the presence or absent of catalyst considering the error ranges (Figure 1). The least proportion of the solid residue fraction and the highest proportion of residual lignin fraction were detected with CoP_2O_6 catalyst, followed by $\beta\text{-CaP}_2\text{O}_6$, $\text{NiMo}/\text{Al}_2\text{O}_3$ and control in that order (Figure 1). Phosphate-based catalysts have significantly lower surface area of $0.5 \text{ m}^2/\text{g}$ compared to the $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst which has a value of $108 \text{ m}^2/\text{g}$, while the acid strength of the former is in the range of +3.3 to +4.8 and that of $\text{NiMo}/\text{Al}_2\text{O}_3$ +1.7 to +2.0. Low acidity corresponds to greater acid strength.⁶ Therefore it is clear that the better performance of the phosphate catalysts relative to the commercial catalyst is not controlled by these properties, but rather by type of the acid type. There are two types of active sites in the phosphate catalysts that are involved with catalytic activities: one belongs to the hydroxyl group or Bronsted site, while the other is the predominant Lewis site. It is therefore likely that it is the Lewis acid sites that play an important role in the improvement of the catalyst selectivity as $\text{NiMo}/\text{Al}_2\text{O}_3$ has only the Bronsted acid sites.

The yields of monomeric phenols in the aqueous and residual lignin fractions were analyzed by GC-MS² and the results are shown in Table 1 and Supplementary Figure 3. It is known that hardwood (*e.g.*, *Eucalyptus grandis*) lignin contains mainly guaiacyl and syringyl units.⁸ The results therefore demonstrated that the presence of the phosphate catalysts selectively produced syringol during the depolymerization process. The highest syringol yields in both aqueous and residual lignin fractions were achieved with the $\beta\text{-CaP}_2\text{O}_6$ catalyst. The total syringol yield with $\beta\text{-CaP}_2\text{O}_6$ was 8.47%, followed by 6.67% with CoP_2O_6 and 5.96% for sulfide $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst. Without catalyst, the total syringol yield was only 1.85% despite having the highest proportion of 1-(4-hydroxyl-3,5-dimethoxyphenyl)-ethanone. Benzoic acid was detected in the aqueous fractions derived from CoP_2O_6 and sulfide $\text{NiMo}/\text{Al}_2\text{O}_3$, while small quantities of 4-hydroxy-3,5-dimethoxy-benzaldehyde was detected

from the aqueous fraction derived from sulfide NiMo/Al₂O₃. Guaiacol was not detected possibly because of the structural features of the purified organosolv lignin. The use of β-CaP₂O₆ and CoP₂O₆ catalysts significantly increased the syringol content from 25.9% (without catalyst) to 74.3% and 53.1% respectively in the aqueous fraction, while the syringol contents in all the lignin residues were no more than 5.7% (Supplementary Figure 3).

FT-IR spectra of residual lignin after depolymerization using the various catalysts are shown in Supplementary Figure 4. Assignments of the major peaks were based on previous publications (and the references therein).^{9, 10} The peaks at 2840 cm⁻¹ – 2975 cm⁻¹ were assigned to C–H stretching in aromatic methoxyl groups and in methyl or methylene groups of side chains. These peaks became very significant after depolymerization due to the formation of lignin subunits with these groups.

The peaks at 1605 cm⁻¹, 1512 cm⁻¹ and 1426 cm⁻¹ are assigned as the characteristic vibrations of aromatic skeletal structures in lignin. The peaks at 1512 cm⁻¹ and 1426 cm⁻¹ are not significant in the residual lignin after depolymerization with NiMo/Al₂O₃ compared to others possibly due to the reduced proportion of aromatic skeletal structures. The peak at 1462 cm⁻¹ is related to C–H deformation in lignin, which was significant in all the lignin samples. The peak at 1326 cm⁻¹ is assigned to C–O stretching of syringyl rings. Despite similar levels of syringol in all the residual lignins, this peak was very weak with NiMo/Al₂O₃, indicating perhaps of the conversion of the syringyl subunits to other compounds and/or the selective removal of other subunits. The peak at 1261 cm⁻¹ is assigned to guaiacyl ring breathing with C–O stretching. This peak was very weak in the TOL but increased in residual lignins after depolymerization possibly due to the conversion of the other subunits to the guaiacyl units. The peak at 1218 cm⁻¹ is related to ring breathing with C–O stretching of both syringyl and guaiacyl structures. It was not clear why the peak intensity of the NiMo/Al₂O₃ derived

sample was much weaker compared to those of other samples. The peak at $\sim 1150\text{ cm}^{-1}$ is associated with the C–O–C antisymmetric bridge stretching vibration in cellulose and hemicelluloses. The low peak intensities in all the residual lignin samples indicated a very low content of carbohydrates. The peaks at $\sim 1118\text{ cm}^{-1}$ and $\sim 1124\text{ cm}^{-1}$ are assigned to aromatic C–H in-plane deformation of syringyl units. These peak intensities of the NiMo/Al₂O₃ derived sample are weaker. For each of the spectrum, the ratio of the peak area associated with the *p*-hydroxyphenyl propane units at 1161 cm^{-1} to that of the syringyl units at 1124 cm^{-1} , an indication of the relative proportion of the *p*-hydroxyphenyl propane units, was in the order of CoP₂O₆ > β -CaP₂O₆ > NiMo/Al₂O₃ = no catalyst > TOL. In summary, some of the characteristics syringyl peaks were reduced in intensity with the residual lignin obtained with NiMo/Al₂O₃, possibly due to the conversion of syringyl subunits to 4-hydroxy-3,5-dimethoxy-benzaldehyde and 1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone in the aqueous phase (Table 1).

β -CaP₂O₆ catalyst was used to evaluate the effect of temperature on lignin depolymerization in the water solvent system. The highest syringol yield (9.77%) in the aqueous fraction was achieved at 300 °C, while the highest syringol yield (4.95%) in residual lignin fraction was achieved at 350 °C (Table 2). The total syringol yields at 300 °C and 350 °C were similar, 13.82% and 13.77% respectively. However, the solid residue fraction was negligible at 300 °C whereas it was 6.00% at 350 °C (Figure 2). The syringol content in aqueous phase was the highest at 250 °C and decreased thereafter (Supplementary Figure 5) due to the formation of higher proportions of other monomers (Table 2).

Previous studies have shown that alcohol-water solvent could improve lignin depolymerization^{2, 11} possibly due to increased lignin solubility and therefore decreased mass diffusion limitation. In this study, depolymerization of lignin was also investigated in a

methanol-water (50/50, wt/wt) solvent system. Depolymerization was conducted in the presence of β -CaP₂O₆ at 300 °C for 1 h. As shown in Figure 2, the proportion of aqueous fraction formed with methanol/water is 11.20%, higher than that (6.29%) with water. The solid residue content was negligible and similar to that with water. However, the syringol content in aqueous fraction with methanol/water is 45.70%, 18.70% lower than that with water (Supplementary Figure 5), indicating the production of other undetected water soluble lignin depolymerization products. The syringol contents in the aqueous phase and the lignin residue obtained at 300 °C for the methanol water mixture were 5.12% and 11.55%, respectively, leading to a total of 16.67% (Table 2).

A number of heterogeneous catalysts (*e.g.*, supported metal catalysts such as Pd, Pt, Ru, Ni, Co-Mo, and Ni-Mo supported on C, Al₂O₃, and SiO₂-Al₂O₃) have been used for the depolymerization of lignins as summarized in a review paper.¹ In one of these studies, a maximum guaiacol yield of 10% was achieved from lignosulfonate with Ni/C at 200 °C via hydrogenolysis, followed by a guaiacol yield of 4.7% from Kraft spruce lignin with Pd-Nafion SAC in aqueous formic acid solution at 300 °C.¹² Guaiacol and syringol derivatives were also obtained in previous studies, which included 4-propylguaiacol (7.8%) and 4-methylguaiacol (5.0%) from organosolv switchgrass lignin with Pt/C in the mixture of formic acid and ethanol solution via hydrodeoxygenation at 350 °C¹³ and higher yields of propenylguaiacol (12%) and propenylsyringol (36%) from with Ni/C in alcohol via a hydrogenolysis process.¹⁴ Other phenols such as pyrocatechol and resorcinol were also obtained in these studies but the yields of these products were generally low, less than 5.0%.¹ These studies indicated that these types of catalysts are able to selectively produce monolignol derivatives from lignin. Although in the present study, the total syringol yield of 16.7% was lower than that reported in our previous study with SBA-15 catalyst,² it is worth noting that the β -CaP₂O₆ catalyst, is of lower cost than the SBA-15 catalyst. The results

indicated that the β -CaP₂O₆ catalyst is more selective towards syringol formation as only smaller proportions of other phenolic compounds are produced relative to the SBA-15 catalyst. The β -CaP₂O₆ catalyst can be readily recovered by calcination of the solid residue in air. However, it should be noted that while the recyclability and the structure of the catalysts after depolymerization were not studied in the present study, the post-reaction pH of the aqueous phase dropped to pH 5.5, an indication of catalyst deactivation. From our previous study on glucose conversion to HMF, ⁶ Ca leaching was 8.4%, though under more severe conditions than the present study.

In summary, the study demonstrated that β -CaP₂O₆ did produce reasonable yields of syringol from lignin. Preliminary results showed that reaction temperature and the type of solvent system had impacts on the yield of syringol produced from eucalyptus wood lignin. It is recommended future studies should be focused on the catalyst recyclability, optimization of reaction conditions, and understanding the reaction mechanism.

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Legends of Tables and Figures

Tables

Table 1 Effect of catalysts on the yields of phenolic monomers at 250 °C for 1 h.

Table 2 Effect of reaction temperature and solvent on the yields of phenolic monomers with β -CaP₂O₆ catalyst.

Figures

Figure 1 Effect of catalysts on major fractions after lignin depolymerization at 250 °C for 1 h.

Figure 2 Effect of reaction temperature and solvent on major fractions after lignin depolymerization with β -CaP₂O₆ catalyst.

Table 1

Catalysts	Monomers in aqueous phase (%)				Syringol in residual lignin (%)	Total syringol (%)
	Syringol	1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone	4-Hydroxy-3,5-dimethoxy-benzaldehyde	Benzoic acid		
No catalyst	1.32	2.55	-	-	0.53	1.85
CoP ₂ O ₆	3.79	0.05	-	2.09	2.88	6.67
β-CaP ₂ O ₆	4.88	0.55	-	-	3.59	8.47
Sulfided NiM _o /Al ₂ O ₃	2.45	0.47	0.09	2.11	3.51	5.96

Table 2

T (°C)	Monomers in aqueous phase (%)						Syringol in residual lignin (%)	Total syringol (%)
	Syringol	1-(4-Hydroxy-3,5- dimethoxyphenyl)- ethanone	Butylated hydroxytoluene	4-Hydroxy- 3,5- dimethoxy- benzaldehyde	1-(2,4,6- Trihydroxy-3- methylphenyl)- 1-butanone	Benzoic acid		
200	0.11	-	-	-	-	-	0.09	0.20
250	4.88	0.55	-	-	-	-	3.59	8.47
300	4.05	-	-	-	-	1.30	9.77	13.82
350	4.95	0.25	0.5	-	0.44	0.22	8.62	13.57
300 (Methanol/water)	5.12	-	-	-	-	0.55	11.55	16.67

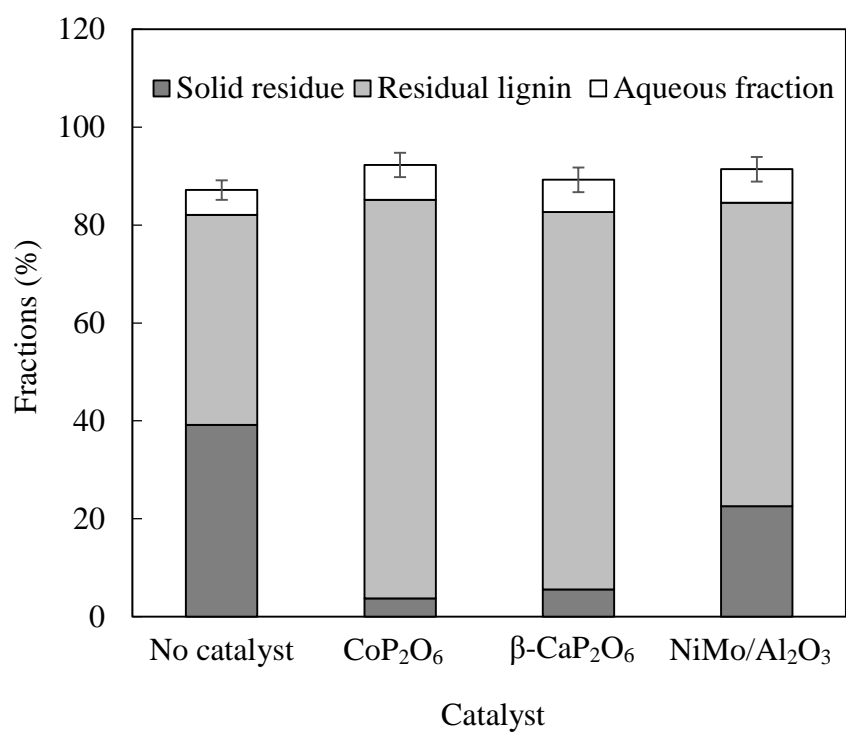


Figure 1

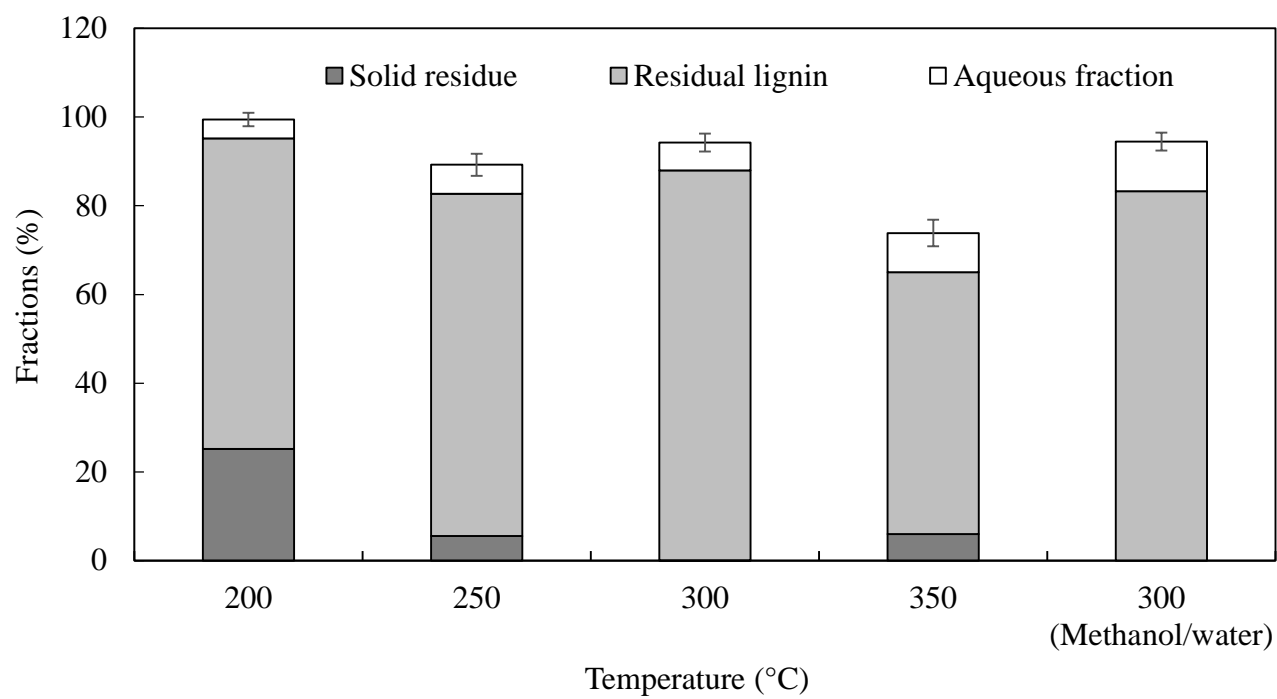


Figure 2