

Co(salen) catalysed oxidation of synthetic lignin-like polymer: NaOH effects

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An attempt has been made to selectively oxidise synthetic lignin-like polymer for fine chemicals. The G- and S-type polymers (G- and S- type lignin model polymers) were synthesized using simple aromatic compounds as starting materials and then oxidised to benzaldehydes by reacting them with Co(salen) catalytic system. The reaction was characterized by measuring the change of the polymer with FTIR, C-13 NMR and GC-MS spectroscopy. The results obtained by the FTIR and C-13 NMR showed that the effects of NaOH were important and higher yield of benzaldehydes characterized by GC-MS in the presence of NaOH in the course of catalytic oxidation of the polymer demonstrated these effects. From the results, the catalyst could suitably be used in green procedures for lignin transformation.

Keywords: Co(salen), catalyst, catalytic oxidation, lignin model polymer, NaOH effect, FTIR, C-13 NMR, GC-MS.

INTRODUCTION

Co(II)-salen is a four-coordinate complex that readily adds ligands to become five or six-coordinate. The remarkable feature of the structure is a capability to form four bonds with a metal ion using two phenol hydroxyls and unshared electrons pairs of two imino nitrogens. They can form cobalt-superoxo complexes and dimeric peroxy complexes upon exposure to molecular oxygen or H₂O₂ (Fig. 1)¹⁻³. This complex is relatively easy to prepare, cheap, stable in water and small in size, and a variety of its derivatives have been widely used as catalysts for various oxidation reactions. The first example of the use of Co(salen) to catalyse phenol oxidation with dioxygen was published in 1967⁴⁻⁸.

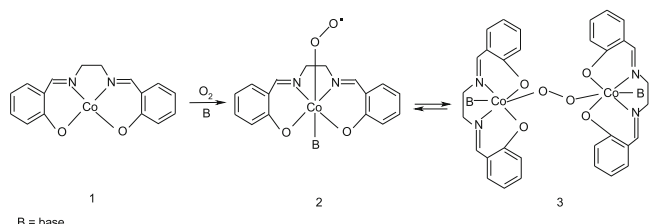


Figure 1. Co(II)-salen exists in two different forms

These complexes can catalyze the oxidation of substrates that serve as models for lignin phenolic subunits. In particular it was demonstrated that they were able to oxidize lignin model compounds in high yields. Arylglycerol- β -aryl ethers, phenylcoumarans and apocynol showed very high conversion values within 30 min in catalytic oxidation⁹⁻¹¹. A series of biomimetic oxidation of lignin and lignin model compounds using Co(salen) have been successfully studied in our laboratory¹²⁻¹⁴. From this and related studies, the oxidation occurs selectively in all experiments and the high catalytic activity was reached with the complex. Co(salen)-catalysed oxidations appear to allow the creation of high-value products to extend the role of lignin for future applications.

In this paper Co(salen) was used for further studies on the reactions of lignin model polymer in catalytic oxidation and the NaOH effect in catalytic system was

illustrated. Synthetic lignin-like polymer was chosen as the model substrate for this study because it is more able to resemble natural lignin in structure. Model polymer studies in lignin are important as they can enlighten the mechanism of the catalytic reaction¹⁷⁻¹⁹.

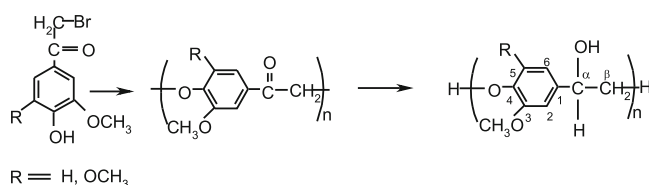
EXPERIMENTAL

Co(salen) synthesis

Co(salen) was prepared according to the published literature⁴. The salen (N, N-bis(salicylaldehyde ethylenediamine) was prepared in 88% yield by condensation reactions of ethylenediamine with salicylaldehyde in methanol. The cobalt complex, Co(salen), was synthesised from the salen and a slight excess of (CH₃CO-O)₂Co · 4H₂O in refluxing CH₃OH.

Synthesis of lignin model polymer

Lignin model polymers composed of only the β -O-4 structure were prepared using simple aromatic compounds as starting materials referring to the methods of Kishimoto et al.¹⁷ (Scheme 1). The commercially available 4-hydroxy-3-methoxy-acetophenone (guaiaacyl type, G-type), 4-hydroxy-3, 5-dimethoxyacetophenone (syringyl type, S-type) was dissolved in anhydrous 1,4-dioxane-diethyl ether (3 : 4, v/v). The mixture was added bromine, then kept at 0 for 1 h to obtain the bromide. Adding K₂CO₃ as the catalyst, the bromide was dissolved in anhydrous DMF, stirred under nitrogen at 50 for 3 h, and polymerized to the given polymer. The given polymer was reduced with NaBH₄ in DMSO to obtain the G- and S-type lignin model polymer. The molecular weight (Mw) of the polymer was determined by gel permeation chromatography (GPC). The Mw of G-type polymer was 5753, and the value of S-type polymer was 7501. The Mw of the polymer was comparable to that of technical lignin. The chemical structure of the polymer was characterized by FTIR and ¹³C-NMR.



Scheme 1. Synthesis of S- and G- type lignin model polymer

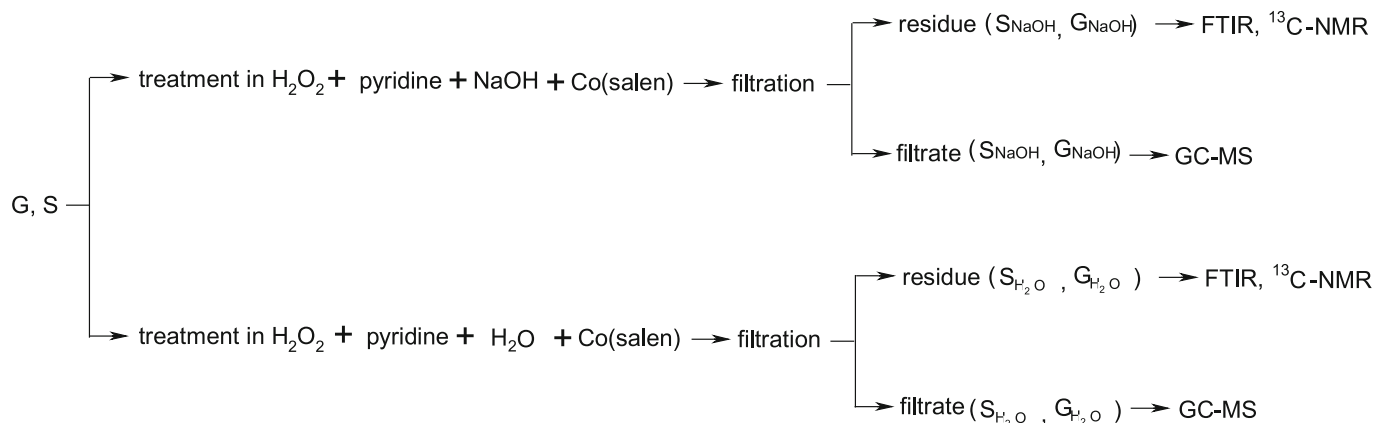


Figure 2. Programmable route of experiment

Catalytic experiments

As shown in Figure 2, the standard procedure was to dissolve the lignin model polymer (30 mg), hydrogen peroxide (0.6 mL, 30%) and pyridine (0.96 mL, 0.5g · L⁻¹) in water (10 mL) and adjust the pH with 0.9 mg NaOH (pH ~12). After that the Co(salen) (4.0 mL, 0.5g · L⁻¹) was added. The reaction flask was evacuated and the ambient pressure oxygen (≥99.5%) was bubbled constantly through the solution at a rate (2.5 cm³/min) low enough to avoid evaporation of the solvent. The mixture was then stirred at 90 for 1 h. The reaction was stopped by cooling the solution to ambient temperature, after which the reaction mixture was filtered with fritted glass filter. The final residue (S_{NaOH}, G_{NaOH}) was collected for FTIR and ¹³C-NMR analysis. The pH of the filtrate was adjusted to 12 with 2M NaOH and soluble organic products were extracted with methylene dichloride. The organic phase was separated and the residual filtrate was adjusted to pH 2 with 2M HCl and soluble organic products were similarly extracted. The two organic phases were merged, dried with sodium sulphate, filtered and finally concentrated to 1mL for analysis of reaction product with GC-MS (S_{NaOH}, G_{NaOH}).

In addition, NaOH was replaced with water to evaluate the NaOH effect in catalytic reaction.

FTIR

FTIR spectra of lignin model polymer (S, G) and residual polymer (S_{NaOH}, G_{NaOH}) were obtained on a Bruker Tensor 27 spectrophotometer using KBr pellets in wavelength bands from 4000 to 400 cm⁻¹.

C-13 NMR spectrometry

All ¹³C-NMR spectra were recorded under quantitative conditions, which were accomplished by using a pulse sequence (inverse-gated) that eliminated the nuclear overhauser effect (NOE) and had a sufficiently long pulse delay, allowing for all nuclei to be fully relaxed before the next pulse. The pulse delay commonly used

for lignin, which had been established and verified in the literature was 10 seconds²⁰.

Samples were dissolved in d₆-DMSO and the spectra were recorded on Bruker DRX 500 apparatus at 318 K with TMS as internal reference (δ 0.00) in a 5 mm diameter tube. Some of the acquisition parameters used during the recording of the spectra included 9–15 k number of acquisitions, 90° pulse width (pl = 8 usec, pl 1 = 1.00 db), 222 ppm sweep width, and a 10-second pulse delay. The total acquisition time for recording each spectrum was typically quite long, ranging from 24 to 36 hours. During processing, a line broadening of 10.0 Hz was used to obtain acceptable line widths.

GC-MS

Separation and identification of oxidation products were performed using gas chromatography-mass spectrometry (GC-MS) with a Agilent Technologies HP 6890/ 5973 system fitted with a fused silica column (HP-INNOWAX, 30 m × 0.25 mm i.d., 0.25 μm film thickness). Each sample was injected into a deactivated glass liner inserted into the GC injection port and using He as the carrier gas (1.0 mL min⁻¹). The GC oven was programmed from 80 (with a 5 min initial delay) to 290 (held 40 min) using a 4 min⁻¹ temperature ramp. The GC injector and GC-MS interface were maintained at 290. The mass spectrometer was operated in the electron ionization mode (EI, 50 eV). Compound identification was performed using GC retention times and by Mainlib database.

RESULTS AND DISCUSSION

Lignin model polymers were degraded during the catalytic oxidation. According to Figure 3 and Figure 4, the β-O-4 linkage was cleaved, aromatic ring was opened, and the side chain was oxidized. In these cases the lignin model polymers were oxidized, yielding benzaldehydes as the main products with good selectivity (Fig. 5, 7.2 min) and sometimes more exotic products were obtained, such as quinone compounds (Fig. 5, 24.0 min)²¹. In the

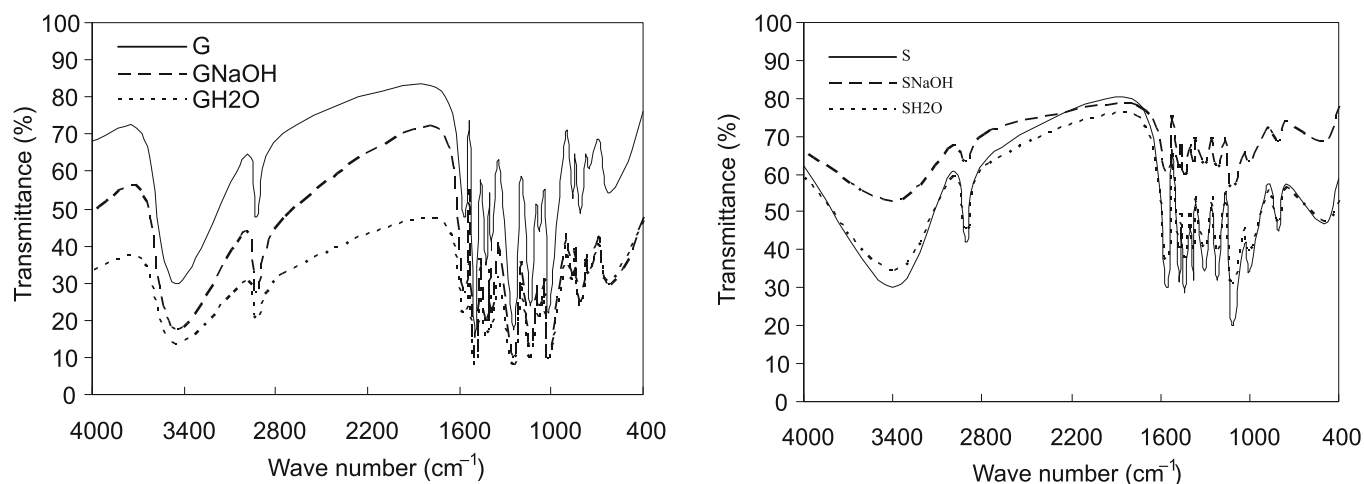


Figure 3. FTIR spectra of lignin model polymer. 1135 cm^{-1} , β -O-4; 1250 cm^{-1} , OH; 1423 cm^{-1} , ph-OH; 1500 cm^{-1} , Ar-; 2923 cm^{-1} , CH_3O^-

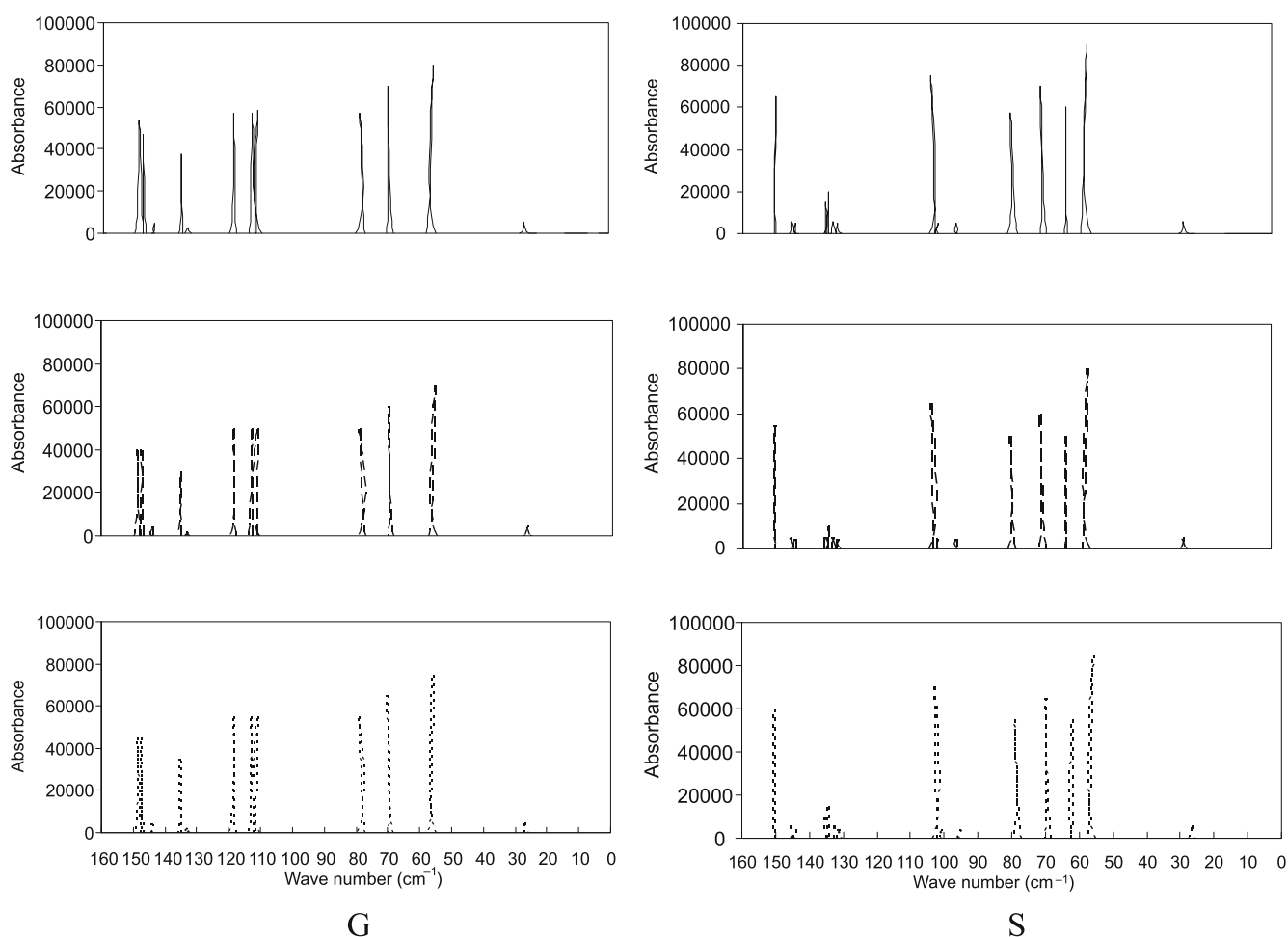


Figure 4. C-13 NMR spectra of lignin model polymer. G: 26.7 ppm, $\text{CH}_3(\beta^-)$, non-phenolic end units; 55.7 ppm, CH_3O^- ; 70.2 ppm, C_{α^-} ; 80.1 ppm, C_{β^-} ; 111 ppm, C_2^- ; 113 ppm, C_5^- ; 118.6 ppm, C_6^- ; 133 ppm, $\text{C}_{1,4,7}^-$, phenolic end units; 135.2 ppm, C_1^- ; 144 ppm, $\text{C}_{4,7}^-$, phenolic end units; 147.4 ppm, C_4^- ; 148.6 ppm, C_3^- . S: 26.7 ppm, $\text{CH}_3(\beta^-)$, non-phenolic end units; 55.7 ppm, CH_3O^- ; 62.2 ppm, C_{α^-} , non-phenolic end units; 70 ppm, C_{α^-} ; 79 ppm, C_{β^-} ; 95.4 ppm, C_6^- , non-phenolic end units; 101 ppm, C_2^- , non-phenolic end units; 103 ppm, $\text{C}_{2,6}^-$; 131.2 ppm, $\text{C}_{1,7}^-$; 132.7 ppm, $\text{C}_{4,7}^-$; 134.3 ppm, C_4^- ; 135.1 ppm, C_1^- ; 144.2 ppm, C_1^- , non-phenolic end units; 145.5 ppm, $\text{C}_{3,5,7}^-$; 150.2 ppm, $\text{C}_{3,5}^-$

mechanistic studies by our group based on spectrometry¹³, it was suggested that the mechanism involves the initial formation of a superoxo complex, which performs a two electron oxidation of the substrate. A radical superoxo complex abstracts the phenolic hydrogen atom to produce phenoxy radical, which is then reacted with another superoxo complex (Scheme 2). Similar step was

observed in the oxidation of benzylic alcohols catalysed by the copper enzyme galactose oxidase^{22, 23}.

The structure of the substrate had a crucial effect on the outcome of the reaction, as seen from Figure 3 to Figure 5. Under identical conditions, S-lignin model polymer yielded smaller amounts of oxidation products, probably because of the more stable property of the S-polymer towards destruction by H_2O_2 . Another reason was the

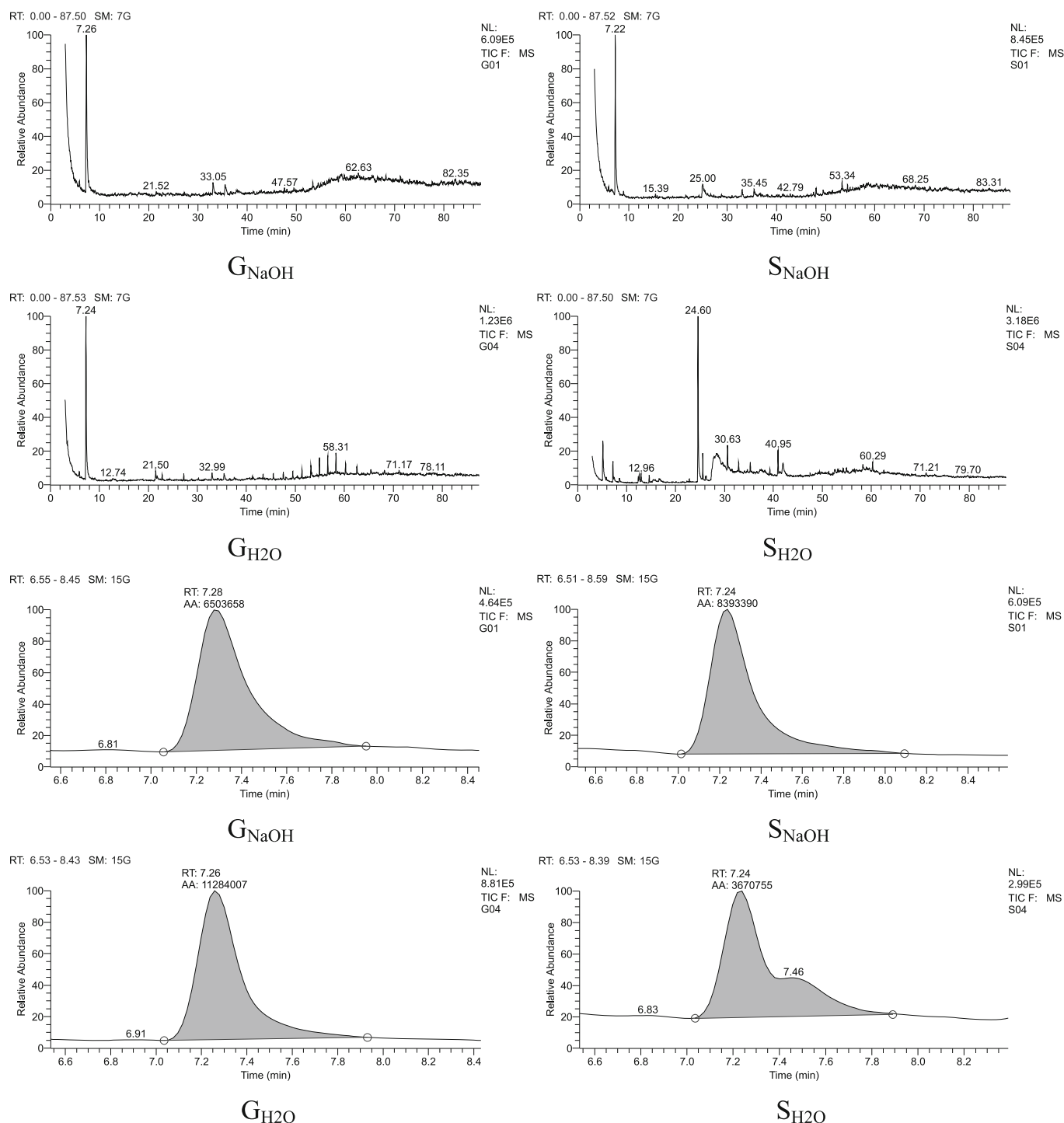
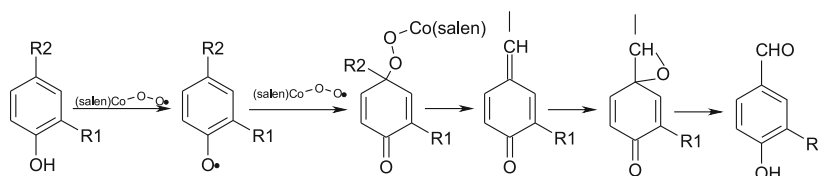


Figure 5. Total ion chromatograms of S and G sample for GC-MS detection



Scheme 2. Postulated mechanism of phenol oxidation reactions catalysed by Co(salen)

explanation that phenoxyl radical was generated in a lower concentration when the second electron donative CH_3O -group was introduced into the ring^{24, 25}.

The state of the coordinated oxygen species of Co(salen) complex influences the reactivity of the complex depending on the structure of the ligand and reaction conditions. The less reactive binuclear, bridged peroxy complex is favoured in the equilibrium solution of

Co(salen) oxygen adducts, but the equilibrium can be shifted towards the more catalytically active mononuclear superoxo complex by tuning the reaction conditions. There was need for addition of NaOH as OH^- evidently acted on the state of Co(salen) complex. With addition of NaOH, as lignin model polymers there were weaker signals of the corresponding structures in FTIR (Fig. 3) and C-13 NMR spectra (Figure 4). Comparison of the

spectra of G_{NaOH} and $G_{\text{H}_2\text{O}}$ indicated that after addition of NaOH, the peaks at 1135 cm^{-1} (β -O-4), 1250 cm^{-1} (OH), 1423 cm^{-1} (ph-OH), 1500 cm^{-1} (Ar-) in FTIR spectra were decreased, and the signals of the band between 0 and 160 ppm in C-13 NMR spectra were weakened; while as products there were stronger signals of the corresponding benzaldehydes in GC-MS spectra (Fig. 5). These results confirmed that NaOH is an important component of the reaction system for Co(salen) catalyzed-oxidation of lignin model polymer. This is because, in aqueous solutions, a hydroxide anion acts as an axial ligand that facilitates coordination with oxygen^{26,27}. In a study of the oxidation of 3,4-dimethoxybenzyl alcohol in aqueous alkaline media using Co(sulfosalen) as catalyst, Sippola and Krause²⁸ found that at higher pH, more of the phenolic OH groups were deprotonated to more easily oxidised phenolates, which is another reason for the more easily degradation of lignin model polymer by Co(salen) when NaOH was added to the reaction system.

CONCLUSION

The substituents CH_3O - on the ring of lignin model polymer seem to have an important role in catalytic oxidation by Co(salen) as catalyst. S-lignin model polymer with two CH_3O -substituents is more stable than G-lignin model polymer with one CH_3O -substituent. The observed variations in catalytic activity can be caused by addition of NaOH. By adding NaOH catalytic activity can be increased. This is also supported by the fact that after addition of NaOH, as lignin model polymers there were weaker signals of the corresponding structures in FTIR, C-13 NMR spectra, while as products there were stronger signals of the corresponding benzaldehydes in GC-MS spectra.

This is first trial to study for NaOH effects generated in Co(salen) catalysed oxidation using synthetic lignin-like polymer as substrate, in respect to catalytic activity. Based upon this study, the addition of NaOH can be expected to increase catalytic activity of Co(salen). However, in this study the catalyst was used in homogeneous medium under very basic condition, hence further intensive research on reusability of the catalyst and use of low alkali should be considered.

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