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## **CATALYTIC CONVERSION OF KRAFT LIGNIN USING PAPER-LIKE CO(SALEN) AS AN EFFECTIVE CATALYST**

*Co(salen) powders were homogeneously scattered over a ceramic fibre network to give a catalyst paper and the Co(salen) paper was tested for the oxidative degradation of a kraft lignin using H<sub>2</sub>O<sub>2</sub> as an oxidant. Due to the structural effect of the interconnected 3D-network, the catalyst paper exhibited a higher performance in the oxidation of kraft lignin with a oil yield of 23.27 % than the original Co(salen) powder with an oil yield of 10.63 %, along with excellent recycling performance. 2,6-Dimethoxyphenol (2.32 mg/kg kraft lignin), vanillin (3.80 mg/kg kraft lignin), and syringaldehyde (2.63 mg/kg kraft lignin) were found to be the main products in the oil obtained. In addition, the structural changes in the kraft lignin were also studied during the process. The phenolic compounds were formed through side chain oxidation together with the oxidative cleavage of  $\beta$ -O-4 linkage.*

**Keywords:** kraft lignin, Co(salen), catalyst paper, phenolic compounds

### **Introduction**

Kraft lignin is a major by-product of the conversion of lignocellulosics to pulp in the kraft process. It can be used for the production of high value-added chemicals [Santos et al. 2014]. However, due to its complex structure, some novel catalysts were used in order to oxidise kraft lignin, including

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organometallic catalysis, biomimetic catalysis and plasma oxidation [Bozell 2014].

As an important class of organometallic compounds, salen complexes can be used as catalysts in lignin oxidation. Their advantages include simple, easy and economic synthesis and remarkable biomimetic performances [Hurisso, Singer 2013]. As reported in the literature, lignin model compounds with  $\beta$ -O-4 linkage, including phenolic and non-phenolic models, were selectively and effectively degraded by the Co(salen)/O<sub>2</sub> system [Rajagopalan et al. 2008; Cedeno, Bozell 2012; Haikarainen 2005; Zhang et al. 2015]. Similarly, Badamali et al. reported that the Co(salen) supported in SBA-15 could be a more effective biomimetic catalyst for selective oxidation of lignin than neat Co(salen) [Badamali et al. 2011]. Previous work has indicated that zeolite-encapsulation of M(salen) facilitated the stability of M(salen) to enhance the activity of the catalyst in the degradation of lignin [Zhang, Zhou 2012; Zhou 2014a, b, c]. In this case, the degradation efficiency of the lignin depends on the accessibility of the target molecules to the supercages of the catalyst. For this reason, due to the poor accessibility of encapsulated M(salen) and the complex structure of lignin, a more effective process for the immobilisation of M(salen) is clearly needed to reduce spatial restrictions upon the target molecules entering the pores [Bayne et al. 2013].

In recent years, catalyst paper has been used in many reactions to make a structured catalyst. Bortolozzi et al. reported novel catalytic ceramic papers applied to the oxidative dehydrogenation of ethane, showing very high activity for the reaction [Bortolozzi et al. 2013], and Homma and Kitaoka reported that porous paper composites containing ruthenium hydroxide showed significantly higher reactivity than conventional catalysts in catalytic alcohol oxidation [Homma, Kitaoka 2014]. Hence, in this study, catalyst paper composed of ceramic fibre and Co(salen) was prepared using a papermaking technique, and its catalytic performance and stability were tested in the oxidation of kraft lignin with hydrogen peroxide as an oxidant.

## Materials and methods

### Kraft lignin

Kraft lignin was supplied by the Research Center of Pulp and Paper Engineering of Kunming University of Science and Technology (China). The kraft lignin was produced by the kraft pulping of bamboo (*D. brandisii*) using NaOH and Na<sub>2</sub>S. The kraft lignin was purified in the following way in order to obtain a pure sample: heating in 80% dioxane containing 0.05 M HCl, filtering, washing with 80% dioxane, collecting filtrates, neutralizing with solid NaHCO<sub>3</sub>, evaporating under reduced pressure, adding acidic deionised water (pH 2), centrifuging,

freeze-drying the precipitate, washing with methylene chloride, and then drying under a vacuum. The kraft lignin possessed the following composition after purifying: acid insoluble lignin 87.02%, acid soluble lignin 3.12% (purity 91%), total sugars 3.32% and ash content 5.35%.

### Preparation of catalyst paper

Co(salen) was prepared according to the method described in the literature [Cozzi 2004] with minor modifications, and pulverized into powder with 100 mesh-pass size.

The catalyst paper composing ceramic fibre and Co(salen) was prepared using a papermaking technique. A ceramic fibre suspension (79.82 wt%  $\text{Al}_2\text{O}_3$ , 19.78 wt%  $\text{SiO}_2$ , with an average length of ca. 0.5 mm) containing 0.4g Co(salen) powder was vigorously mixed with 0.1 g polydiallyldimethylammonium chloride (PDADMAC), 5.0 g alumina sol and 0.1 g anionic polyacrylamide (A-PAM). The pulp fibre suspension containing 0.5 g bleached hardwood kraft pulp (400ml CSF) was added to the mixture. The final concentration for papermaking was 0.5 w/v%, handsheets were then prepared according to the TAPPI Test Method T205. The wet sheets were dried at 105°C for 1h, pressed at 350 kPa for 5 min, and calcined at 350°C for 12 h to remove the pulp fibres.

An ICP-AES (PerkinElmer Optima 8300 apparatus, USA) was used to determine the cobalt content in the catalyst paper after acidification of the sample using nitric acid.

Mercury intrusion analysis was carried out using a Pore-master 33P (YUASA IONICS Co. Ltd) to determine the pore diameter and surface area of the catalyst papers.

XRD patterns were recorded on a Rigaku Dmax X-ray diffractometer (Nifiltered,  $\text{CuK}\alpha$  radiation).

DR UV-Vis spectra were obtained in the range of 200–800 nm on a PerkinElmer Lambda Bio40 spectrophotometer equipped with an integration sphere.

### Kraft lignin oxidation test

According to previous studies on salen complexes [Zhang, Zhou 2012; Zhou 2014a, b, c], the following oxidation conditions were used in this study. Kraft lignin (1.0 g), the catalyst (0.2 g) and 30%  $\text{H}_2\text{O}_2$  (1.0 g) were used, with 100 mL deionised water also added to the mixture in this study. A reaction was performed at 130°C for 0.5 h in a batch reactor equipped with a condenser with constant stirring. After the reaction, the catalyst paper was washed with secondary deionised water and dried for recycling tests. The mixture was

separated by filtration to obtain solid and liquid products. The solid products were dissolved in tetrahydrofuran (THF), and filtered. Residual lignin dissolved in the THF was recovered by vacuum drying for HSQC NMR analysis. The liquid products were obtained through extraction using ethyl acetate, and vacuum dried to obtain an oil.

A blank experiment (without a catalyst) was carried out as the control experiment.

Parallel experiments were also repeated at least three times to ensure the test's reliability.

The oil yield was calculated gravimetrically (oil/kraft lignin, %).

Identification of the compounds in the oils was performed on an Agilent HP6890-5973 GC-MS, equipped with a quartz capillary column (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas. The temperature started at 50°C, then increased to 280°C at 10°C/min (and held for 5 min at this temperature). Compounds were identified by comparing them to authentic samples and the database. A quantitative analysis of the oil components was carried out using a GC-FID under the same conditions as GC-MS, using the external standard method, as it is simple to use and easy to calculate.

The lignin samples (80 mg of the sample in 0.5 ml of DMSO-*d*<sub>6</sub>) were characterised using 2D HSQC NMR on a Bruker AV 600 MHz NMR spectrometer (Germany) to obtain the structural changes in the conversion of the kraft lignin. HSQC spectra were recorded using the Bruker standard pulse program. All chemical shift values were recorded in ppm relative to TMS [tetramethylsilane]. The solvent peak was used as the internal reference.

The molecular weight of the acetylated kraft lignin and residual kraft lignin were determined using GPC with an HPLC Waters 244 equipped with Sephadex LH 60 gel columns. Determination was performed at 280 nm using a Beckman UV detector. Polystyrene samples with various molecular weights were used for calibration.

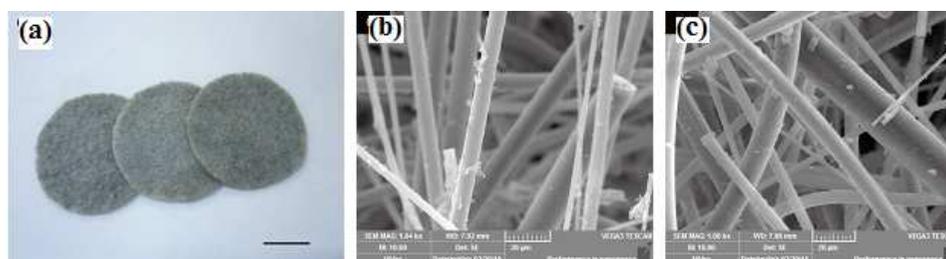
## Results and discussion

### Characterisation of catalyst paper

The white of the pulp changed to the grey of catalyst paper after the treatment, thus confirming the successful preparation of the paper using a typical papermaking procedure. As depicted in figure 1a, the appearance of the catalyst paper was similar to cardboard material and the Co(salen) in the sheets was easy to handle and recover compared to the original Co(salen) in powders. The PDADMAC and APAM improved the retention of the Co(salen) powders in the sheets, thanks to the flocculation mechanism involved in adsorbing, bridging

effect, [ZakrajSek 2014]. Besides, after the pulp fibres were thermally removed, the physical strength of the catalyst paper was achieved through binder treatment using alumina sol, as the ceramic fibre, unlike pulp fibre, has no interfibre bonds [Koga et al. 2010].

In addition, the fibre network structure (fig. 1b) significantly increased the pore size of the catalyst paper (16.20  $\mu\text{m}$ ) (table 1) compared to Co(salen)/NaY (2.30 nm) [Zhou 2014c], which is important for the accessibility of the reactants to the catalyst [Mlekodaj et al. 2014]. The cobalt content of the catalyst paper was also maintained at a high level (8.2 %) compared to the Co(salen)/NaY ( $\sim$  2.3 %) [Zhou 2014c]. In any case, as indicated by the data from the ICP and EDX analysis, some Co(salen) particles were believed to have been deposited on the external surface of the catalyst paper. Other supported catalysts also showed similar results [Pineda et al. 2012; Pineda et al. 2011].



**Fig. 1.** Optical image of the catalyst paper (a), SEM image of the fresh catalyst paper (b), and the reused catalyst paper (c)

**Table 1.** Metal content and textural properties of various catalysts

Sample	Metal content		Textural properties		
	ICP [wt%]	EDX [wt%]	$S_{\text{BET}}$ [ $\text{m}^2 \text{g}^{-1}$ ]	Pore volume [ $\text{mL g}^{-1}$ ]	Pore diameter [ $\mu\text{m}$ ]
Ceramic fibre paper	–	–	4262470	4118	36.47
Co(salen)	18.33	–	–	–	–
Co(salen)/CP	8.20	2.32	2464543	2448	16.20
Co(salen)/CP-reused	8.07	2.06	2464337	2427	16.12

As expected from the XRD patterns, the Co(salen) powder in the pores of the support decreased the peak intensity in the XRD diagrams. Some additional diffraction peaks were observed up to  $60^\circ 2\theta$ , considered an indicator of the external deposition of the Co(salen) powder (fig. 2). However, the structure of the support framework remained during the sorption/desorption process, as shown in the XRD patterns [Sagiri et al. 2014].

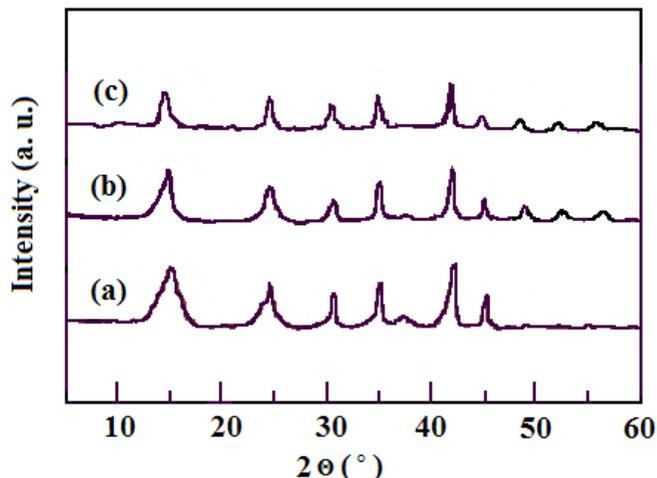


Fig. 2. XRD spectra of (a) ceramic fibrr paper, (b) Co(salen)/CP, (c) reused Co(salen)/CP

In the DR UV-vis spectra (fig. 3), all the samples showed characteristic bands in the 220–420 nm and 420–680 nm range, corresponding to charge-transfer and d-d transitions, respectively. After introducing Co(salen) into the ceramic fibre paper, a blue shift was observed due to the interaction between the support and the Co(salen). The spectra retained their original shape in comparison, confirming that the Co(salen) was successfully introduced into the ceramic fibre paper [Poltowicz et al. 2006].

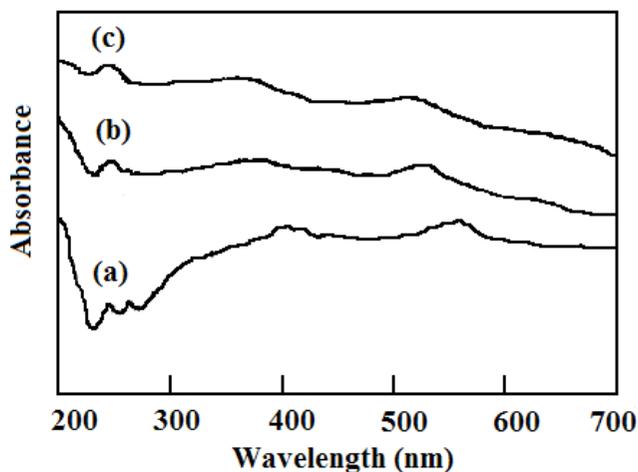
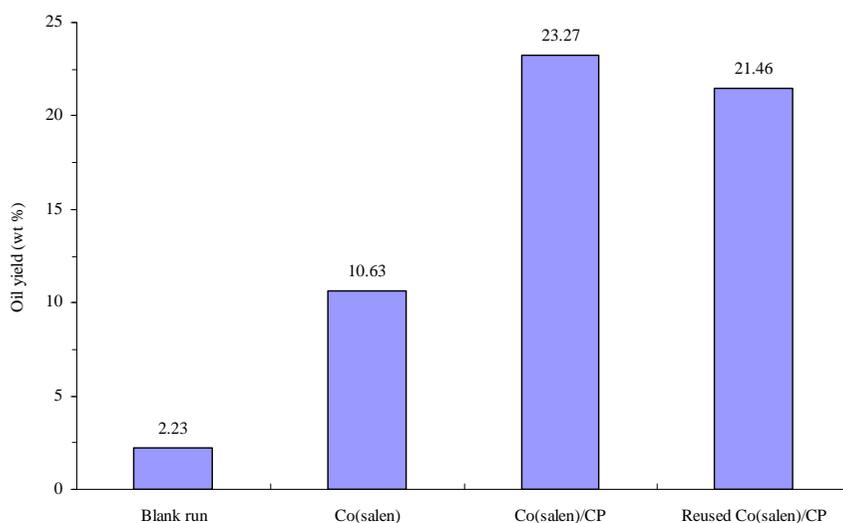


Fig. 3. DR UV-vis spectra of (a) Co(salen), (b) Co(salen)/CP; (c) reused Co(salen)/CP

### Catalytic oxidation of kraft lignin

Figure 4 shows the oil yields from the oxidation of the kraft lignin using different catalysts. The catalytic effects clearly depended on the catalysts used. The Co(salen)/CP showed the highest oil yield (23.27 wt%), which was twice as high as the oil yield obtained by the Co(salen). This means, therefore, that the oil yield obtained by the catalyst paper was relatively high compared to earlier reported results [Erdocia et al. 2014; Toledano et al. 2012; Zhou 2014b]. The larger pore sizes of the catalyst paper, giving high accessibility, may be the reason for this improved catalytic performance.



**Fig. 4.** Oil yield (oil/kraft lignin, %)

Oxidation of the kraft lignin gave the main compounds, 2,6-dimethoxyphenol, vanillin, syringaldehyde, as presented in table 2. Other compounds (2-methoxy-4-vinylphenol, catechol, guaiacol, 4-hydroxy-3-methoxyphenyl propanone, 4-hydroxy-3-methoxy benzeneacetic acid and 4-hydroxy-3,5-dimethoxyphenyl ethanone) in small amounts were also formed in the selective oxidation of the kraft lignin. Otherwise, the Co(salen)/CP significantly favoured the formation of these compounds, as indicated in table 2.

**Table 2. Yield of main compounds in oils (mg/g kraft lignin)**

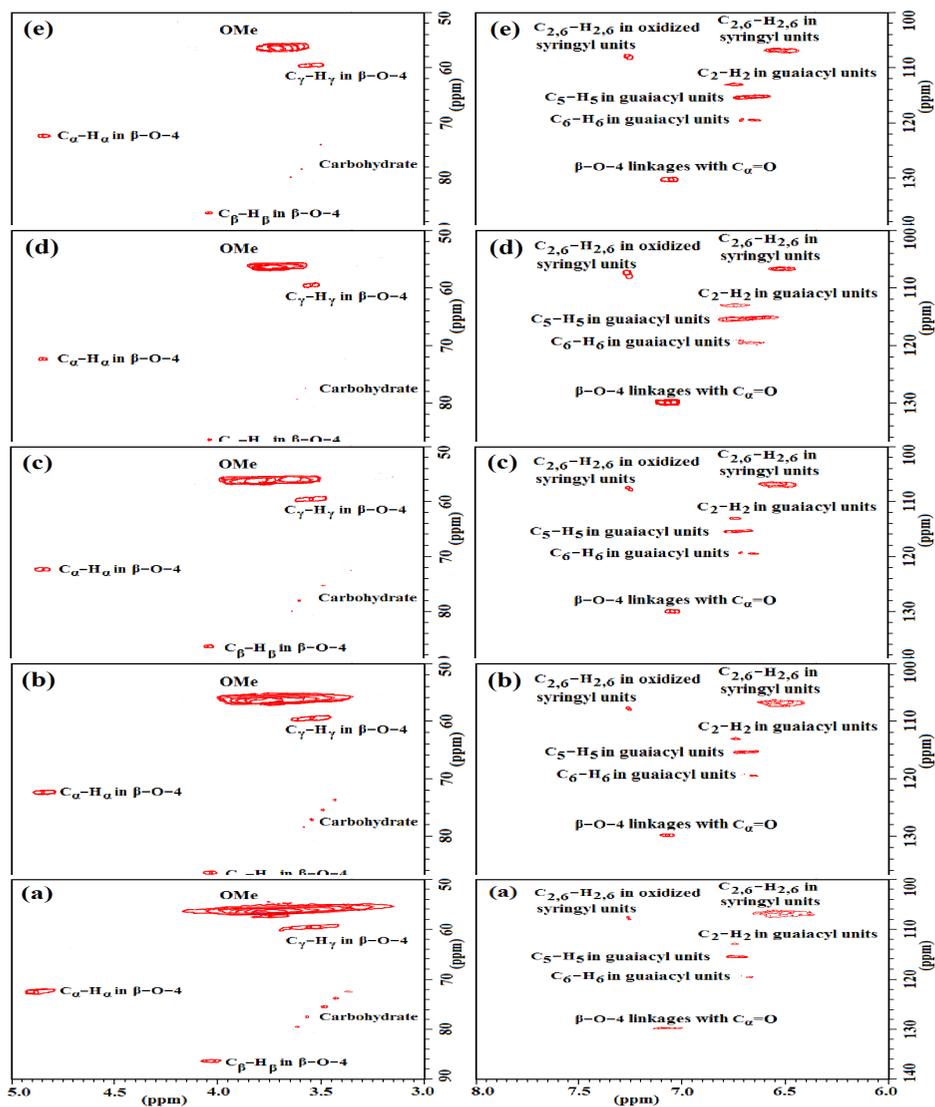
Catalyst	2,6-Dimethoxyphenol	Syringaldehyde	Vanillin
Blank run	0.16	0.18	0.31
Co(salen)	0.84	1.16	1.57
Co(salen)/CP	2.32	2.63	3.80
Co(salen)/CP-reused	2.15	2.48	3.37

The phenolic compounds were produced through side chain oxidation together with the oxidative cleavage of the  $\beta$ -O-4 linkage. In the HSQC spectra (fig. 5), a reduction in the peaks corresponding to  $C_{\alpha}$ -H $_{\alpha}$ ,  $C_{\beta}$ -H $_{\beta}$ ,  $C_{\gamma}$ -H $_{\gamma}$  in the  $\beta$ -O-4 linkage was found, and an increase in the peaks of the  $\beta$ -O-4 linkage with  $C_{\alpha}$ =O after the treatments.

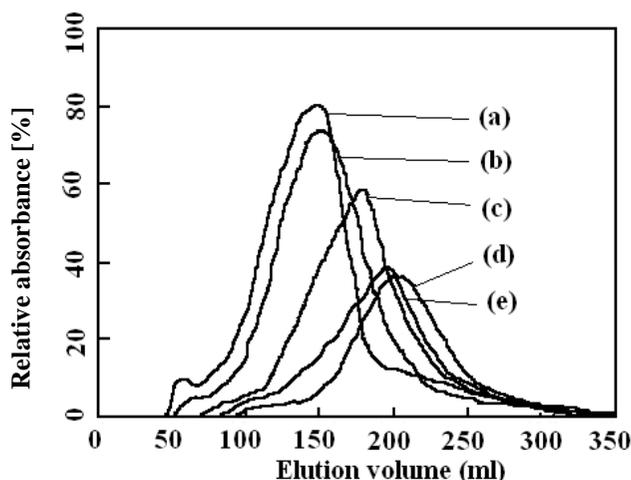
GPC analyses further confirmed changes in the structure of the kraft lignin. As shown in fig. 6, the kraft lignin was slightly degraded during the blank experiment, in which the residual kraft lignin still had a high molecular weight, while the degradation of the kraft lignin increased from the Co(salen) experiment to the Co(salen)/CP experiment. Meanwhile, the results clearly show that the kraft lignin was highly degradable by Co(salen)/CP, which was in accordance with the results as mentioned above. This is likely attributable to the fact that the  $\beta$ -O-4 linkages in the kraft lignin were further cleaved to produce more lignin fragments in the Co(salen)/CP experiment in comparison to the Co(salen) experiment.

### Reusability of catalyst paper

The catalyst paper was reused after its use in degrading the kraft lignin to test its recycling performance. According to the spectra in fig. 2c and fig. 3c, the structural integrity of the catalyst paper was relatively well retained after the first recycling, as shown by the SEM image of the reused catalyst paper (fig.1c), indicating that the catalyst paper (Co(salen)/CP) was stable and recyclable under the reaction conditions. The textura data also confirmed that only a small decrease in the pore size of the catalyst paper was observed as compared to the fresh catalyst paper (table 1). The first reuse of the Co(salen)/CP provided a similar degradation of the kraft lignin (figures 4, 5 and 6; table 2), when compared to the fresh catalyst paper. Furthermore, the catalyst paper gave most of its activity after 4 runs and may be reused up to ten times in kraft lignin oxidation.



**Fig. 5.** HSQC NMR spectra of (a) kraft lignin, (b) residual kraft lignin obtained in the blank experiment, (c) residual kraft lignin obtained in Co(salen) experiment, (d) residual kraft lignin obtained in Co(salen)/CP experiment, (e) residual kraft lignin obtained in reused Co(salen)/CP experiment



**Fig. 6.** GPC spectra of (a) kraft lignin, (b) residual kraft lignin obtained in the blank experiment, (c) residual kraft lignin obtained in Co(salen) experiment, (d) residual kraft lignin obtained in Co(salen)/CP experiment, (e) residual kraft lignin obtained in reused Co(salen)/CP experiment

## Conclusions

A paper-structured Co(salen) catalyst was successfully prepared using a papermaking method and used in the oxidation of kraft lignin, with  $\text{H}_2\text{O}_2$  as the oxidant. The catalyst paper demonstrated itself to be twice as active as the Co(salen) powders with a oil yield of 23.27 % and a phenolic compound yield of 2.32 mg 2,6-dimethoxyphenol, 2.63 mg syringaldehyde, and 3.80 mg vanillin/kg kraft lignin, which was due to the excellent porosity of the catalyst paper and a well defined paper structure, as well as the biomimetic performance of the Co(salen). In addition, reuse of the catalyst paper caused similar degradation of the kraft lignin compared to fresh catalyst paper. Thus, Co(salen) catalyst paper is a suitable catalyst for the practical conversion of kraft lignin. However, further studies are still needed to investigate applications on an industrial scale.

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