

# ZEOLITE-ENCAPSULATED Co(II)[H<sub>4</sub>]SALEN AND [H<sub>2</sub>]SALEN COMPLEXES: PULP BLEACHING CATALYSTS WITH ENHANCED BLEACHABILITY

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Salen complexes are an important class of coordination compounds, which have been used to catalyze a wide variety of reactions with exceptional selectivity. Considerable efforts have been made by our research group focusing on additional developments, including the heterogenization of catalytic systems and hydrogenation for application in catalytic delignification of pulp. [H<sub>2</sub>] and [H<sub>4</sub>]salen type complexes of cobalt encapsulated in zeolite cages were synthesized and characterized by spectroscopic techniques. Their catalytic properties were then evaluated in the catalytic delignification of pulp using peracetic acid (CH<sub>3</sub>COOOH) as an oxidant. The encapsulation and hydrogenation of the complexes yielding increased spatial separation, which strongly enhanced the activity of complexes, were found to play a key role in the selective delignification of pulp. With encapsulated and hydrogenated complexes as catalysts, pulp was selectively delignified to a high brightness. The catalysts that were developed could suitably be used in green bleaching for the pulp industry.

**Keywords:** tetrahydro-salen complex, encapsulation, pulp delignification, heterogeneous catalysts, bleachability

## INTRODUCTION

From a chemical point of view, lignins are considered as complex polyphenols. The heterogeneity of lignin polymers exists in molecular composition and linkage types between the phenylpropane monomers, syringyl- (S), guaiacyl- (G), and p-hydroxyphenyl- (H) units. These are derived from the monolignols sinapyl-, coniferyl-, and coumaryl-alcohol, respectively (Fig. 1).<sup>1,2</sup> Lignin is the main source of color in pulp due to the presence of a variety of chromophores, either naturally present in the wood or created in the pulp mill. Chemical pulps (kraft and sulphite) contain less than 5% residual lignin. Subsequent bleaching is required to remove essentially all of the residual lignin from the pulp to achieve the high level of brightness expected of fine papers, but conventional bleaching with chlorine compounds is becoming unpopular because of the chlorinated organic by-products involved. New bleaching processes, which do not depend on chlorine compounds, are being developed.<sup>3-5</sup>

Totally chlorine-free or TCF bleaching uses oxygenic chemicals. The use of TCF bleaching is the safest process for the environment as it does not release toxins into the environment. Current TCF sequences are likely to have lower yields than chlorine sequences when the bleach sequences have the same incoming bleach plant kappa and final brightness target.<sup>6,7</sup> The need for highly selective removal of lignin without depolymerization of the cellulose in pulp presents an opportunity for catalytic methods, which typically have high levels of specificity.<sup>8,9</sup>

At the same time, the biomimetic catalysts offer an alternative for chemical processes. Biomimetic catalysis generally refers to the chemical catalysis that mimics certain key features of enzymes. These features include high enzyme-substrate binding affinities, high catalytic turnovers of enzyme-catalyzed reactions, and substantial rate accelerations relative to uncatalyzed reactions.<sup>10</sup> Moreover, their stability and selectivity may be

improved by chemical modifications of the active sites by altering the immobilization procedures. The immobilization of active sites within solid host materials can lead to the creation of highly active and selective catalysts that can facilitate highly selective transformation.<sup>11,12</sup> Badamali and co-workers found that a  $\beta$ -O-4 lignin model phenolic dimer degraded faster in Co(salen) catalysed oxidation than in Co(salen)/SBA-15 catalysed oxidation.<sup>13</sup> Recent developments in catalysis have allowed us to develop the reduced and encapsulated salen complexes for catalytic delignification in pulp bleaching. Our group has provided evidence for the distribution of activity within a crystal, supporting catalytic delignification. Our findings indicate that the activity in catalytic delignification could be higher if Cu([H<sub>2</sub>]salen) was encapsulated in NaY by the impregnation (IM) and ship-in-a-bottle (SB) method.<sup>14</sup> [H<sub>4</sub>]salen complexes were also reported by some researchers to have a positive effect on activity due to the more flexible complexes and the improved increased spatial separation where salen ligands are converted to tetrahydro-salen ligand ([H<sub>4</sub>]salen) by the hydrogenation of C=N to C-N in the present of NaBH<sub>4</sub>. The reduced derivatives have shown higher activity than the parent [H<sub>2</sub>]salen complexes and are an alternative ligand system for oxidation catalysis.<sup>15,16</sup> This information, along with that discussed above, suggests that the encapsulation and hydrogenation of salen complexes play more

than one role in catalytic oxidation. This, however, was not clearly examined in selective delignification in pulp bleaching.

This paper systematically studies the multi-role of encapsulation and hydrogenation of salen complexes in delignification of pulp over different catalysts and shows its relationship with the nature of complex and delignification.

## EXPERIMENTAL

### Materials

All chemicals are commercially available and were used as received without further purification, unless otherwise noted.

Laboratory oxygen delignified eucalyptus (*E. urophylla* × *E. grandis*) kraft pulp (46.4% ISO brightness, 13.0 kappa number, 1130 ml g<sup>-1</sup> viscosity and 83.34 N m g<sup>-1</sup> tensile index) was used for the catalytic TCF bleaching. Before bleaching, the pulp was thoroughly washed with tapwater and distilled water to remove all residual black liquor and stored at 0 °C.

### Instrumentation

X-ray powder diffraction (XRD) patterns of the samples were recorded on a Rigaku Dmax X-ray diffractometer (Ni-filtered, CuK $\alpha$  radiation). The Fourier transform infrared (FTIR) spectra were recorded on an Equinox 55 FT-IR spectrometer in KBr. An atomic absorption spectrometer, Shimadzu AA-6800, was used for the estimation of cobalt. Diffuse reflectance (DR) UV-Vis measurements in the range of 200-800 nm were performed on a Perkin-Elmer Lambda Bio40 spectrophotometer equipped with an integration sphere.

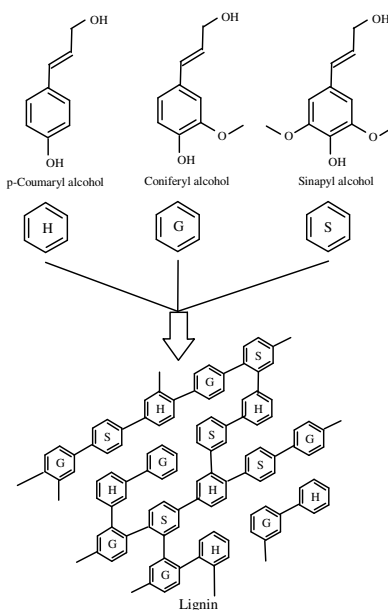
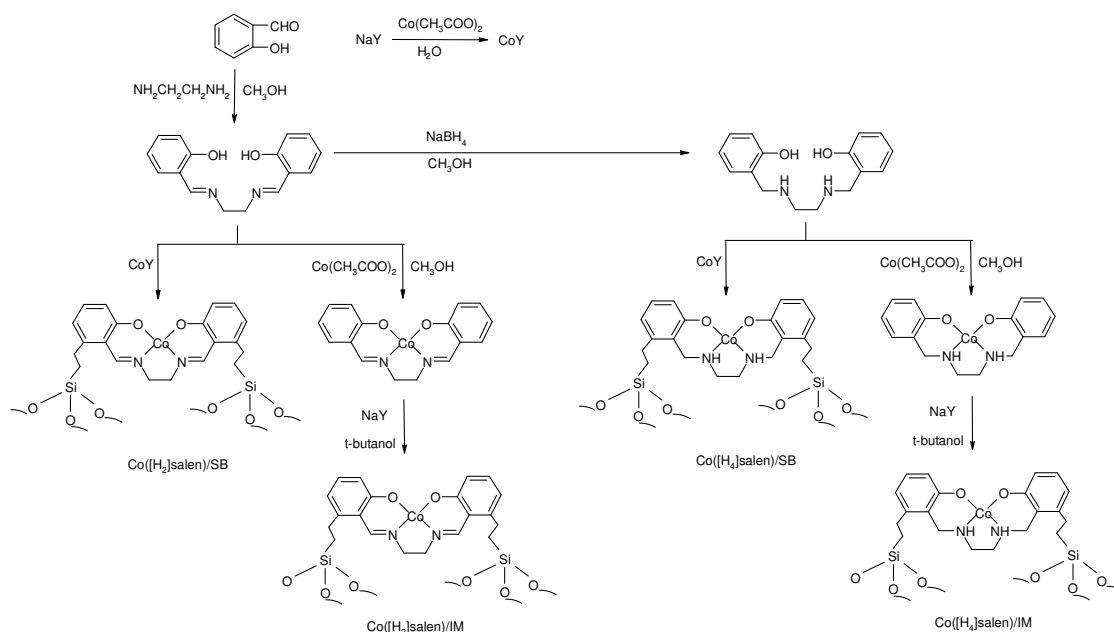


Figure 1: Structure of lignin



Scheme 1: Preparation of Co(II)  $[\text{H}_4]\text{salen}$  and  $[\text{H}_2]\text{salen}$  complexes and immobilization on NaY

The surface area (by the BET method) was determined by adsorption and desorption of nitrogen at the temperature of liquid nitrogen (77 K), using volumetric adsorption set-up (Micromeritics ASAP-2020, USA).

#### Preparation of zeolite-encapsulated Co(II) $[\text{H}_4]\text{salen}$ and $[\text{H}_2]\text{salen}$ complexes

Co(II)  $[\text{H}_4]\text{salen}$  and  $[\text{H}_2]\text{salen}$  complexes were encapsulated in NaY by the impregnation method (IM) and ship-in-a-bottle method (SB). The encapsulated catalysts were designated by the following notation: complex/encapsulation method.

The preparation of Co(II)  $[\text{H}_4]\text{salen}$  and  $[\text{H}_2]\text{salen}$  complexes and the following encapsulations on NaY via the 'IM' and 'SB' processes are depicted in Scheme 1.

$[\text{H}_4]\text{salen}$  and  $[\text{H}_2]\text{salen}$  ligands were prepared by following the procedures reported in the literature.<sup>17,18</sup>

$[\text{H}_2]\text{salen}$  (N, N'-bis(salicylidene)-ethylenediamine) was synthesized by dropwise addition of ethylenediamine (4.5 mmol), to a methanolic solution (18 mL) of salicylaldehyde (9 mmol). The reaction mixture was stirred for 30 min in an ice-water bath with a condenser. After standing for 15 min, a yellow precipitate of  $[\text{H}_2]\text{salen}$  was formed, which was filtered out, washed with petroleum ether, and dried in vacuum.  $[\text{H}_4]\text{salen}$  was obtained by stirring 0.011 mol  $\text{NaBH}_4$  with 0.01 mol  $[\text{H}_2]\text{salen}$  in  $\text{CH}_3\text{OH}$  at ambient temperature for 2 h. The solid product was washed with water and dried in vacuum. The purity of the ligands was confirmed by IR and H-1 NMR before coordination to Co(II) cation.

$\text{Co}([\text{H}_2]\text{salen})$  and  $\text{Co}([\text{H}_4]\text{salen})$  were prepared following a literature method.<sup>19</sup> 1.16 g of  $[\text{H}_2]\text{salen}$  ( $[\text{H}_4]\text{salen}$ ) was dissolved in 50 mL of hot methanol,

followed by the addition of 1.08 g  $\text{Co}(\text{CH}_3\text{COO})_2$  in 6.7 mL of hot deionized water. Then the mixture was refluxed for 60 min. The precipitate obtained was filtered out, washed with methanol, vacuum dried and characterized.

$\text{Co}/\text{Y}$  was obtained by ion-exchanging NaY with  $\text{Co}^{2+}$  ions at room temperature in an aqueous solution of cobalt acetate (0.08 M) with a liquid/solid ratio of 20 (mL/g).

The  $\text{Co}([\text{H}_2]\text{salen})$  ( $\text{Co}([\text{H}_4]\text{salen})$ ) was supported on NaY by impregnation: 150 mg of  $\text{Co}([\text{H}_2]\text{salen})$  ( $\text{Co}([\text{H}_4]\text{salen})$ ) complex was dissolved in *t*-butanol and added to 300 mg of NaY molecular sieve. The amount of solvent was just enough to cover the mixture. Then the mixture was refluxed for 6 h under nitrogen gas flow. The solid resulting after filtering was extracted with *t*-butanol and acetonitrile using a Soxhlet extractor until the extract was colorless. Then, the solid was allowed to vacuum dry to obtain the final encapsulated complex.

$\text{Co}/\text{Y}$  was mixed well with excessive  $[\text{H}_2]\text{salen}$  ligand ( $[\text{H}_4]\text{salen}$ ) (ligand/metal=3, M/M), and sealed into a round flask. Then, the mixture was heated for 24 h at 150 °C under high vacuum conditions. Uncomplexed ligands were removed by extraction with acetone, and uncoordinated  $\text{Co}^{2+}$  ions were removed by ion-exchange with NaCl aqueous solution (0.1 M). The sample was further washed thoroughly with deionized water, and air-dried for 60 min to give the  $\text{Co}([\text{H}_2]\text{salen})/\text{SB}$  ( $\text{Co}([\text{H}_4]\text{salen})/\text{SB}$ ).

#### Catalytic TCF bleaching trials

In this study, catalytic TCF bleaching sequences consisting of four stages included a treatment with a catalytic agent and several bleaching stages, such as

alkaline extraction stage with hydrogen peroxide addition and two hydrogen peroxide stages, designated as Cat, Ep, P<sub>1</sub> and P<sub>2</sub>, respectively. After each stage, the pulp was washed thoroughly with deionized water in a Büchner funnel and then pressed to 30% consistency.

A series of catalytic bleaching trials (Cat) were performed using Co([H<sub>2</sub>]salen), Co([H<sub>4</sub>]salen), Co([H<sub>2</sub>]salen)/SB, Co([H<sub>2</sub>]salen)/IM, Co([H<sub>4</sub>]salen)/SB, Co([H<sub>4</sub>]salen)/IM for 120 min at 70 °C. Oxygen delignified eucalyptus kraft pulp (15 g, o.d. pulp) obtained with 30% consistency, was combined with the catalyst (0.03% on o.d. pulp), CH<sub>3</sub>COOOH (0.5% on o.d. pulp), and deionized water to obtain a 5% pulp consistency. Control experiments were also carried out under identical conditions in the absence of the catalyst to examine the ability of the catalyst.

Alkaline extraction with 0.5% (on o.d. pulp) addition of H<sub>2</sub>O<sub>2</sub> (Ep) was performed by heating the pulp at a consistency of 10% at 70 °C for 60 min in 0.0375M NaOH and using MgSO<sub>4</sub> (0.1% on o.d. pulp) and DTPA (0.05% on o.d. pulp) as stabilizer at this stage.

The consistency of pulp at stages P<sub>1</sub> and P<sub>2</sub> was maintained at a value of 10%. NaOH, MgSO<sub>4</sub>, Na<sub>2</sub>SiO<sub>3</sub>, DTPA, H<sub>2</sub>O<sub>2</sub> were used as bleaching chemicals. P<sub>1</sub>-stage: NaOH 1.5% (on o.d. pulp), MgSO<sub>4</sub> 0.1% (on o.d. pulp), Na<sub>2</sub>SiO<sub>3</sub> 1.0% (on o.d. pulp), DTPA 0.1% (on o.d. pulp), H<sub>2</sub>O<sub>2</sub> 2.0% (on o.d. pulp), and 80 °C for 150 min; P<sub>2</sub>-stage: NaOH 1.0% (on o.d. pulp), MgSO<sub>4</sub> 0.05% (on o.d. pulp), DTPA 0.1% (on o.d. pulp), H<sub>2</sub>O<sub>2</sub> 1.5% (on o.d. pulp), and 80 °C for 90 min.

All experiments were run at least three times.

### Analytical methods

Kappa number, a measure of residual lignin in the pulp, was determined according to TAPPI T 236 om-99. Pulp viscosity (T 230 om-08), a measure of its strength

properties depending on molecular mass, was obtained using the capillary viscometer method. Brightness of pulp (T452) was measured on the samples obtained in each bleaching sequence. For assessing physical properties, sample sheets (T 205 sp-06) were formed by means of a handsheet former. The handsheet weight varied from 60 to 65 g/m<sup>2</sup>. The tensile index (T 220 sp-10) of pulp handsheets was measured.

## RESULTS AND DISCUSSION

### Characterization of the catalyst

#### Chemical analysis and XRD

The analytical data of neat and encapsulated Co(II) [H<sub>4</sub>]salen and [H<sub>2</sub>]salen complexes are given in Table 1. As expected, elemental analysis of the complexes indicates that the encapsulated complexes contained less cobalt than the neat complexes. The amount of cobalt was higher in the sample obtained by the 'IM' rather than by the 'SB' method, due to the higher probability of retention of the complex inside the supercage during the synthesis.<sup>20</sup> Since the complexes were present within the supercages of the NaY structure, the surface area (S<sub>BET</sub>) and pore volume (V<sub>BJH</sub>), as well as the pore diameter (D<sub>BET</sub>), decreased compared with those of pure NaY (Table 1).<sup>21</sup> XRD considerations of the complexes encapsulated within NaY indicate that Co(II) [H<sub>4</sub>]salen and [H<sub>2</sub>]salen complexes were essentially unaltered after the encapsulation procedure (Fig. 2).<sup>22</sup>

Table 1  
Characteristics of neat and encapsulated Co(II) [H<sub>4</sub>]salen and [H<sub>2</sub>]salen complexes

Sample	Co content (wt%)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>BJH</sub> (cm <sup>3</sup> g <sup>-1</sup> )	D <sub>BJH</sub> (nm)	D <sub>BET</sub> (nm)
NaY	-	584.38	0.32	7.62	3.22
Co([H <sub>2</sub> ]salen)	18.33	-	-	-	-
Co([H <sub>2</sub> ]salen)/IM	2.46	227.65	0.13	5.02	2.28
Co([H <sub>2</sub> ]salen)/SB	2.26	375.45	0.23	5.75	2.46
Co([H <sub>4</sub> ]salen)	18.17	-	-	-	-
Co([H <sub>4</sub> ]salen)/IM	1.34	388.71	0.23	5.87	2.35
Co([H <sub>4</sub> ]salen)/SB	0.79	485.79	0.30	6.88	2.46

Specific surface area, S<sub>BET</sub> (m<sup>2</sup> g<sup>-1</sup>); pore volume, V<sub>BJH</sub> (cm<sup>3</sup> g<sup>-1</sup>); pore diameter, D<sub>BJH</sub> (nm), D<sub>BET</sub> (nm)

### FTIR spectroscopy

The characterization of neat and encapsulated complexes by FTIR spectroscopy was done comparatively (Fig. 3). In general, the similarity of the FTIR spectra provided evidence that the complex structure remained unchanged upon

encapsulation, in agreement with the XRD results. The FTIR spectra of neat and encapsulated Co([H<sub>2</sub>]salen) complexes (Fig. 3, b, c, d) were characterized by the presence of a band at about 1630 cm<sup>-1</sup> due to the stretching of the C=N bond, while Co([H<sub>4</sub>]salen) derivatives (Fig. 3, e, f, g)

showed a band at about 1500-1300  $\text{cm}^{-1}$  due to the presence of the C-N bond. In conclusion, the appearance of the bands at 568  $\text{cm}^{-1}$  (Co-N), 470  $\text{cm}^{-1}$  (Co-O), 1500  $\text{cm}^{-1}$  (aromatic ring), 3220  $\text{cm}^{-1}$  (N-H) provided further conclusive evidence of the successful encapsulation of Co(II)  $[\text{H}_4]\text{salen}$  and  $[\text{H}_2]\text{salen}$  into the NaY.<sup>23</sup>

#### DR UV-vis spectroscopy

DR UV-vis spectra of the complexes are shown

in Figure 4. It indicates that the neat and encapsulated complexes presented peaks at 200-250 nm, and 300-350 nm, corresponding to the absorption of  $[\text{H}_4]\text{salen}/[\text{H}_2]\text{salen}$  and  $\text{Co}([\text{H}_4]\text{salen})/\text{Co}([\text{H}_2]\text{salen})$ . Moreover, the absorptions of DR UV-vis of these complexes were different. Generally, the weaker absorptions of encapsulated and hydrogenated samples in the DR UV-vis spectra confirmed the small change in the geometry and the stability of the complexes.<sup>24,25</sup>

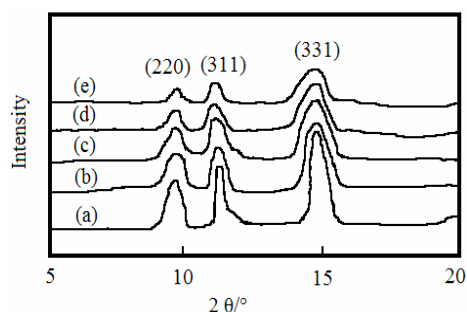


Figure 2: XRD spectra of (a) NaY, (b) Co( $[\text{H}_2]\text{salen}$ )/IM, (c) Co( $[\text{H}_2]\text{salen}$ )/SB, (d) Co( $[\text{H}_4]\text{salen}$ )/IM, (e) Co( $[\text{H}_4]\text{salen}$ )/SB

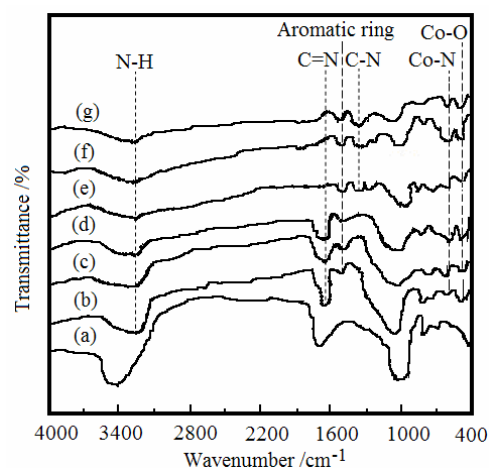


Figure 3: FTIR spectra of (a) NaY, (b) Co( $[\text{H}_2]\text{salen}$ ), (c) Co( $[\text{H}_2]\text{salen}$ )/IM, (d) Co( $[\text{H}_2]\text{salen}$ )/SB, (e) Co( $[\text{H}_4]\text{salen}$ ), (f) Co( $[\text{H}_4]\text{salen}$ )/IM, (g) Co( $[\text{H}_4]\text{salen}$ )/SB

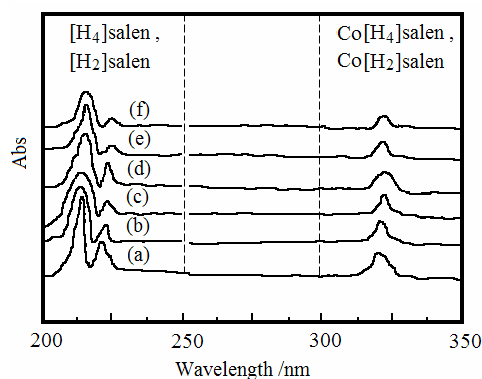


Figure 4: DR UV-vis spectra of (a) Co( $[\text{H}_2]\text{salen}$ ), (b) Co( $[\text{H}_2]\text{salen}$ )/SB, (c) Co( $[\text{H}_2]\text{salen}$ )/IM, (d) Co( $[\text{H}_4]\text{salen}$ ), (e) Co( $[\text{H}_4]\text{salen}$ )/SB, (f) Co( $[\text{H}_4]\text{salen}$ )/IM

#### Catalytic delignification of pulp

Figures 5 and 6 show the selectivity of delignification and pulp brightness for the catalytic bleaching using different catalysts and  $\text{CH}_3\text{COOOH}$  as oxidant. It can be seen that after the complexes were introduced into the support, the

heterogeneous ones afforded a high value of selectivity of delignification (Fig. 5) and pulp brightness (Fig. 6). The  $[\text{H}_4]$  complexes proved to be more efficient than  $[\text{H}_2]$  complexes in pulp delignification with complexes. The selectivity of delignification per mole of metal using

Co([H<sub>2</sub>]salen), Co([H<sub>2</sub>]salen)/SB, Co([H<sub>2</sub>]salen)/IM, Co([H<sub>4</sub>]salen), Co([H<sub>4</sub>]salen)/SB, Co([H<sub>4</sub>]salen)/IM achieved values of 550, 6477, 5347, 647, 17879, 10768, respectively, and pulp brightness reached 84.37%ISO, 87.17%ISO, 86.08%ISO, 85.30%ISO, 87.55%ISO, 86.99%ISO, respectively. However, SB-encapsulated Co(II) [H<sub>4</sub>]salen and [H<sub>2</sub>]salen complexes obtained a higher value of selectivity and brightness. Obviously, well isolated active sites increase activities of the catalysts, as reported in many studies.<sup>26-28</sup> The influence of the metal content in NaY should also be considered. The content of cobalt in SB-encapsulated Co(II)

[H<sub>4</sub>]salen and [H<sub>2</sub>]salen complexes was lower, which is probably related to radicals affecting the oxidation degree of lignin and carbohydrates.<sup>29,30</sup>

Although the catalytic pretreatment was introduced as an initial bleaching stage, TCF-experimental paper properties are better than those of the TCF-industrial process. The tensile indexes of the papers pretreated with different catalysts were of 60-75 N·m·g<sup>-1</sup>. In conclusion, the TCF-experimental sequence with these catalytic pretreatments attained good results, surpassing those obtained by the TCF-industrial sequence.<sup>31,32</sup>

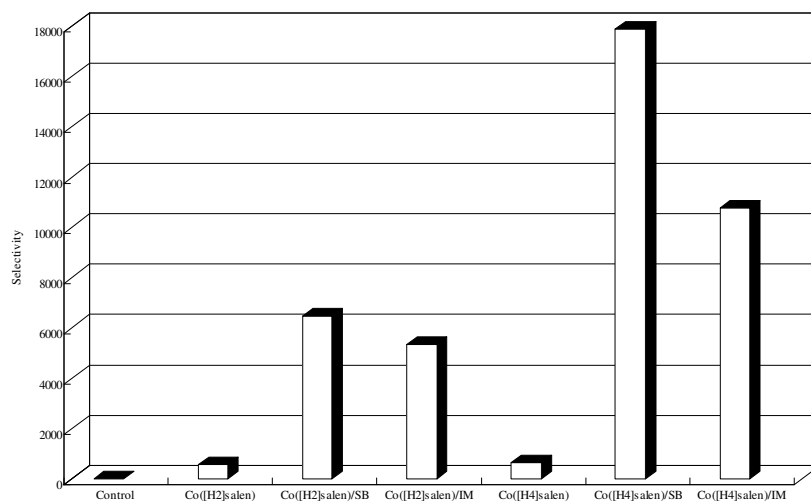


Figure 5: Selectivity for CatEp bleaching (Selectivity =  $\frac{(K_{\text{oxygen delignified pulp}} - K_{\text{CatEp pulp}})}{(V_{\text{oxygen delignified pulp}} - V_{\text{CatEp pulp}})}$ )  
Per mole metal ion

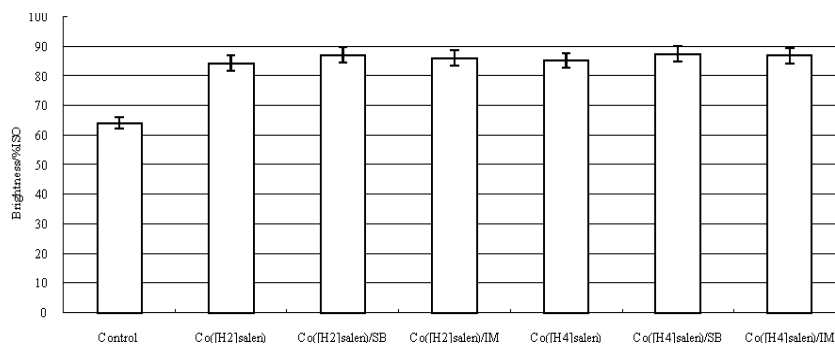


Figure 6: Pulp brightness for CatEpP<sub>1</sub>P<sub>2</sub> bleaching

## CONCLUSION

The encapsulation and hydrogenation of Co([H<sub>2</sub>]salen) has a beneficial effect in catalytic delignification of pulp in the presence of CH<sub>3</sub>COOOH. In addition to the catalysis

modification depending on the encapsulation method, this work shows that catalysis may cause an increase in the selectivity of delignification and brightness of pulp – the properties of the papers bleached by the TCF-experimental sequence and

pretreated with different catalysts are better than those of the samples subjected to the TCF-industrial process. Using spectroscopic methods, the positive effect of encapsulation and hydrogenation of Co([H<sub>2</sub>]salen) on the activity in catalytic delignification may be explained as due to the greater dispersion of the metal active sites.

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