Selective Oxidation of Kraft Lignin over Zeolite-Encapsulated Co(II) [H$_4$]salen and [H$_2$]salen Complexes

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ABSTRACT: The Co([H$_4$]salen) and the corresponding Co([H$_2$]salen) complexes were encapsulated in NaY by the impregnation (IM) and flexible ligand ship-in-a-botttle (SB) method for oxidation of kraft lignin to obtain chemical compounds. The neat and encapsulated complexes were characterized by XRD, FTIR, DR UV–Vis spectroscopy and BET, which showed the observed changes in the molecular structure to be correlated to the enhanced activity of the complexes. GC-MS confirmed that the catalytic reactions of kraft lignin in the presence of peracetic acid produced major products including 2-methoxy phenol, 2-hydroxy benzaldehyde, 4-hydroxy-3,5-dimethoxyphenyl ethanone. The encapsulated complexes exhibited improved reactivity compared to the corresponding neat complexes. Additionally, there was a greater improvement in TOF value for complexes upon IM-immobilization as compared to SB-immobilization. The improved salen, that is, [H$_4$]salen, was beneficial to the enhancement of catalytic activity as compared to [H$_2$]salen, as revealed by the high TOF values due to the incorporation of a modified coordination environment of the central cobalt cation by C=N hydrogenation. Actually, Co([H$_4$]salen)/IM was proved to be most active. Lignin conversion and TOF were high over the neat cobalt complexes when using 100% H$_2$O as the solvent, and the values were high over the corresponding encapsulated analogues when using 80% H$_2$O + 20% CH$_3$OH as the solvent. It can be found that encapsulation and hydrogenation of the complexes can improve the selectivity to 2-methoxy phenol in the oxidation of kraft lignin. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40809.

**KEYWORDS:** biomimetic; biopolymers and renewable polymers; cellulose and other wood products; porous materials

INTRODUCTION

Lignin is the second most abundant renewable polymer on the planet and a heterogeneous polymer in lignocellulosic residues. Lignin is the only naturally synthesized polymer with an aromatic backbone. It generally contains three precursor aromatic alcohols including coniferyl alcohol, sinapyl, and *p*-coumaryl. These precursors form the guaiacyl- (G), syringyl- (S) and *p*-hydroxyphenyl (H) subunits in the lignin molecule, respectively. Oxidative coupling of these monomers creates a complex structure in lignin which is highly recalcitrant to degradation.[1,2]

Traditionally, lignin is usually obtained as a byproduct of pulping processes with respect to the specificities of further transformations within the biorefinery cascades. Noteworthy, due to environmental concerns, increasing oil prices and the economic problems, many pulp and paper mills have started to look for new ways of recycling and for cost effective methods, including

wider usage of renewable sources. Usually, a pulp and paper mill produces only paper and recycles the chemical used for pulping, producing energy for internal use. However, paper mills have clear potential of additionally being biorefineries by utilising a larger part of the organic components in the wood, for example, hemicellulose and lignin. By isolating lignin from the black liquor, it can be used as a fuel in a lime kiln or be further upgraded as a renewable material (Figure 1).[3–5] In fact, from an economic point of view, it would be profitable to use kraft lignin for more valuable products, rather than for combustion to gain energy, by either degradation (phenols, aromatics)[6,7] or cross-linking (adhesives, carbon fiber).[8–10]

The controlled breaking of carbon-carbon and carbon-oxygen bonds in lignin represents a very selective depolymerization that could produce a whole series of monomeric, aromatic species. The effective degradation of kraft lignin and its selective transformation is a key process in various potential applications,
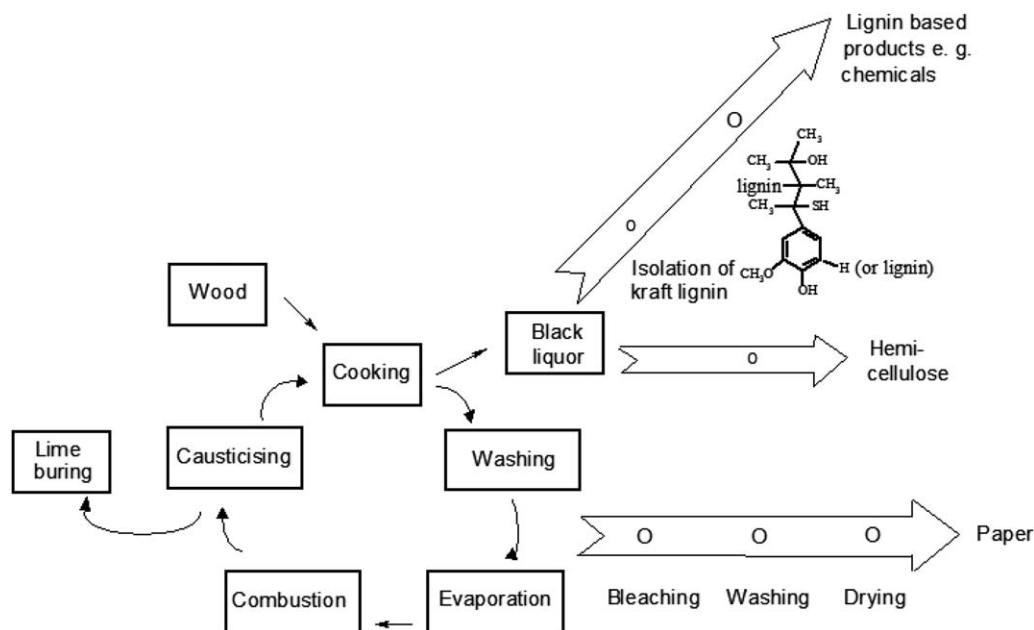
Figure 1. An overview of the process of kraft pulping with the potential point for withdrawal and isolation of kraft lignin and production of chemicals.

which justifies the search for catalysts. Therefore, the development of an effective, selective, and robust catalyst remains a major challenge in targeted functionalization of kraft lignin within biomass refinery processes.[11,12]

The salen-type complexes ([H$_2$]salen) are an important class of organometallic compounds, which are considered as promising candidates because of their easy synthesis and excellent catalytic performances in a wide variety of reactions with oxidants like oxygen and hydrogen peroxide. For these reasons, they can be used as catalysts in the field of lignin and wood chemistry. In particular, it was demonstrated that they were able to oxidize in high yields lignin model compounds.[13–15] Bozell et al.[16] have reported that Co(salen) along with oxygen as the oxidant constituted the most promising biomimetic degradation of lignin. Similarly, Canevali et al.[17] have studied the oxidation mechanism of apocynol catalyzed by Co(salen) in the homogeneous phase using either chloroform or pyridine as solvent. About 90% conversion was obtained after 48 h of reaction.

Salen ligand can be easily converted to tetrahydro-salen ligand ([H$_4$]salen) by the hydrogenation of C=N to C-N in the present of NaBH$_4$. Previously, the spectroscopic, electrochemical and structural properties and coordination chemistry of a limited number of metal tetrahydro-salen complexes, such as Cu(II), Co(II), Fe(III) and Mn(II) tetrahydro-salen, were studied. The hydrogenation would increase N basicity and make the complex more flexible.[18–21]

However, these reported [H$_2$]salen and [H$_4$]salen complexes often deactive with time due to easy formation of dimeric oxo- and peroxo-bridged species. Therefore, metal [H$_2$]salen and [H$_4$]salen complexes encapsulated in the pores and voids spaces of zeolites and zeolite materials have been receiving special attention as inorganic mimics of enzymes, often referred to as zeozymes. In addition, they behaved functionally similar to heterogeneous

catalysts as well as homogeneous catalysts.[22–25] Badamali et al.[26] have studied the oxidation behavior of apocynol, an important lignin model compound using a Co(salen)/SBA-15 based heterogeneous catalytic system in the presence of hydrogen peroxide as oxidant. The active Co(salen) complex seemed to be stabilised within the mesoporous host, rendering a supported catalyst twice as active as the homogeneous Co(salen)complex. Cu(II), Co(II), and Fe(III) tetrahydro-salen complexes encapsulated in zeolite-Y have been reported to show improved catalytic activity in oxidation of cycloalkanes with H$_2$O$_2$ in comparison with the corresponding metal salen complexes.[27]

From this and related studies, molecular sieve based heterogeneous salen and tetrahydro-salen complexes appeared to be a promising alternatives for the selective degradation of kraft lignin. In our laboratory, we have found that the catalytic activity of copper (II) salen complexes zeolite-encapsulated by the "impregnation" (IM) and flexible ligand "ship-in-a-botttle" (SB) method was enhanced significantly in the selective delignification of kraft pulp.[28] These results encouraged us to extend these neat and encapsulated tetrahydro-salen and salen complexes to the transformation of kraft lignin and performed the catalytic oxidation of kraft lignin for chemical compounds. Here we synthesized zeolite-encapsulated Co(II) tetrahydro-salen and salen complexes by the IM and SB method. The catalysts were analyzed using a variety of techniques and their catalytic performances in oxidation of kraft lignin using CH$_3$COOOH as oxidant were then evaluated. Peracids have been used mainly for the preparation of metal-oxo complexes to model the high-valent states of heme-containing enzymes. Peroxyacetic acid is a powerful oxidation agent, only few articles have been devoted to its use as stoichiometric oxidant in metallosalen-catalyzed oxidations. Peroxyacetic acid has been shown to be practical oxidants in homogeneous and heterogeneous epoxidation catalysis.[29,30]
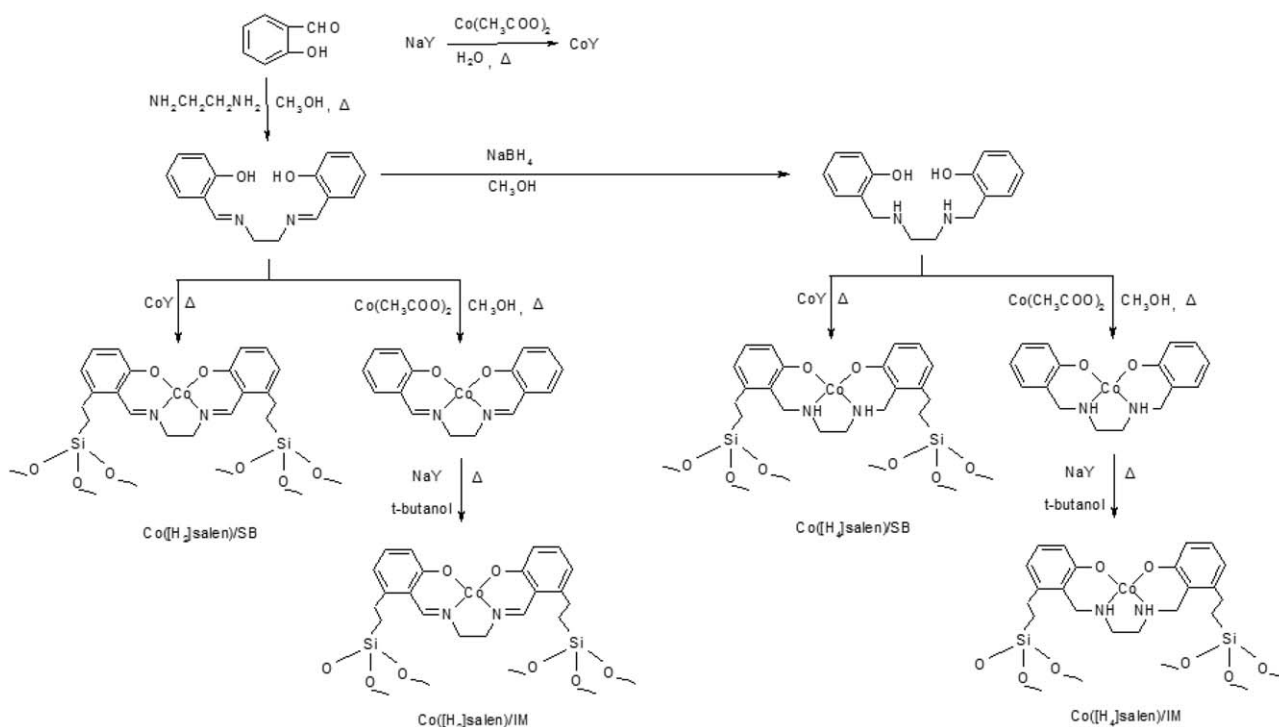
Scheme 1. The preparation of the Co(II) [H$_4$]salen and [H$_2$]salen complexes and the immobilizations on NaY.

In contrast to the large number of studies for the use of lignin, relatively little efforts have been placed in the encapsulated tetrahydro-salen and salen complexes from which important aromatic compounds can potentially be obtained from the conversion of kraft lignin.

EXPERIMENTAL

Materials

All starting materials described herein were commercially purchased from Sinopharm Chemical Reagent, Shanghai, China and used as received without further purification, unless otherwise noted. The NaY molecular sieve was activated by heating at 200°C for 2 h in vacuum and then used to prepare encapsulated Co(II) tetrahydro-salen and salen complexes following a procedure described in Scheme 1. The solvents for the organic syntheses were dried prior to use according to standard procedures.[31]

Eucalyptus (*E. urophylla* × *E. grandis*, 24.5% lignin), from Yunnan Province of China, was cooked by the conventional laboratory-scale kraft method with NaOH and Na$_2$S. Black liquor was collected from the reaction vessel. DTPA was slowly added with agitation to black liquor to facilitate metal-ion removal followed by the addition of aqueous sulfuric acid (2 *M*) until a pH of between 2 and 3 was reached causing some of the kraft lignin to precipitate. The solution and resulting precipitate was kept at 0°C overnight and thawed at room temperature. The precipitate was separated by centrifugation, then freeze dried and kept frozen until purification. The crude kraft lignin was heated in 80% dioxane containing 0.05 *M* HCl at reflux for 2 h in a nitrogen atmosphere, filtered through a

medium sintered glass funnel at 0°C, and sequentially washed up with 80% dioxane. All filtrates were collected, neutralized with solid NaHCO$_3$, and then evaporated under reduced pressure. The liquid after rotary evaporation was slowly added to the acidic deionized water (pH 2), precipitate was centrifuged and freeze-dried. The kraft lignin sample obtained was washed with methylene chloride (three times 150 mL) and dried under vacuum with phosphorus pentoxide to give pure kraft lignin. The purity was 88.70% klason lignin, 8.87% acid soluble lignin, 0.81% carbohydrate, 0.84% ash, the elemental composition was 56.4% C, 6.5% H, 1.3% N, 36.8% O, molecular weight was 3031.

Instrumentation

X-ray power diffraction (XRD) patterns of the samples were recorded on a Rigaku Dmax X-ray diffractometer (Ni-filtered, CuKa radiation). The Fourier transform infrared (FTIR) spectra were recorded on Equinox 55 FT-IR spectrometer in KBr. 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. The surface area (by 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) [H$_4$]salen and [H$_2$]salen Complexes

Co(II) [H$_4$]salen and [H$_2$]salen complexes were encapsulated in NaY by IM and SB methods. The encapsulated catalysts were

Table I. Characteristics of Neat and Encapsulated Co(II) [H$_4$]salen and [H$_2$]salen Complexes

Sample	Co content (wt %)	S_{BET} (m^2 g^{-1})	V_{BJH} (cm^3 g^{-1})	D_{BJH} (nm)	D_{BET} (nm)
NaY	–	584.38	0.32	7.62	3.22
Co([H$_2$]salen)	18.33	–	–	–	–
Co([H$_2$]salen)/IM	2.46	227.65	0.13	5.02	2.28
Co([H$_2$]salen)/SB	2.26	375.45	0.23	5.75	2.46
Co([H$_4$]salen)	18.17	–	–	–	–
Co([H$_4$]salen)/IM	1.34	388.71	0.23	5.87	2.35
Co([H$_4$]salen)/SB	0.79	485.79	0.30	6.88	2.46

S_{BET}, specific surface area (m^2 g^{-1}); V_{BJH}, pore volume (cm^3 g^{-1}); D_{BJH}, D_{BET}, pore diameter (nm).

designated by the following notation: complex/encapsulation method.

The preparation of Co(II) [H$_4$]salen and [H$_2$]salen complexes and the following immobilizations on NaY via IM and SB process were depicted in Scheme 1.

Preparation of [H$_2$] salen and [H$_4$]salen Ligands. [H$_4$] salen and [H$_2$]salen ligands were prepared by following the procedures reported in the literature.[32,33] [H$_2$]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 a ice-water bath with a condenser. After standing for 15 min, the yellow precipitate of [H$_2$]salen was formed which was filtered out, washed with petroleum ether, and dried in vacuum. [H$_4$]salen was obtained by the stirring of 0.011 mol NaBH$_4$ with 0.01 mol [H$_2$]salen in CH$_3$OH at ambient temperature for 2 h. The solid product was washed with water and dried in vacuum. The purity of the ligands were confirmed by IR and H-1 NMR before coordination to Co(II) cation.

Preparation of Co([H$_2$]salen) and Co([H$_4$]salen)
Co([H$_2$]salen) and Co([H$_4$]salen) were prepared followed by a literature method.[27] Co([H$_2$]salen) (Co([H$_4$]salen)) was prepared by the following method: 1.16 g of [H$_2$]salen ([H$_4$]salen) was dissolved in 50 mL of hot methanol, followed by the addition of 1.08 g Co(CH$_3$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.

Preparation of Co/Y. Co/Y was obtained by ion-exchanging NaY with 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).

Preparation of Co([H$_2$]salen)/IM and Co([H$_4$]salen)/IM
The Co([H$_2$]salen) (Co([H$_4$]salen)) was supported on the NaY by impregnation: 150 mg of Co([H$_2$]salen) (Co([H$_4$]salen)) complex was dissolved in t-butanol and added to 300 mg of the NaY molecular sieve. The amount of solvent was just enough to cover the mixture; then refluxed for 6 h under nitrogen gas flow. The resulting solid after filtering was extracted with t-butanol and acetonitrile using soxhlet extractor to the

colorless. Then the solid was allowed to vacuum dry to obtain the final encapsulated complex.

Preparation of Co([H$_2$]salen)/SB and Co([H$_4$]salen)/SB. CoY was mixed well with excessive [H$_2$]salen ligand ([H$_4$]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 condition. Uncomplexed ligand and complex were removed by extraction with acetone, and uncoordinated 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 Co([H$_2$]salen)/SB (Co([H$_4$]salen)/SB).
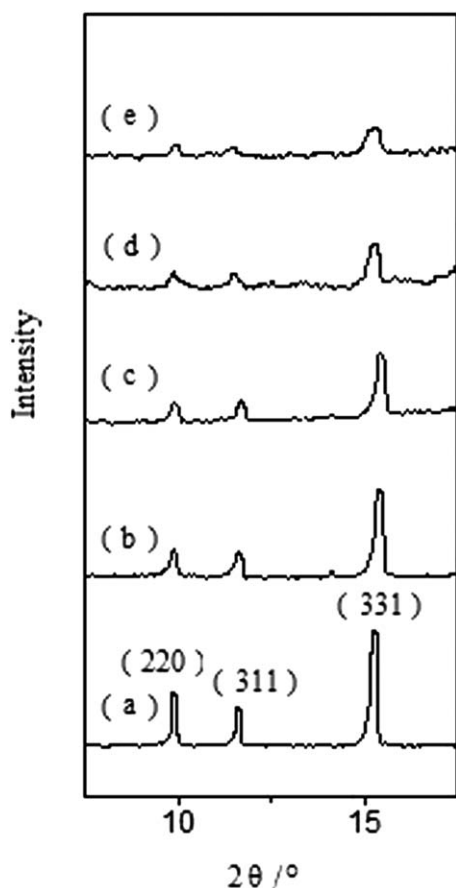
Typical Catalytic Trials
Reactions were conducted at 70°C for 3 h in a batch reactor. In a typical run, 1.0 g kraft lignin along with 1.0 g CH$_3$COOOH, 100 mL solvent (100% H$_2$O, 80% H$_2$O + 20% CH$_3$OH) and 0.2 g catalyst were added into a 500 mL two-necked flask equipped with a condenser. After the reaction was finished (3 h), the flask was cooled to room temperature, and the sample was taken. The flask was thoroughly rinsed with deionized water. Products and residual kraft lignin were separated from the aqueous mixture by three sequential extractions using trichloromethane (60.0 mL). The bottom trichloromethane phases were collected and analyzed using a GC-MS, and products were identified and compared with pure standards when available. Prior to conducting reactions, extraction efficiencies of the potential reaction components using trichloromethane or diethyl ether were determined. Extraction efficiencies were generally higher when trichloromethane was used, compared to diethyl ether.

Two additional blank experiments that use only peracetic acid, only zeolite support was conducted at the conditions same as that of catalytic experiments.

RESULTS AND DISCUSSION

Characterization of the Catalyst

Chemical Analysis and XRD. The analytical data of neat and encapsulated Co(II) [H$_4$]salen and [H$_2$]salen complexes were given in Table I. The cobalt amount of the complex encapsulated was lower in sample obtained by IM and SB methods than that of the complex unencapsulated. However, it maybe noted that in Table I as the hydrogenation on the C=N, the cobalt
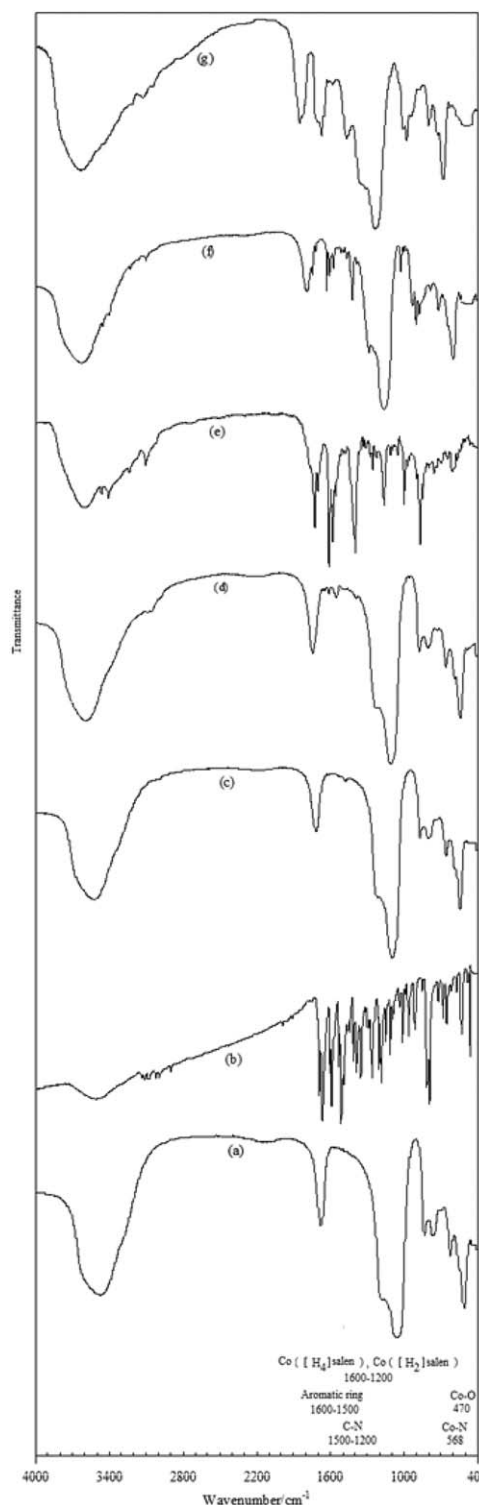
to contrast matching between the NaY framework and organic moieties which were located inside the channels of the support.[34] Moreover, as for Co([H$_4$]salen)/IM [Figure 2(d)], Co([H$_4$]salen)/SB [Figure 2(e)], the intensity shifted to lower

Figure 2. XRD spectra of (a) NaY, (b) Co([H$_2$]salen)/IM, (c) Co([H$_2$]salen)/SB, (d) Co([H$_4$]salen)/IM, and (e) Co([H$_4$]salen)/SB.

amount decreased in [H$_4$]salen complex. The amount of cobalt was higher in sample obtained by IM rather than the SB method due to the low, but finite, solubility of the sample in the synthesis medium. A another probable explanation was that the probability of retention of the complex inside the supercage during the synthesis was higher for complex obtained by IM.[34] Thus, the cobalt amount increased in the following order (Table I): Co([H$_4$]salen)/SB < Co([H$_4$]salen)/IM < Co([H$_2$]salen)/SB < Co([H$_2$]salen)/IM < Co([H$_4$]salen) < Co([H$_2$]salen).

Compared to the pure NaY, the encapsulation of Co(II) [H$_4$]salen and [H$_2$]salen complexes led to a pronounced decrease of the surface area (S_{BET}) and the pore volume (V_{BJH}) as well as a pronounced decrease of the pore diameter (D_{BJH}, D_{BET}) of NaY since the complex molecules occupied part of supercages of the mesoporous material. Similar trends have also been observed previously.[33] It was, however, noted that the changes in S_{BET}, V_{BJH}, and D_{BJH} were even largerer observed for IM-complexes as compared to those for SB-complexes and the changes were largerer for [H$_2$]salen complexes as compared to those for [H$_4$]salen complexes, suggesting that IM-complexes and [H$_2$]-complexes possibly occupied more supercages.
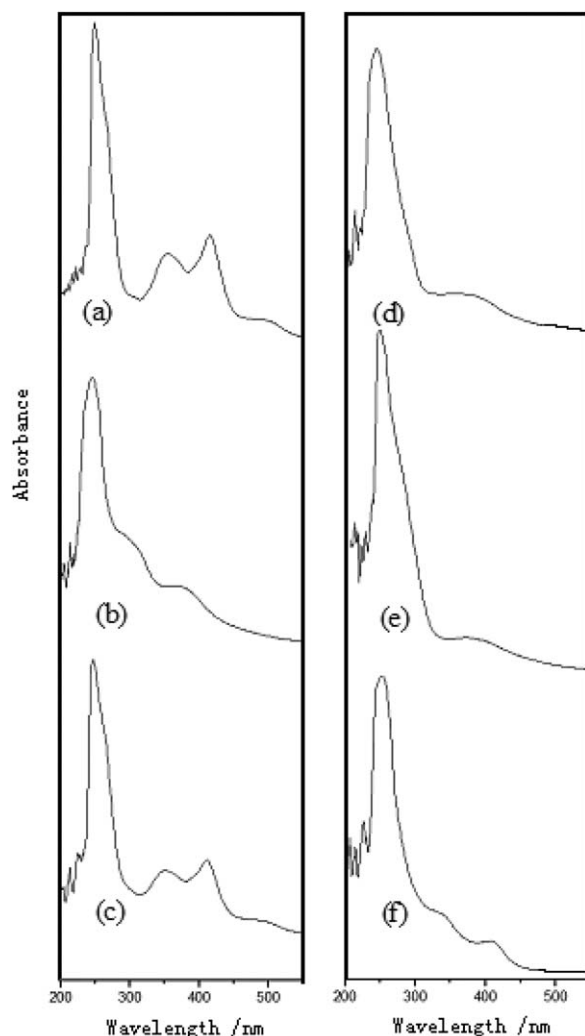
XRD measurements (Figure 2) showed that for the hybrid materials, the relative intensities of the prominent diffraction peaks decreased after the introduction of complex mainly due

Figure 3. FTIR spectra of (a) NaY, (b) Co([H$_2$]salen), (c) Co([H$_2$]salen)/IM, (d) Co([H$_2$]salen)/SB, (e) Co([H$_4$]salen), (f) Co([H$_4$]salen)/IM, and (g) Co([H$_4$]salen)/SB.

Figure 4. DR UV–Vis spectra of (a) Co([H$_2$]salen), (b) Co([H$_2$]salen)/SB, (c) Co([H$_2$]salen)/IM, (d) Co([H$_4$]salen), (e) Co([H$_4$]salen)/SB, and (f) Co([H$_4$]salen)/IM.

value as compared to Co([H$_2$]salen)/IM [Figure2(b)], Co([H$_2$]-salen)/SB [Figure 2(c)], indicating that the hydrogenation allows a flexible positioning of the complex of its surroundings.[35] Similar trends have also been observed by Yang et al.[36] The XRD results confirmed that the crystallinity and morphology of NaY were preserved during the encapsulation of the Co(II) [H$_4$]salen and [H$_2$]salen, which had no obvious influence on the structure of the zeolitic matrix.

FTIR. The infrared spectra were depicted in Figure 3. Vibrations in the range of 1600–1500 cm^{-1}, which attributed to the aromatic ring, were observed in all the samples. The bands in the range of 1500–1200 cm^{-1} for Co([H$_4$]salen), Co([H$_4$]salen)/IM, and for Co([H$_4$]salen)/SB [Figure 3(e–g)] were attributed to C-N adsorptions, which were absent in the spectra of Co([H$_2$] salen), Co([H$_2$]salen)/IM, and Co([H$_2$]salen)/SB [Figure 3(b–d)], indicating the hydrogenation reaction of NaBH$_4$ with C=N.[37]

The characteristic adsorptions of the encapsulated complexes/SB in the range of 1600–1200 cm^{-1}, which indicated the presence

of Co([H$_2$]salen), Co([H$_4$]salen) in the NaY, of which no adsorptions were observed, were weaker than those of the encapsulated complexes/IM due to their low concentration in the NaY.[38]

The identification at the band of 568 cm^{-1} (Co-N) and 470 cm^{-1} (Co-O) and the comparison of the FTIR spectra of the neat and the encapsulated complexes demonstrated a successful formation and encapsulation of Co([H$_2$]salen), Co([H$_4$]salen) into the NaY by the coordination.[39] The appearance of the spectra of the embedded complexes was very similar to that of the free complexes. Obviously, the structure of the complex was maintained in the immobilized state. The wavenumber shifts and relative intensity changes of the vibration bands showed significant guest/host interactions.[40]

DR UV–Vis. The DR UV–Vis spectra of the neat and encapsulated Co(II) [H$_4$]salen and [H$_2$]salen complexes were presented in Figure 4. The complexes exhibited intense adsorptions at 200–300 nm attributable to ligand transfer bands in all cases.[41,42] The DR UV–Vis spectra of the free and encapsulated complexes showed intense ligand-to-metal charge transfer adsorptions in the range of 310–420 nm.[43,44] Nevertheless, these bands shifted to lower wavelength region upon hydrogenation, [Figure 4(d–f)]. Compared to the neat Co(II) [H$_2$]salen [Figure 4(a)] and [H$_4$]salen complexes [Figure 4(d)], there was no distinct change of these bands upon their encapsulation in NaY [Figure 4(b,c,e,f)]. However, a small shift to low wavelength was observed in the DR UV–Vis spectra of SB-encapsulated complexes [Figure 4(b,e)], the ligand-to-metal charge transfer bands in the range of 310–420 nm shifted to lower value as compared to the neat complexes [Figure 4(a,d)], indicating the small change in metal-ligand geometry and stability of Co(II) [H$_4$]salen and [H$_2$]salen complexes due to encapsulation in NaY.[45–47]

The UV–Vis spectra of the neat and encapsulated Co(II) [H$_4$]salen and [H$_2$]salen complexes were recorded in CHCl$_3$ due to the low solubility of the complexes in other organic solvents. The complexes spectra were similar in the position and intensity of the bands characteristic to free complex, further confirming the presence and change of Co(II) [H$_4$]salen and [H$_2$]salen complexes in NaY.

Catalytic Oxidation of Kraft Lignin

Three oxidation products have been identified in the GC-MS chromatogram by comparing with pure standards when available (Figure 5). Isolated products from extraction with trichloromethane included several high-value products commonly obtained from lignin oxidation, such as 2-methoxyphenol, 2-hydroxy benzaldehyde, 4-hydroxy-3, 5-dimethoxyphenyl ethanone.[48] 2-Methoxyphenol is the main product.

To measure the action of the catalysts, lignin conversion, TOF and selectivity were calculated for each experiment from GC-MS data. Table II summarized the catalytic results for the oxidation of kraft lignin over various catalysts. The encapsulated complexes showed higher activity than the corresponding neat complexes. The higher TOF was observed in the case of heterogeneous catalysts. The observed changes in the molecular and
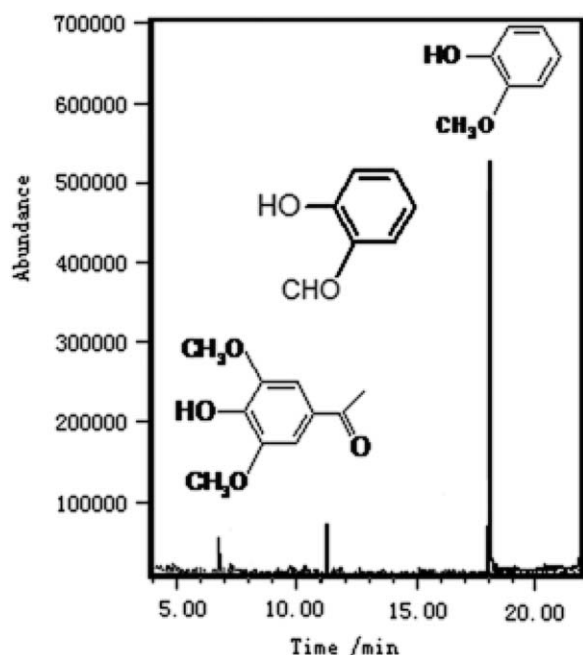
Figure 5. A representative GC-MS chromatogram of the trichloromethane phase collected after reaction.

electronic structure of the complexes on encapsulation were, perhaps, responsible for the enhancement in catalytic activity.[49,50] Despite of this, Co([H$_4$]salen)/IM and Co([H$_4$]salen)/SB (Table II, entries 4 and 5) showed higher activity than the corresponding Co([H$_2$]salen)/IM and Co([H$_2$]salen)/SB (Table II, entries 2 and 3). It was the same case with the neat complex

Co([H$_4$]salen) (Table II, entry 4) as compared to Co([H$_2$]salen) (Table II, entry 1), as revealed by the higher TOF values. This was consistent with the results reported in the literature that the hydrogenation was beneficial to the enhancement of catalytic activity due to the more flexible [H$_4$]salen and the greater site-isolation of Co([H$_4$]salen) as compared to Co([H$_2$]salen).[27,42] Additionally, it appeared that the method of encapsulation had a marked effect on oxidation by Co(II) [H$_2$]salen and [H$_4$]salen complexes. There was a greater improvement in TOF value for Co(II) [H$_2$]salen and [H$_4$]salen complexes upon the IM-encapsulation (Table II, entries 2 and 5) as compared to the SB-encapsulation (Table II, entries 3 and 6).

By contrast, the catalytic performances of the complexes were highly dependent on the type of solvents. The conversion and TOF of kraft lignin were low over the neat cobalt complexes, Co([H$_2$]salen) and Co([H$_4$]salen), when using (80% H$_2$O + 20% CH$_3$OH) as the solvent, and the values were obviously increased over the corresponding encapsulated complexes, Co([H$_2$]salen)/IM, Co([H$_2$]salen)/SB, Co([H$_4$]salen)/IM and Co([H$_4$]salen)/SB, when methanol was added to the system (Table II). The system composed of Co([H$_4$]salen)/IM, H$_2$O, CH$_3$OH was proved to have highest lignin conversion, TOF value. Several factors have been adduced to explain the rise in the value: (1) the use of methanol for solvolysis of lignin ethers or capping radicals or reaction with these disrupted linkages and affecting lignin depolymerization;[51,52] (2) the cobalt loading; (3) the differences in the location, interaction with the NaY framework and accessibility;[53] (4) the presence of uncomplexed metal ions;[54] (5) an increase in the site-isolation of complex and discretization of active species on hydrogenation.[42]

Table II. Catalytic Results of Neat and Encapsulated Cobalt Complexes in Oxidation of Kraft Lignin

Entry	Catalyst	Solvent	Lignin conversion (%)	TOF (h^{-1})	Product selectivity (mol %)	
					2-Methoxy phenol	Others
Blank	Only peracetic acid	H$_2$O	2.37	–	Minor	Minor
		H$_2$O+CH$_3$OH	2.83	–	Minor	Minor
Blank	Only NaY support	H$_2$O	1.12	–	Trace	Trace
		H$_2$O+CH$_3$OH	1.78	–	Trace	Trace
1	Co([H$_2$]salen)	H$_2$O	23.34	0.041	72.96	27.04
		H$_2$O+CH$_3$OH	14.91	0.026	70.16	29.84
2	Co([H$_2$]salen)/IM	100% H$_2$O	9.97	0.13	76.93	23.07
		H$_2$O+CH$_3$OH	18.06	0.24	74.30	25.70
3	Co([H$_2$]salen)/SB	H$_2$O	6.53	0.094	75.86	24.14
		H$_2$O+CH$_3$OH	16.20	0.23	73.93	26.07
4	Co([H$_4$]salen)	H$_2$O	20.47	0.037	74.62	25.38
		H$_2$O+CH$_3$OH	17.82	0.032	71.62	28.38
5	Co([H$_4$]salen)/IM	H$_2$O	18.55	0.45	78.64	21.36
		H$_2$O+CH$_3$OH	46.00	1.11	76.99	23.01
6	Co([H$_4$]salen)/SB	H$_2$O	6.90	0.28	76.08	23.92
		H$_2$O+CH$_3$OH	18.98	0.78	74.59	25.41

Solvent: 100%H$_2$O; 80%H$_2$O + 20%CH$_3$OH.
TOF (h^{-1}), turnover frequency, the number of moles of lignin converted per mole metal ion per hour;
Other, 2-hydroxy benzaldehyde, 4-hydroxy-3, 5-dimethoxyphenyl ethanone.

On the other side, the catalysts were evaluated by the selectivity since the selectivity is very important in conversion processes. It was found that encapsulated complexes (both [H₂] and [H₄] complexes, Table II, entries 2, 3, 5, and 6) as compared to neat complexes, and [H₄] salen complexes (both neat and encapsulated complexes, Table II, entries 4–6) as compared to [H₂] salen complexes, showed high selectivity, which suggested that isolatation and hydrogenization of cobalt [H₂] and [H₄] salen complexes can improve the selectivity to 2-methoxy phenol in the oxidation of kraft lignin. The similar effects of encapsulation and hydrogenization on the [H₂] and [H₄] complexes were observed by Yang et al.[36] in the aerobic epoxidation of styrene. These results demonstrated that, in our series of biomimetic oxidation of lignin,[28,55–59] the use of encapsulation and hydrogenization on [H₂] and [H₄] salen complexes is well suited to transform kraft lignin for chemicals.

CONCLUSION

Co(II) [H₂]salen and [H₄]salen complexes were encapsulated inside the pores and cages of NaY. Biomimetic activity of the encapsulated complexes in the selective oxidation of kraft lignin was investigated. The encapsulation and the hydrogenization of the Co([H₂]salen) complexes had a beneficial effect in the oxidation of kraft lignin. Enhanced activity, and in some cases improved selectivity, were obtained using the encapsulated and the hydrogenised complexes. The possible reasons for the different complexes were investigated using spectroscopic methods. These observations lead us to believe that, with encapsulation and hydrogenization of salen complexes, the efficiency and effectiveness of catalytic protocols in lignin oxidation could easily match or exceed that with common technology, possible applications of these complexes, either for lignin oxidation or for biomass oxidation, are thus worth to be considered.

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