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Towards lignin valorisation: Comparing homogeneous catalysts for the aerobic oxidation and depolymerisation of organosolv lignin

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Abstract

Lignin is a unique potential source of aromatic chemicals derived from renewable resources. Homogeneous oxovanadium, copper and cobalt complexes exhibit intriguing selectivity for the aerobic oxidation of complex lignin models, affording some control of C-C, C-H and C-O bond cleavage. In this work these catalysts are compared, along with a metal-free variant, for their performance in oxidation and depolymerisation of organosolv lignin, as determined by gel permeation chromatography (GPC), quantitative-heteronuclear single quantum correlation (q-HSQC) and ^{31}P NMR spectroscopy of derived phosphite esters. Although most catalysts oxidized the lignin extracts, the oxovanadium(V) complexes, $[VO(O^iPr)L_n]$ (L_n = dipic or $(HQ)_2$ where dipic = dipicolinate and HQ = 8-oxyquinoline) demonstrated the highest degree of lignin depolymerisation. Further ligand development is achieved with a tethered base (pyridine) in the novel BPAMP(V^V)(O)(O^iPr) catalyst [H_2PAMP = *N,N*-bis(3,5-di-*tert*-butyl-2-phenol)-*N*-(methylpyridine)amine]. Efficient oxidation and some degree of depolymerisation is achieved with this new bifunctional catalyst without the addition of exogenous base.

1 Introduction

The quest for new energy and raw material sources as alternatives to those currently derived from fossil fuels is one of the principal technical challenges of the 21st century.[1,2] Lignocellulose is the most abundant non-food source of biomass and the last decade has seen an enormous growth of bio-based chemical processes involving catalytic transformations of carbohydrates and associated feedstocks.[3-6] As a potential source of aromatic chemicals, lignin macromolecules could also be attractive if more selective catalytic depolymerisation processes could be identified and implemented.[7-21] We[22-26] and others[27-33] have recently demonstrated the utility of oxovanadium and copper complex catalysts for controlling the aerobic oxidation of lignin models, and, in three cases, real lignin extracts. In this work we compare a number of catalysts for the oxidation of organosolv lignin to assess the degree of depolymerisation and nature of the oxidative bond cleavage selectivity and resulting functional group formation.

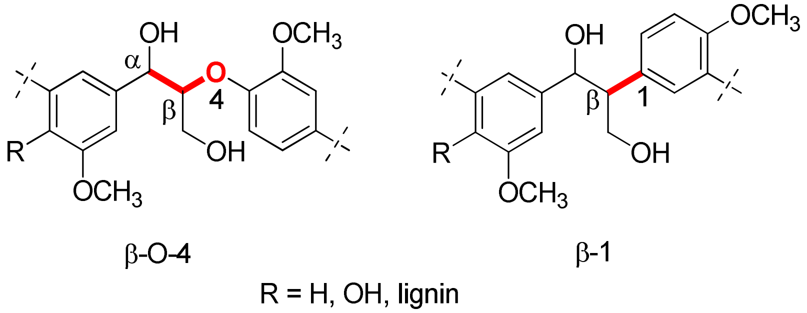

Figure 1. Phenolic and non-phenolic β-O-4 and β-1 linkages in lignin.

Due to the structural complexity and variability of lignin, models containing the prominent β-O-4 and/or β-1 linkages have been used for many catalytic studies (Figure 1).[9] Reductive approaches,[34-36] non-oxidative C-O bond cleavage[27] selective oxidation of C-H bonds[32] and tandem approaches[37,38] have all been employed for the degradation of lignin models. In previous studies we[22-24] and Hanson and co-workers[39] showed that oxovanadium(V) complexes, **1** and **2** (Figure 2), in the presence of base afford the aryl ketone product via a 2e- redox deprotonation pathway (Base-Assisted Redox Deprotonation, BARD). Subsequent cleavage of the Cα-Cβ bond in the aryl ketone then gives aldehyde and acid products. In a complementary reaction, Toste and co-workers showed that complex **3** selectively breaks the Cβ-O-4 bond to give phenol and ene-one products.[27] In contrast, the Cu catalyst system **4** leads to direct cleavage of the Cα-Cβ bond to give primarily the aldehyde product, presumably through a single-electron transfer pathway[26,32,33] reminiscent of peroxidase enzymes.[40,41] For the phenolic variants of these lignin models (R = OH), complexes **1** and **2** (but not **3**) catalyze $\mathrm{C_{aryl}}$-$\mathrm{C_{\alpha}}$ bond cleavage, as reported previously using Co Schiff base complex catalyst **6** (Figure 2).[42,43]

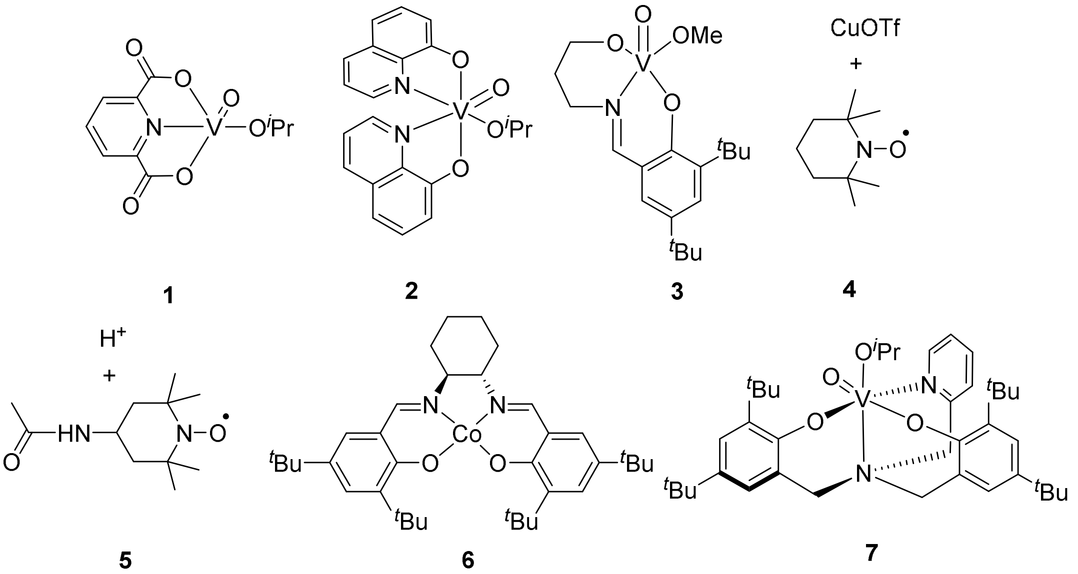

Figure 2. Oxovanadium(V) complexes (**1**, **2** and **3**), CuOTf/TEMPO (**4**), 4-acetamido-TEMPO/acid (**5**) and (salen)cobalt(II) (**6**) and bifunctional oxovanadium(V) (**7**) catalysts for the oxidation of lignin models/extracts (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl; OTf = trifluoromethanesulfonate).

Compared to the model systems described above, extending these studies to lignin extracts is difficult in terms of product analysis and catalyst optimisation, due to the heterogeneity of the lignin substrate. To illustrate, Toste and co-workers reported the decomposition of organosolv lignin (derived from *M. giganteus*) using oxovanadium catalyst **3**.[30] Evidence for depolymerisation of the lignin oxidation was provided by GPC and 2D NMR data that showed decreased intensity for correlations involving β-O-4 linkages and formation of enones (products of redox-neutral C-O bond cleavage). Stahl and co-workers developed a metal-free method for the oxidation of aspen lignin, employing 4-acetamido-TEMPO **5** under acidic conditions. Two-dimensional NMR data revealed that all guaiacyl [4-(2-methoxyphenol)] and syringyl [4-(2,6-dimethoxyphenol)] units were transformed, establishing that the β-O-4 linkages were oxidized to aryl ketone-containing β-ether units though C-H bond cleavage.[31] Bozell and co-workers used the (salen)cobalt(II) catalyst **6** for the aerobic oxidation of organosolv lignin (from tulip poplar) and obtained various quinones, representing 3.5% of the initial weight of lignin.[42] However, the latter three reports do not address the relative molecular weights of the lignin before and after oxidation. Thus, the various studies on catalytic lignin degradation have employed different conditions and taken different approaches to analyze the products. In some cases, the extent of depolymerisation was not evaluated, making it difficult or impossible to compare the different approaches/catalysts.

To our knowledge, the methods published by Chornet *et al.* and Song *et al.* represent the state-of-the-art for obtaining valuable aldehyde products from lignin oxidation,[44] although comparing the various approaches is again challenging due to the different types of analyses applied in each case. The Chornet method utilized Kraft lignin, treated under 1400 kPa (14 atm) of pure oxygen with 135 wt. % NaOH, 5 wt. % $CuSO_4$ and 0.5 wt. % $FeCl_3$ at 160 ^oC for 1 hr, yielding 14 wt. % of aldehydes.[7] Song and co-workers used 5 wt. % $CuSO_4$ supported in ionic liquid using 2500 kPa (25 atm) of pure oxygen at 175 ^oC and reported 30 wt. % yield of aldehydes from commercially-available organosolv lignin.[15] The requirements for pure oxygen, super-stoichiometric sodium hydroxide and high temperature/pressure are clearly drawbacks to the Chornet approach and Song's method also requires high temperature and oxygen pressure.

In pursuit of a milder oxidative degradation of lignin, using air as the oxidant, we report herein the first comparative studies of catalyzed oxidative lignin depolymerisation using oxovanadium(V) catalysts **1** and **2** and CuOTf/TEMPO catalyst **4**. We also assessed previously reported catalysts **3**[30], **5**[31] and **6**[42], as well as the benchmark method of Chornet,[7] under standardized conditions, insofar as possible. New bifuntional vanadium catalyst **7** which incorporates a tethered pyridine base to promote an internal BARD mechanism is also studied. We evaluated the depolymerisation using GPC, quantitative-HSQC and ^{31}P NMR spectroscopy (after derivatisation to phosphite esters).

2 Materials and Methods

Preparation of Lignin Substrate

The organosolv lignin (Lignol) was obtained by extraction of mixed-hardwood[45] with 1:1 (v/v) ethanol/water. Before use, volatile components were removed by heating under *ca.* 10 mTorr vacuum at 150 ^oC for 4 h.

Preparation of BPAMP(V^V)(O)(O^iPr) (7)

To a solution of H_2BPAMP (420 mg, 0.771 mmol) in 3 mL of CH_2Cl_2 was added dropwise a solution of $V(O)(O^iPr)_3$ (207 mg, 0.849 mmol) in 1 mL of CH_2Cl_2. A rapid change of colour was observed to dark-purple from light-green. The reaction was stirred under nitrogen for 18 hours, then the solvent was removed under vacuum and replaced by acetonitrile. The mixture was placed at -35 °C for 18 h and the precipitate was washed with cold acetonitrile. The purple filtrates were placed at -35 °C for 2 hours and then filtered again through Celite, resulting in a separation of both isomers. The *trans* isomer was isolated as a dark purple solid (184 mg, 40% yield) by evaporating the acetonitrile filtrates. **7a**: ^{1}H NMR (CD$_3$CN, 300 MHz): δ 8.97 (d, 1H, J = 5.8 Hz, Ar), 8.45 (s, 1 H, Ar), 7.49 (td, 1H, J = 7.7, 1.7 Hz, Ar), 7.09 (d, 2H, J = 2.4 Hz, Ar), 7.03 (d, 2H, J = 2.4 Hz, Ar), 6.69 (d, 1H, J = 7.7 Hz, Ar), 5.44 (sept, 1H, J = 6.0 Hz, V-OC*H*) 4.46 (d, 2H, J = 12.4 Hz, Ar-C*H*$_2$), 3.77 (s, 2H, pyr-C*H*$_2$), 3.45 (d, 2H, J = 12.4 Hz, Ar-C*H*$_2$), 1.36 (d, 6H, J = 5.8 Hz, (C*H*$_3$)$_2$), 1.31 (s, 18H, ^{t}Bu), 1.24 (s, 18H, ^{t}Bu); ^{13}C{^{1}H} NMR (CD$_3$CN, 75.5 MHz): δ 156.5, 156.5, 152.2, 141.7, 139.1, 125.2, 124.9, 122.5, 62.1, 55.6, 34.6, 33.9, 30.8, 29.3; ^{51}V NMR (CD$_3$CN, 78.9 MHz): -473.9 ppm (s); IR (NaCl plate): $\nu_{V=O}$ = 918 cm^{-1}; The *cis* isomer was isolated as a brown solid (92 mg, 18% yield) from filtration of the cold solution of the isomer mixture. **7b**: ^{1}H NMR (CD$_3$CN, 300 MHz): δ 8.55 (d, 1H, J = 5.0 Hz, Ar), 7.41 (dt, 1H, J = 1.7, 7.7 Hz, Ar), 7.04 (m, 4H, Ar), 6.77 (m, 1H, Ar), 5.97 (sept, 1H, J = 6.5 Hz, V-OC*H*), 4.69 (d, 2H, J = 13.4 Hz, Ar-C*H*$_2$), 3.91 (s, 2H, pyr-CH$_2$), 3.84 (d, 2H, J = 13.4 Hz, Ar-C*H*$_2$), 1.64 (d, 2H, J = 6.1 Hz, (C*H*$_3$)$_2$), 1.26 (s, 18H, ^{t}Bu), 1.23 (s, 18H, ^{t}Bu). Due to rapid isomerization, ^{13}C NMR for **7b** was not possible. ^{51}V NMR (CD$_3$CN, 78.9 MHz): -514.1 ppm (s). IR (NaCl plate): $\nu_{V=O}$ = 960 cm^{-1}; Anal. Calcd for $C_{39}H_{57}O_4N_2V$: C 70.04 H 8.59 N 4.19; Found: C 69.98 H 8.60 N 4.26.

Procedure for the Catalytic Oxidation of Organosolv Lignin

The catalytic oxidation reactions involving catalysts **1**, **2**, **4, 5** and **7** (a mixture of isomers **7a** and **7b** was used) were carried out in a 24-well plate reactor (Freeslate) under 8.2 atm of synthetic air (8% O_2 in Ar), at 100 °C with constant stirring (400 rpm). After 18 h, 400 μL aliquots were removed and analyzed by GPC, q-HSQC and ^{31}P NMR spectroscopy (see Electronic Supplementary Information (ESI) for details). Lignin oxidation/depolymerisation reactions utilizing oxovanadium(V) complexes **1** and **2** were carried out using 10 wt. % catalyst and 10 wt. % base (trimethylamine (Et$_3$N) or diisopropylamine (DIPA)). The CuOTf/TEMPO catalyst **4**, consisted of 10 wt. % CuOTf, 10 wt. % TEMPO and 100 wt. % 2,6-lutidine in dimethylformamide (DMF), the mixture was then heated at 100 °C for 18 h.[26] For catalysts **3**, **5** and **6**, we used the reported conditions (solvents, temperature and catalyst loading) in order to avoid variability in the catalyst performance, although O_2 pressure in our experiment was lower than that reported for the Co catalyst. For catalyst BPAMP(V^V)(O)(O^iPr) **7**, 10 wt. % catalyst was used for all experiments. The oxovanadium(V) catalyst **3** (10 wt. %) was tested in an 8:1 (v/v) ethyl acetate (EtOAc)/tetrahydrofuran (THF) mixture and heated at 80 ^oC for 24 h in a sealed vial under atmospheric pressure of air. For the metal-free system **5**, we used 5 wt. % 4-acetamido-TEMPO, 10 wt. % concentrated HNO_3 and 10 wt. % concentrated HCl (37%) in 19:1 (v/v) CH_3CN/H_2O. The reaction mixture was then heated at 65 ^oC using 8.2 atm of synthetic air for 24 h. For catalyst **6**, we used 10 wt % [Co] complex, 100 wt. % pyridine in 1:1 (v/v) MeOH/ dimethyl sulfoxide (DMSO), at 100 ^oC with 8.2 atm of synthetic air for 18 h. The Chornet method (135 wt. % NaOH, 5 wt. % $CuSO_4$ and 0.5 wt. % $FeCl_3$ heated at 160 °C with 8.2 atm of synthetic air for 18 h) was modified using THF as solvent instead of water in order to facilitate the GPC analysis (Extraction of the aqueous mixture with organic solvents such as ethyl acetate gave non-representative samples). While the amount of soluble base is reduced, both metal salts dissolved readily under these basic conditions.

GPC Analysis

The GPC instrument was calibrated using polystyrene standards although these have been shown to be of limited value for absolute MW determination of branched macromolecules such as lignin (see ESI for details).[46,47] We thus opted for a qualitative comparison of the data from the control and catalytic reactions, in which the lignin was subjected to identical conditions (solvent, temperature, *etc.*) without some or all components of the catalyst. Average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (PDI) for the control and the catalytic experiments are reported in Table 1. For GPC analysis an aliquot of the reaction mixture was evaporated and dissolved in THF.

NMR Experiments

For q-HSQC, an aliquot of the reaction mixture was evaporated under reduced pressure and dissolved in 1 mL of DMSO-d_6. A modified version of the method reported by Heikkinen and co-workers was used.[48] All the structural units of the lignin substrate were assigned based on the lignin database and reported literature.[49,50] q-HSQC NMR spectra of the control experiments in different solvents (EtOAc, *n*-butyl acetate, DMF, MeOH/DMSO and DMSO) showed no real changes in the lignin in the oxygenated aliphatic or aromatic regions.

For ^{31}P NMR spectroscopic analysis 25 mg of the evaporated aliquot of the reaction mixture was dissolved in 0.5 mL of pyridine/$CDCl_3$ (1.6:1) and 50 µL 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) was added along with 6 µL cyclohexanol as internal standard.[51]

3 Results and Discussion

GPC Analysis

Control experiments with organosolv lignin substrate and Et_3N yielded a broad peak in the GPC corresponding to a polystyrene MW of *ca.* 870 Da with several lower molecular weight components eluting at longer times (Figure 3, Table 1). While use of catalyst **1** has a clear effect on reducing the average molecular weight, the best performance was obtained using catalyst **2** which gives the largest MW shift and a major increase in the lower molecular weight components (Mw = 758 Da *vs.* Mw = 575 Da). The lower performance of catalyst **1** can be explained in part by its reaction with water to form less active dioxo anionic species, as observed in previous studies.[52] Catalysts **1** and **2** were tested in EtOAc, THF and *n*-butyl acetate as solvents and ethyl acetate was found to be most effective for depolymerisation of the organosolv lignin.

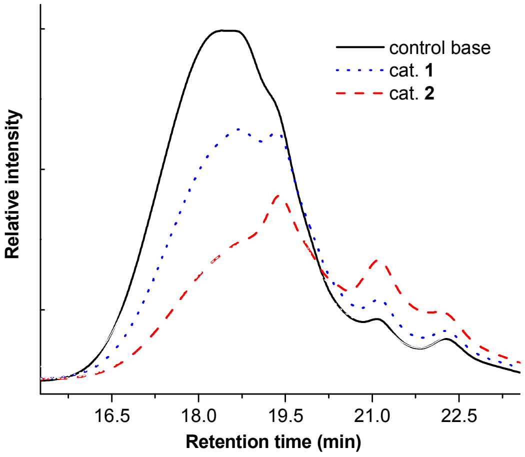

Figure 3. GPC data (THF solvent, elution rate: 1 mL/min, 245.5 nm detection) for the catalytic oxidation of organosolv lignin using **1** (10 wt. % **1** and 10 wt. % Et_3N) and **2** (10 wt. % **2** and 10 wt. % Et_3N) compared with the control experiment (10 wt% Et_3N). For all runs: solvent = EtOAc; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

Table 1. GPC data for different catalyst systems and control experiments (THF solvent, elution rate: 1 mL/min, 254.4 nm detection).

Entry	Experiment	Mw (Da)	Mn (Da)	PDI
1	Organosolv lignin[a]	2526	850	2.97
2	**1**[b]	758	429	1.80
3	**2**[b]	575	324	1.77
4	Control (no catalyst) for **1** and **2**[b]	870	525	1.66
5	**3**[c]	808	411	1.97
6	Control (no catalyst) for **3**[c]	1085	456	2.38
7	**4**[d]	413	229	1.80
8	Control in DMF (no Cu)[d]	817	347	2.36
9	Control TEMPO and 2,6-lutidine (no Cu)[d]	493	239	2.06
10	**5**[e]	502	330	1.52
11	Control (no 4-acetamido-TEMPO) for **5**[e]	606	452	1.34
12	**6**[f]	760	242	3.14
14	Control (no catalysts) for **6**[f]	723	241	3.00
15	**7**[g]	1110	564	1.96
16	Chornet method[h]	835	445	1.88

[a] For untreated organosolv lignin, M_w = 1606 Da and M_n = 637 Da. [b] 10 wt. % catalyst and 10 wt. % Et_3N. For all runs: Solvent = EtOAc; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h. [c] 10 wt. % catalyst. For all runs: solvent = 8:1 (v/v) EtOAc/THF; temperature = 80 °C; sealed vial under atmospheric pressure of air; reaction time = 18 h. [d] 10 wt. % catalyst, 10 wt. % TEMPO and 100 wt. % 2,6-lutidine. For all runs: solvent = DMF; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h. [e] 5 wt. % 4-acetamido-TEMPO, 10 wt. % HNO_3 (70%) and 10 wt. % HCl (37%). For all runs: solvent = 19:1 (v/v) CH_3CN/H_2O; temperature = 65 °C; pressure of synthetic air = 8.2 atm;

reaction time = 24 h. [f] 10 wt. % catalyst and 100 wt. % pyridine. For all runs: solvent = 1:1 (v/v) MeOH/DMSO; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h. [g] 10 wt. % catalyst. For all runs: Solvent = EtOAc; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h. [h] 135 wt. % NaOH, 5 wt. % $CuSO_4$ and 0.5 wt. % $FeCl_3$. For all runs: solvent = THF; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

The control reaction in DMF solvent led to a more pronounced bimodal distribution and while addition of catalyst system **4** (CuOTf/TEMPO/2,6-lutidine in DMF) effected a modest shift to lower molecular weights, the major difference lies in the significant increase in the amount of the lower molecular weight component eluting at *ca.* 21 min (Figure 4). However, nearly identical results were obtained when only TEMPO and 2,6-lutidine were present (*i.e.*, without CuOTf), suggesting that radical processes, not mediated by the metal, are contributing to the depolymerisation process (Table 1).

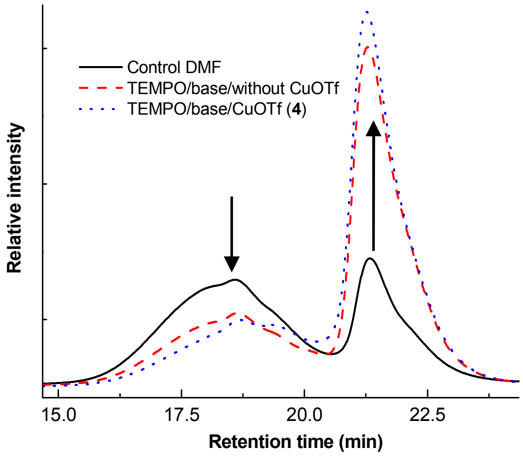

Figure 4. GPC data (THF solvent, elution rate: 1 mL/min, 245.5 nm detection) for the catalytic oxidation of organosolv lignin using **4** (10 wt. % CuOTf, 10 wt. % TEMPO and 100 wt. % 2,6-lutidine), compared with the control experiment (no catalyst, TEMPO or base) and an experiment with TEMPO and base only. For all runs: solvent = DMF; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

In contrast to the results using catalysts **1** and **2**, oxovanadium catalyst **3** showed the same features and retention times as the control experiment. This catalyst can operate anaerobically, exhibiting a preference for C_{alkyl}-O bond cleavage, and the mechanism is thought to proceed through aryloxy radicals;[27] perhaps these radicals initiate reactions leading to new polymeric networks, precluding significant molecular weight reduction for the organosolv lignin used in the present study.

Metal-free catalyst **5** and cobalt complex **6** showed also no difference in the retention times between the catalytic and control experiments (see Table 1 and ESI). Previous reports showed that catalyst **5** oxidizes benzylic C-H bonds in lignin models.[31] Here, we have observed the same effect in terms of lack of decrease of the molecular weight on organosolv lignin. The lower lignin depolymerisation activity that we observed for catalyst **6** (*vs.* previous report using aspen lignin) may be explained by our replacement of 3.4 atm O_2 in the original method with synthetic air (8% O_2 in Ar, 8.2 atm). Catalyst **6** is also sensitive to the amount of free phenolic moieties in lignin; lower activity for C_{aryl}-C_{alkyl} bond cleavage has been observed for low phenolic-containing lignin.[42]

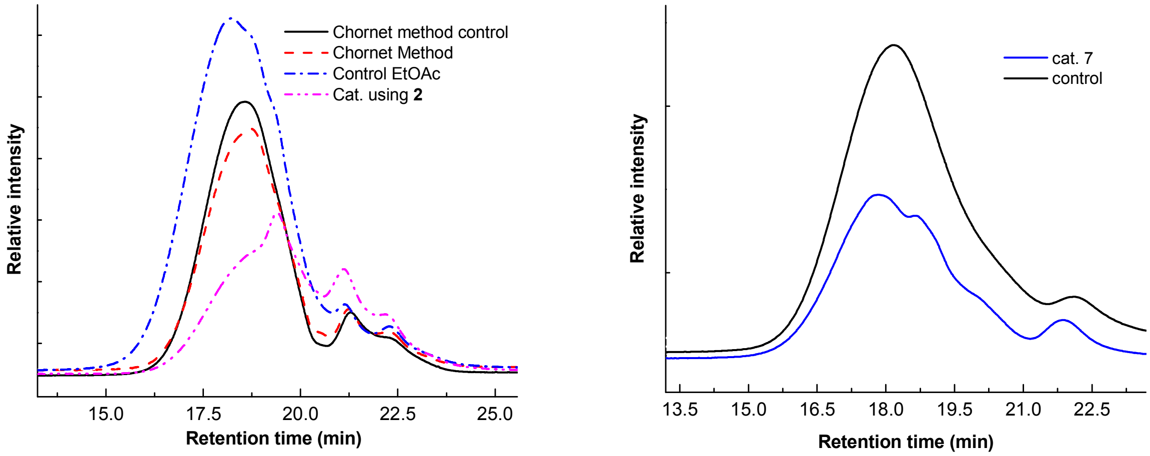

Figure 5. GPC data (THF solvent, elution rate: 1 mL/min, 245.5 nm detection) (left) for the catalytic oxidation of organosolv lignin using the Chornet method (THF, 135 wt. % NaOH, 5 wt. % $CuSO_4$ and 0.5 wt. % $FeCl_3$), Chornet control (THF and 135 wt. % NaOH) and catalyst **2** (EtOAc, 10 wt. % **2**, 10 wt. % Et_3N). (Right) catalytic oxidation of organosolv lignin using **7** (EtOAc, 10 wt. % **7**) and control (EtOAc). For all runs: temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

We then compared the performance of catalyst **2** to the benchmark method reported by Chornet and co-workers (Figure 5, left).[7] Use of the stronger base (135 wt. % NaOH in the Chornet control) gave a narrower MW distribution than heating the lignin in pure EtOAC or with Et_3N in EtOAc (as seen in Figure 3). The GPC chromatograms revealed, however, only minimal depolymerisation when the Chornet method was used (Cu and Fe salts plus NaOH). Indeed, of the catalysts evaluated in this work, only catalyst **2**, operating under synthetic air pressure, induced a significant decrease in the molecular weight of the organosolv lignin substrate.

The bifunctional oxovanadium catalyst **7**, showed a significant decrease in the molecular weight in EtOAc without the need for additives (Figure 5, right). The incorporated pendant pyridine in the ligand scaffold acts as the external base. As reported previously, analogous oxovanadium catalysts require base for both the initial alcohol oxidation and the subsequent C-C bond cleavage.

q-HSQC NMR Analysis

The q-HSQC NMR spectroscopic analysis allows for the evaluation of the reactivity of the various linkages (Figure 6) in the organosolv lignin when subjected to the different homogeneous catalysts. Looking first at the aromatic nucleus, catalytic oxidation of organosolv lignin using catalyst **2** (EtOAc, 10 wt. % **2** and 10 wt. % Et_3N) converts all of the syringyl units **S** and most of the guaiacyl units **G** to the corresponding carbonyl-containing moieties **S'**, **S''** and **G'**; the **G'2**:**G2** ratio increased to 0.74 from 0.16 in the control (10% base with no catalyst; Figure 7). The small amount of hydroxyphenyl units H were also converted. Further details of the oxidative lignin depolymerisation are provided by assessment of the aliphatic linkages. Correlations due to the major structural units **A-D** (δ 3.0 to 6.0 ppm in the ^{1}H NMR spectrum) that persisted on heating the organosolv lignin for 18 h with 10 wt. % base all disappeared on treatment with catalyst **2** under the same conditions. At shorter reaction times (4 h; Figure S22) correlations due to **A-D** were again absent while those in the aromatic region showed a lower

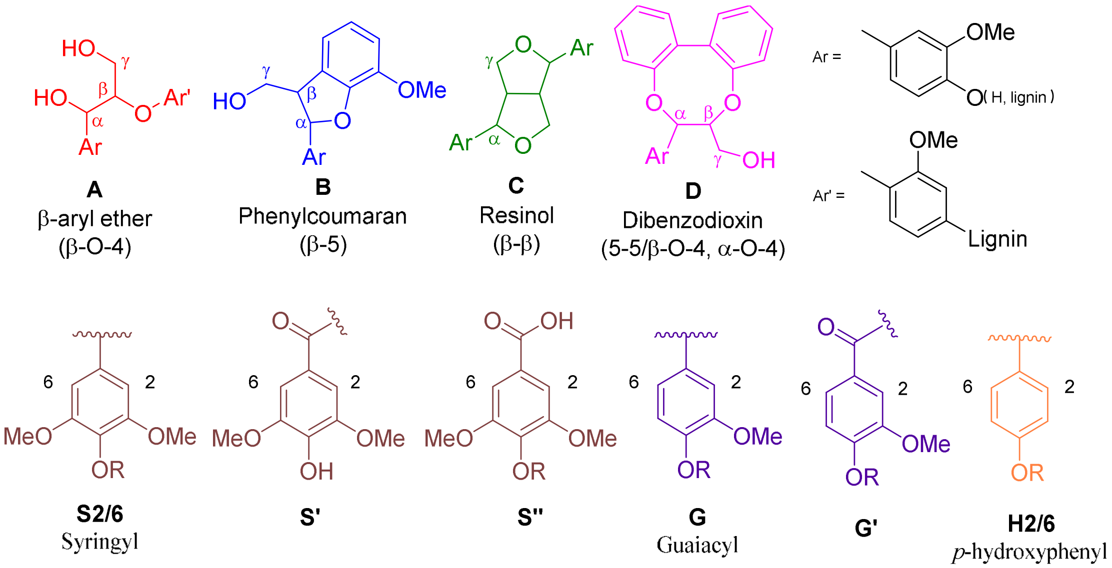

Figure 6. Lignin linkages observed by q-HSQC NMR.

degree of oxidation (**S’** + **S’’**: **S2/6** = 0.90 and **G’2:G** = 0.04).

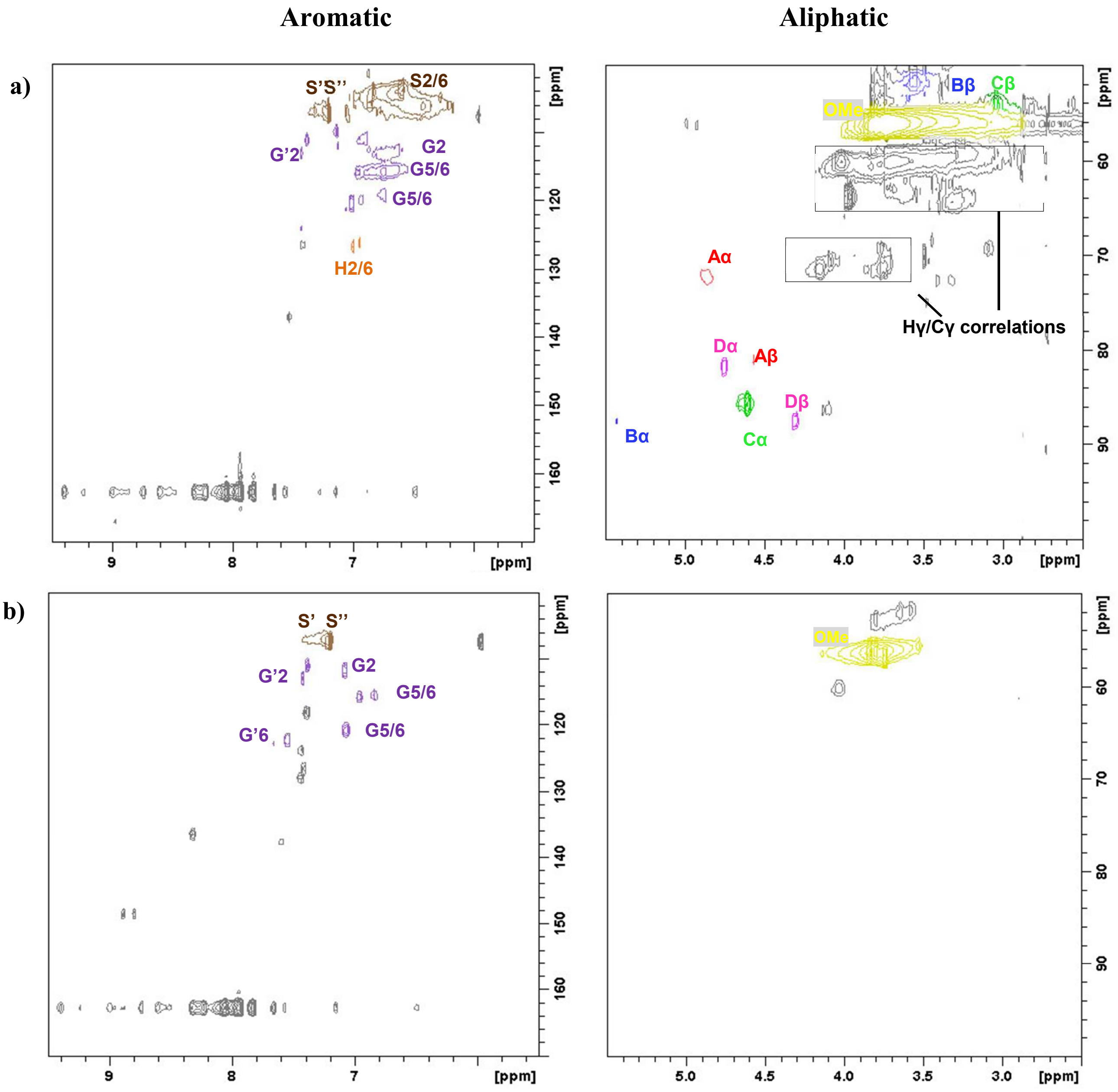

Figure 7. q-HSQC NMR spectra of organosolv lignin for: (a) control experiment (no catalyst) and b) catalytic oxidation using 10 wt. % **2** and 10 wt. % Et_3N. For all runs: solvent = EtOAc; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time = 18 h.

As indicated by the GPC and q-HSQC (Figure S13) data, catalyst **1** showed reduced activity (*vs.* **2**) for the oxidative depolymerisation of organosolv lignin. Previous work showed that reaction of **1** with water (aerobic oxidation by-product) gives a less-active anionic dioxovanadium(V) complex.[52] Indeed, the ^{51}V NMR spectrum after the catalytic run revealed a strong signal at -522 ppm due to this complex.[53] Finally, we note that use of catalyst **2** without base resulted in no change for correlations due to **A-D** in the q-HSQC spectrum, confirming the importance of the BARD pathway for benzylic alcohol oxidation.

On the other hand, the copper catalyst **4** resulted in the breakdown of **A**, **B**, **C** and **D** in addition to **S2/6** being oxidized to mostly **S'** and **S''**, the ratio increased to 0.73 from 0.26 in the control (no catalyst) (Figures 8 and S20). However, paramagnetic interference from residual copper (II) species hindered further investigation on this catalyst.

Similar to experiments with copper catalyst **4**, results from the Chornet method (paramagnetic Cu and Fe salts) prevented us from obtaining noise-free and well-resolved q-HSQC spectra (Figure S27). Filtration through various supports (silica, alumina, Celite) resulted in non-representative samples of the oxidized organosolv lignin. However, the GPC traces showed that the molecular weight was not decreased significantly in either the Chornet control experiment (only base) or the Chornet method (base and metal salts) (Figure 5).

Under our reaction conditions oxovanadium catalyst **3** was only able to oxidize the β-O-4 structural unit **A** in the oxygenated aliphatic region (Figure S18). Correlations corresponding to **H2/6** in the aromatic region disappeared while other structural units remained roughly intact. This is in agreement with the C-O bond cleavage mechanism proposed for this catalyst.[27, 30]

Metal-free catalyst **5** cleaved the major structural units **A**, **B**, **C** and **D,** increasing the oxidized syringyl **S** and guaiacyl **G** units ((**S''** + **S'**)/**S2/6** to 0.82 from 0.76) (see ESI). However, the control experiment (without 4-acetamido-TEMPO) also demonstrated some oxidation of organosolv lignin under our conditions (Figure S24). Contrary to previous reports,[31] we did not observe oxidized **A'** units under our reaction conditions.

As suggested by the GPC data, Co catalyst **6** was not able to oxidize organosolv lignin at the oxygen concentrations employed in this work (Figure S25). All of the major structural units in the oxygenated aliphatic region remained intact and the aromatic region remained similar to organosolv lignin spectrum. The ratios of **S''** + **S'** / **S2/6** and **G'2** / **G2** were almost identical to those in the original organosolv lignin: **S''** + **S'** / **S2/6** = 0.09 and, **G'2** / **G2** = 0.02.

Bifunctional oxovanadium catalyst **7** showed a large decrease on the major units **A**, **B**, **C** and **D**, and most of the aromatic region. The degree of depolymerisation shown by **7** is comparable to catalyst **2**. As demonstrated by GPC, the tethered base in **7** increased the performance for C-C and C-O bond cleavage compare with catalysts **1** and **2**. Detail mechanism of catalyst **7** is currently under investigation in our laboratories.

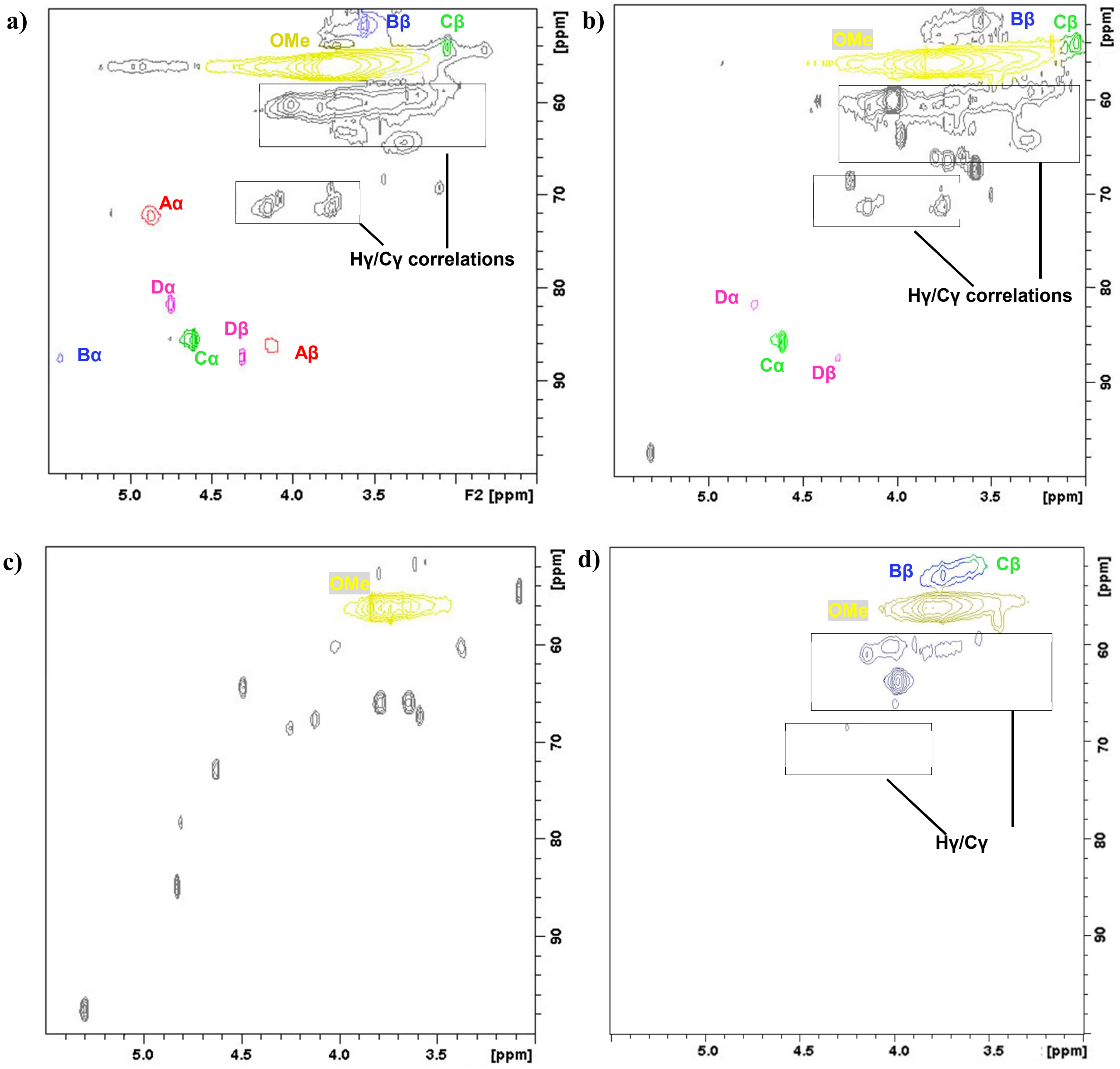

Figure 8. q-HSQC aliphatic regions of (a) organosolv lignin and oxidized material using catalysts (b) **3**, (c) **4** and (d) **7** (see experimental section for reaction conditions).

Quantitative ^{31}P NMR Spectroscopy

Phosphitylation has been shown to be a useful tool for characterizing the various types of aromatic, aliphatic and carboxylic acid O-H bonds in lignin (Figure 9).[51] The control experiment using 10 wt. % base (no catalyst) showed similar composition to the organosolv lignin (Table 2). As expected, concentrations of aliphatic and especially phenolic O-H units (but not carboxylic acids) decreased substantially after treatment of the organsolv lignin with catalyst **2** + Et_3N.

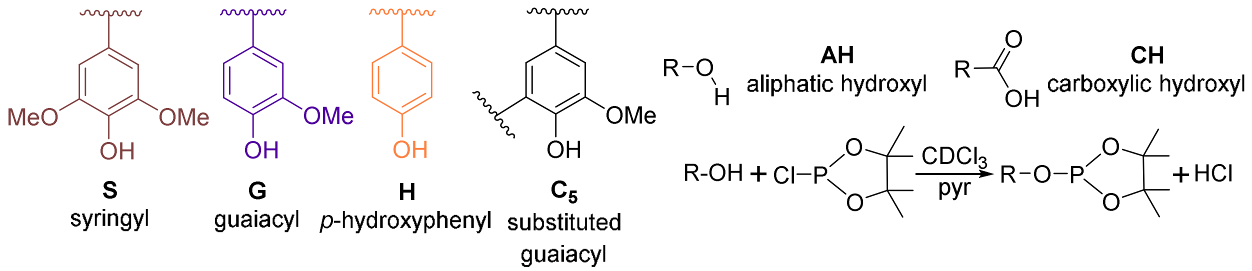

Figure 9. Hydroxyl-containing lignin structural units characterized by ^{31}P NMR spectra of derived phosphite esters.

Table 2. Concentrations (mmol g^{-1} substrate) of lignin-derived phosphite esters as determined by quantitative $^{31}P\{^1H\}$ NMR spectroscopy

$\delta_{(ppm)}{}^{a}$	$\mathbf{G}_{(139.0-140.5)}$	$\mathbf{H}_{(137.5-138.8)}$	$\mathbf{C}_{\mathbf{5}(141.0-144.5)}$	$\mathbf{AH}_{(146.1-150.0)}$	$\mathbf{CH}_{(133.6-136.0)}$
Organosolv lignin	2.68	0.59	8.00	3.29	1.00
Lignin + base control[b,d]	2.25	0.57	6.56	2.08	1.62
Catalyst **2**[c,d]	0.31	0.12	0.72	0.36	1.02
Catalyst **7**[e]	1.75	0.58	5.04	1.63	1.15

[a] Syringyl units **S** are omitted due to overlap with substituted guaiacyl $\mathbf{C_5}$ units at 142.7 ppm. [b] Control experiment using 10 wt. % Et_3N. [c] Catalytic oxidation using 10 wt. % **2** and 10 wt. % Et_3N. [d] For all runs: solvent = EtOAc; temperature = 100 °C; pressure of synthetic air = 8.2 atm; reaction time: 18 h. [e] Catalytic oxidation using 10 wt. % **7**.

We have observed previously that catalyst **2** readily cleaves C_{alkyl}-C_{aryl} bonds in β-O-4[23] and β-1[24] phenolic lignin models.

Catalyst **7** showed similar decreased in the lignin linkages as catalyst **2**, however, lower activity is observed as expected by the GPC and 2D NMR (see above sections).

4 Conclusions

Of the catalysts tested in this work, the bis(8-oxy-quinoline) oxovanadium and bis(phenolate)pyridine oxovanadium catalyst **2** and **7**, respectively, showed the best activity for depolymerisation/oxidation of organosolv lignin, as evidenced by GPC and q-HSQC NMR spectroscopy. A substantial decrease in the molecular weight, quantitative conversion of four common aliphatic linkages, and an increase in oxidized **S** and **G** units, were observed compared to the control experiment. Moreover, significant conversion of phenolic and aliphatic hydroxyls was demonstrated by ^{31}P NMR spectra of derived phosphite esters.

In comparing the performance of several homogeneous catalysts for the aerobic oxidation of organosolv lignin, several additional observations can be made:

1) Whereas copper catalysts **4** exhibit complementary selectivity to oxovanadium catalysts, **1** and **2** in aerobic oxidation of simple lignin models, the former suffers from poor carbon balance with more complex models which translates to inefficient depolymerisation with lignin extracts, likely due to radical recombination. DMF solvent toxicity would also be a drawback for practical industrial applications;
2) Previous work has demonstrated that oxovanadium catalysts such as **3** and **1** in the absence of base tend to favour C-O *vs.* benzylic C-H bond cleavage in a variety of phenolic and non-phenolic lignin models. In these cases, however, generation of phenoxy radicals appears to also be deleterious to achieving efficient depolymerisation of lignin extracts.
3) While both metal-free acetamido-TEMPO catalyst **5** in an acidic medium and oxovanadium catalyst **2** with added base show excellent selectivity for benzylic C-H bond cleavage to the ketone, only catalyst **2** is then able to cleave the ketone C_α-C_β bond, allowing for significant depolymerisation of lignin extracts.
4) Although the detailed mechanism of ketone C_α-C_β bond cleavage is still unclear, preliminary experiments show that this reaction is also promoted by added base.[54] A new generation of base-tethered ligands, such as **7**, afford more efficient and selective oxovanadium catalysts for aerobic oxidation of lignin. Further tuning of the pendant base, however, is needed to achieve improved lignin depolymerisation.

As new exciting results on tandem redox[37,38] and biocat-chemcat[20] approaches to lignin valorisation are being disclosed, a selective and productive homogeneous oxidation catalyst could be a key component.

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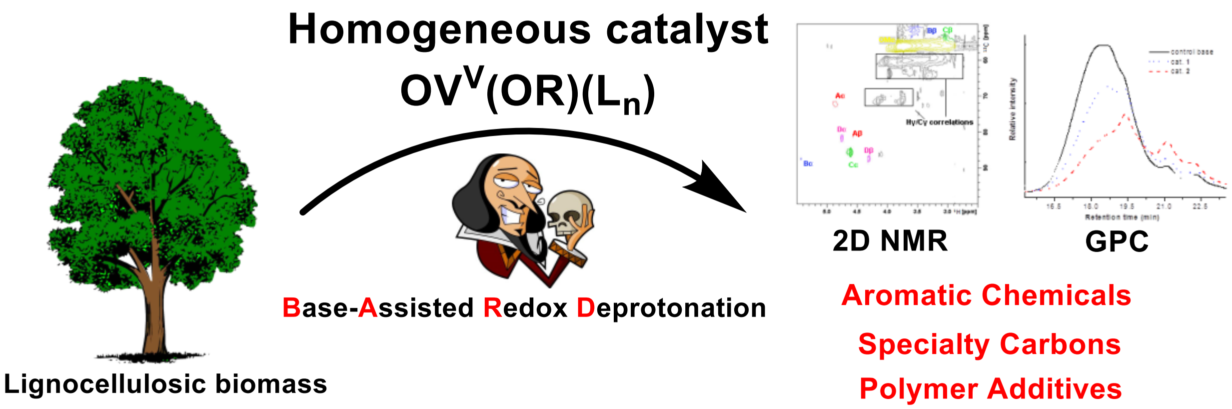

Homogeneous catalyst

$OV^V(OR)(L_n)$

Base-Assisted Redox Deprotonation

Lignocellulosic biomass

2D NMR

GPC

Aromatic Chemicals

Specialty Carbons

Polymer Additives