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Selective Utilization of Methoxyl Group in Lignin to Produce Acetic Acid

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Abstract: Selective transformation of lignin into a valuable chemical is of great importance and challenge due to its complex structure. Herein, we propose the strategy for the transformation of methoxyl group (-OCH_3) which is abundant in lignin into pure highly valuable chemicals. As an example to apply this strategy, the route to produce acetic acid with high selectivity by selective conversion of methoxyl group of lignin was developed. It was demonstrated that the methoxyl group in lignin could react with CO and water to generate acetic acid over $RhCl_3$ in the presence of promoter. The conversions of methoxyl group in the kraft lignin and organosolv lignin could reach 87.3% and 80.4%, respectively, and no by-product was generated. This work opens the way to produce pure chemicals using lignin as the feedstock.

Biomass resources are abundant and renewable[1]. Utilization of biomass as raw materials to produce useful chemical compounds and fuels can liberate us from the reliance on fossil resource, and many researches have been conducted[2]. Lignocellulose is the most abundant form of biomass, with an annual production of around 170 billion metric tons[3], about 20% of which is lignin. Large amount of lignin is produced in the pulp and paper industry as by-product. Simply burning lignin is increasingly recognized as a waste of its potential[4], and efficient utilization of lignin is of great importance for sustainable development of our society. Over the past few decades, researches on the production of alternative fuels, platform compounds,value-added chemicals, and materials from lignin have grown rapidly[5]. Overall, utilization of lignin is mainly at the research stage, and there have been few industrial applications[4b]. So far, general routes to convert lignin into valuable chemicals and fuels focus on breaking it into low-molecular-weight compounds[6], which are further converted into valuable products[7]. In addition, many researches have been carried out to transform lignin model compounds into chemicals or fuels[8]. Although satisfactory results have been achieved with different model compounds, the catalytic systems are usually not efficient for conversion of real lignin. Moreover, it is a great challenge to get a chemical with high selectivity because of the complex structure of lignin. The depolymerized product usually contains numerous compounds.

Lignin is abundant of methoxyl group[1a], as shown in Figure S1. However, selective utilization of methoxyl group in lignin to produce valuable compounds has not received attention. Acetic acid is an important commodity chemical with a broad range of applications, such as producing vinyl acetate monomer (VAM) and aceticanhydride, and as a solvent for purified terephthalic acid (PTA) production[9]. Currently, acetic acid is produced in industry mainly by carbonylation of methanol[10].

Herein, we propose the strategy that a specified class of group (methoxyl group) in lignin is transformed into highly valuable pure chemical. As an example, the route to produce acetic acid by selective conversion of methoxyl group of lignin was developed. It was demonstrated that 87.3% and 80.4% of methoxyl group in the kraft lignin and organosolv lignin could be transformed into acetic acid, respectively. The reaction could be carried out at 120 ºC, which was lower than that for the carbonylation of methanol to acetic acid (about 150–200 ºC)[11].

Kraft lignin, which is a by-product of paper industry, was first studied. The lignin contained 11.0 wt% of methoxyl group determined by the iodine stoichiometry titration method[12], and the apparatus and procedures are discussed in Supplementary Information (Figure S2 and Figure S3). The catalyst system for the production of acetic acid from the lignin was explored. It is known that Rh-based catalyst was efficient for carbonylation reaction, and metal halides can cleave ether bond at appropriate condition[13]. Using $RhCl_3$ as the catalyst, the performances of different metal halide promoters and solvents were studied, and the results obtained at different conditions are presented in Table 1. In this work, the yield of acetic acid is defined as the percentage of the methoxyl group in the lignin that converted into acetic acid. The output is defined as the grams of acetic acid produced from per gram of lignin. No gaseous product was generated in the reaction.

LiI was efficient promoter in the presence of $LiBF_4$, and the activity of LiBr was much lower, while LiCl, NaI, KI, CsI were not effective for the reaction (Table 1, entries 1-6). Solvents often affect a reaction significantly[14]. The reaction did not occur in water or DMSO (Table 1, entries 7 and 8). Acetic acid was produced in toluene, cyclohexane, benzene and chlorobenzene (Table 1, entries 1 and 9-11), and toluene was the optimum organic solvent with a yield of 78.8%, *i.e.*, 0.168 g of acetic acid could be produced from 1 g of lignin considering that lignin contained 11.0 wt% of methoxyl group. Acetic acid is the only product (the NMR spectra are given in Figure S4), and the mass balance was 99.7% at this condition (See supporting information for details). $LiBF_4$ was necessary for the reaction and no acetic acid was produced in the absence of $LiBF_4$ (Table 1, entry 12). Ionic liquids (ILs) have been widely used as reaction solvents[15]. The reaction was also conducted in different ILs (Table 1,

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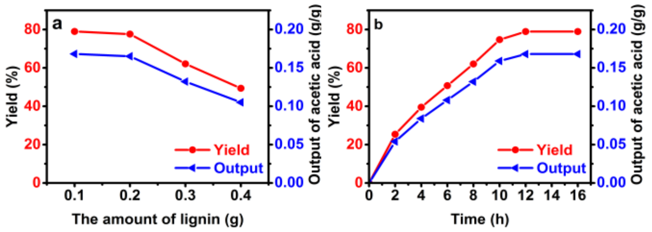
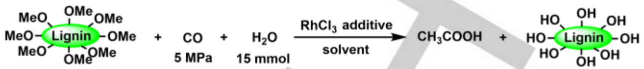


Figure 1. Effects of amount of lignin (a) and reaction time using 0.2 g kraft lignin (b) on the reaction. Reaction conditions: 0.01 g $RhCl_3$, 2 mmol LiI, 1 mmol $LiBF_4$, 5 MPa CO, 1.5 mL toluene, 15 mmol H_2O, 140 ºC, 12 h.

entries 13-17). The reaction could proceed smoothly without adding $LiBF_4$ in $HMimBF_4$ (1-hexyl-3-methylimidazolium tetrafluoroborate) and $BMimBF_4$ (1-butyl-3-methylimidazolium acetate), which contains BF_4^-. The yield of acetic acid was 83.1% in $HMimBF_4$, *i.e.*, 0.177 g of acetic acid could be produced from 1 g of lignin (Table 1, entry 13). The yield of acetic acid was 83.7% in $BMimBF_4$ (Table 1, entry 14). However, no acetic acid was generated in BMimCl (1-butyl-3-methylimidazolium chloride) and BMimOAc (1-butyl-3-methylimidazolium acetate) without $LiBF_4$ (Table 1, entries 15 and 16). The reaction also occurred in BMimCl (1-butyl-3-methylimidazolium chloride) with $LiBF_4$, and 74.7% yield of acetic acid was obtained, *i.e.*, 0.159 g of acetic acid could be produced from 1 g of lignin (Table 1, entry 17). The results further indicated that BF_4^- was necessary for the reaction. The blank test demonstrated that acetic acid could not form without lignin (Table 1, entry 18). We also carried out the reaction without $RhCl_3$, and acetic acid was not produced, but CH_3I was yielded (Table 1, entry 19). It can be known from Entries 12 and 19 that BF_4^- could catalyze the reaction of lignin and LiI to form CH_3I, which is an intermediate for the generation of acetic acid.

The effects of different factors on the reaction were studied (Figure 1 and Figure S5). The effect of amount of lignin on the yield and output is demonstrated in Figure 1a. The yield and output of acetic acid decreased continuously with increasing amount of lignin. This is understandable because the yield and output was on the lignin basis (Figure 1a). The yield and output of acetic acid increased gradually with reaction time prolonging at beginning, and became almost unchanged after 12 h (Figure 1b). The effects of reaction temperature, CO pressure and the amount of water on the yield and output of acetic acid were also studied, and results are given in Figure S5. No acetic acid was produced at 100 ºC and the yield of acetic acid was only 8.4% at 110 ºC, *i.e.*, only 0.018 g of acetic acid could be produced from 1 g of lignin. The yield of acetic acid increased sharply to 55% at 120 ºC, while it increased slowly as the temperature increased from 140 ºC to 160 ºC. At 160 ºC, the yield reached 87.5%, *i.e.*, 0.186 g of acetic acid could be produced from 1 g of lignin (Figure S5a). The yield and output of acetic acid increased continuously with increasing CO pressure at beginning, and was independent of the pressure after 5 MPa (Figure S5b). Water was necessary for the reaction, but too much water in the reaction system was not favorable to the reaction (Figure S5c).

Table 1. Results for the reaction of lignin, CO and H_2O to acetic acid in different catalyst systems.[a]



Entry	Solvent	Additive	Output of acetic acid (g/g)[b]	Yield of acetic acid (%)[c]
1	toluene	LiBr+$LiBF_4$	0.045	21.1
2	toluene	LiCl+$LiBF_4$	0	0
3	toluene	LiI+$LiBF_4$	0.168	78.8
4	toluene	NaI+$LiBF_4$	0	0
5	toluene	KI+$LiBF_4$	0	0
6	toluene	CsI+$LiBF_4$	0	0
7	H_2O	LiI+$LiBF_4$	0	0
8	DMSO	LiI+$LiBF_4$	0	0
9	cyclohexane	LiI+$LiBF_4$	0.165	77.5
10	benzene	LiI+$LiBF_4$	0.114	53.5
11	chlorobenzene	LiI+$LiBF_4$	0.108	50.7
12	toluene	LiI	0	0
13	$HMimBF_4$	LiI	0.177	83.1
14	$BMimBF_4$	LiI	0.174	81.7
15	BMimCl	LiI	0	0
16	BMimOAc	LiI	0	0
17	BMimCl	LiI+$LiBF_4$	0.159	74.7
18[d]	toluene	LiI+$LiBF_4$	0	0
19[e]	toluene	LiI+$LiBF_4$	0	0

[a] Reaction conditions: 0.01 g $RhCl_3$, 2 mmol metal halide, 1mmol $LiBF_4$, 0.2 g kraft lignin containing 11.0 wt% of methoxyl group determined by the reported method[12], 120 ºC in ionic liquids and 140 ºC in organic solvents, 1.5 mL solvent, 12 h. [b] Output is the grams of acetic acid produced per gram of lignin. [c] Yield is the percentage of the methoxyl group in the lignin that converted into acetic acid. The amount of acetic acid was obtained by NMR method using 1,3,5-trioxane as an internal standard. [d] Without lignin. No acetic acid was produced. [e] Without $RhCl_3$. No acetic acid was produced, but CH_3I was detected.

We characterized the lignin before and after reaction by two-dimensional heteronuclear single quantum coherence nuclear magnetic resonance (2D-HSQC NMR)[16], and the spectra are shown in Figure 2. It is known that the signal of methoxyl group in lignin is at 56.4/3.70 ppm[16b], and the corresponding region was colored with yellow in Figure 2. It can be known that the signal of methoxyl group dramatically decreased after reaction. Meanwhile, the signal of the aromatic region also indicates that

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aryl methyl ether structures (guaiacyl units, colored with green) transformed to phenol structures (catechyl units, colored with brown). The lignin was modified to be rich of hydroxyl, which could be advantageous and feasible for further usage and modification.

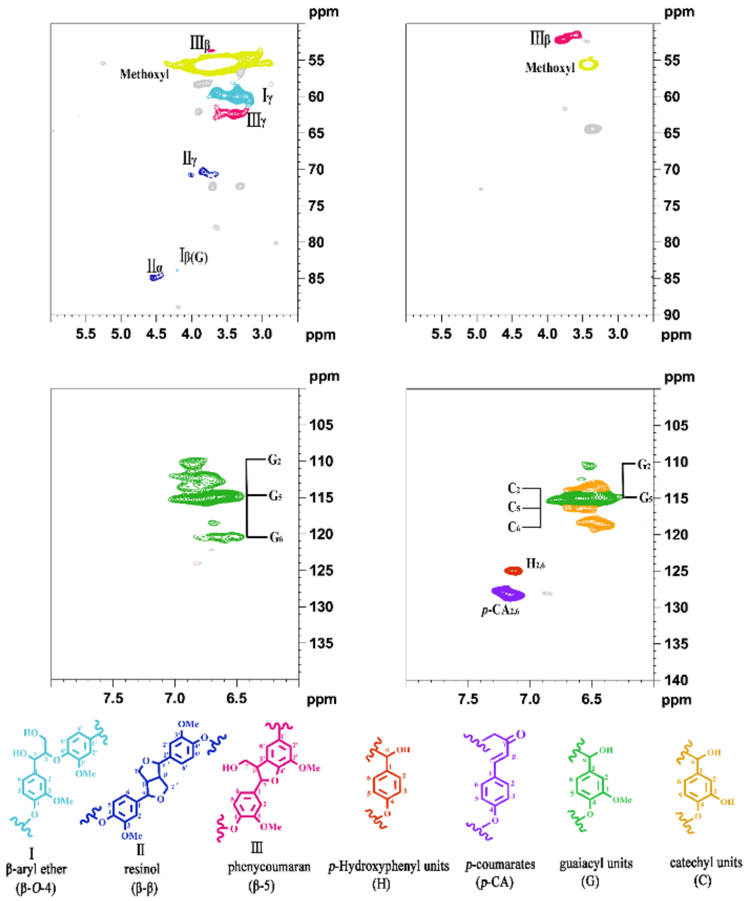


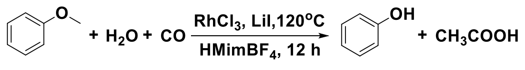
Figure 2. The 2D-HSQC NMR spectra of the lignin before (left) and after (right) reaction. Reaction conditions: 0.01 g $RhCl_3$, 2 mmol LiI, 1 mmol $LiBF_4$, 0.2 g kraft lignin, 5 MPa CO, 1.5 mL toluene, 15 mmol H_2O, 140 °C, 12 h.

The reaction was also conducted with organosolv lignin. The organosolv lignin was obtained by treating milled bamboo with 1,4-dioxane/water mixed solvent using the method developed by Björkman[17]. The methoxyl content in the organosolv lignin was 14.1wt% determined by iodine stoichiometry titration method[12]. At 140 °C, the yield of acetic acid was 80.4%, *i.e.*, 0.219 g of acetic acid could be produced from 1 g of organosolv lignin, and the mass balance was 99.1% at this condition. The organosolv lignin before and after reaction were also characterized by 2D-HSQC NMR (Figure S6). Similarly, the signal of methoxyl group dramatically decreased after reaction and the signal of the aromatic region also indicates that aryl methyl ether structures (guaiacyl units, syringyl units and ferulates, colored with green, purple and light yellow, respectively) transformed to phenol structures (catechyl units and 5-hydroxyguaiacyl units, colored with brown and black, respectively). This indicates that the method is applicable to different types of lignin.

We performed the experiments using deuterated toluene (toluene-d_8) instead of toluene in the reaction of the two lignins. NMR analysis was carried out before and after reaction, and the results are provided in the Figure S7 and Figure S8, respectively. It can be concluded from the results that the solubility of the lignins in toluene before and after reaction was negligible. The results also showed that CH_3COOH was produced even deuterated toluene was used as the solvent, confirming that the methyl in CH_3COOH is from lignin. This is consistent with the conclusion obtained from the blank experiment that no acetic acid was produced without lignin (entry 18 of table 1).

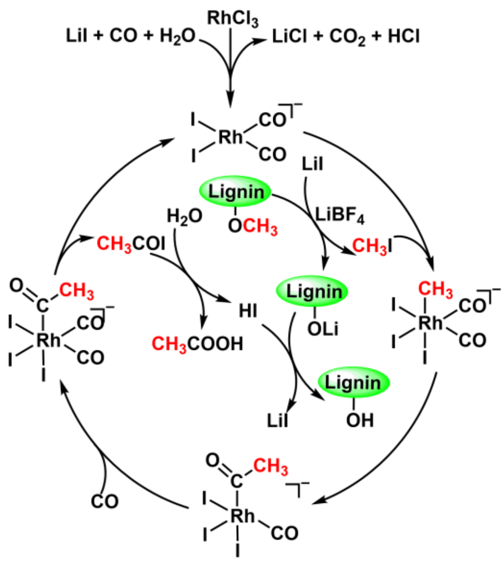
The GPC traces of the two lignins before and after the reaction were given in Figure S9 and Figure S10, respectively. The results showed the GPC traces before and after the reaction were similar, indicating there were no detectable depolymerisation products. We also analyzed the liquid phase (toluene phase) of the reaction mixture by HPLC (Figures S11 and S12). The results indicated that acetic acid was the only detectable product. The result was consistent with the conclusion obtained from NMR analysis that acetic acid was the only product (Figure S4).

Anisole is the simplest model compound of lignin that contains a methoxyl group. We also studied the reaction using anisole (Scheme 1). Acetic acid and phenol were produced, and the conversion of anisole could reach 91.2% without any other product. This is consistent with the results that methoxyl group in lignin can be transformed into acetic acid selectively.



Scheme 1. The reaction of anisole as methyl source to produce acetic acid. Reaction conditions: 0.01 g $RhCl_3$, 2 mmol LiI, 1.5 mL $HMinBF_4$, 5 MPa CO, 15 mmol H_2O.

On the basis of the experimental results and the related knowledge in the literature[18], we propose the possible reaction mechanism, which is shown schematically in Scheme 2. The active component of the catalyst is rhodium carbonyl generated in situ[18]. $LiBF_4$ catalyzed the reaction of methoxyl group and LiI to form CH_3I and lithium phenolate, as can be known from Entries 12 and 19 of Table 1. In addition, trace amount of CH_3I was detected in the reaction mixture (Figure S4), which supports this argument. The sequence involves the oxidative addition of CH_3I to Rh species, CO-insertion, then reductive elimination of acetyl iodide, followed by its hydrolysis to acetic acid and HI. Finally, HI reacts with lithium phenolate and regenerates LiI. It is known that iodide is a necessary component for the carbonylation of methanol to acetic acid, and iodide serves as a promoter[9-10]. However, other iodide sources in our work such as NaI, KI and CsI were not effective for the reaction of lignin, CO and H_2O to form acetic acid (Table 1, entries 2-4). The main reason may be that NaI, KI and CsI could promote the carbonylation reaction but could not break the ether bond. So LiI acts as two roles. One role is breaking the ether bond and the other is promoting the carbonylation of methyl iodide to acetic acid.



Scheme 2. The possible reaction mechanism of the reaction of lignin as methyl source to produce acetic acid

In summary, we have proposed the strategy to produce pure valuable chemical using lignin as the feedstock, in which a specified class of group is utilized in the reaction instead of depolymerization of lignin. To demonstrate the feasibility of this method, the route to produce acetic acid using the methoxyl group in lignin as the feedstock have been developed. For producing acetic acid from lignin, CO and water, the yields can reach 87.3% and 80.4%, respectively, when kraft lignin and organosolv lignin are used as the feedstocks. In these cases, 0.186 g and 0.219 g of acetic acid can be obtained from 1 g lignin, and no byproduct is generated. The unique advantage of this method is that chemical with high purity can be obtained from lignin. We believe that the strategy that transforms a class of group in lignin selectively into product with high purity can be used to produce other chemicals, which needs many researches in the future.

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Keywords: Transformation • lignin• carbon monoxide • water • acetic acid

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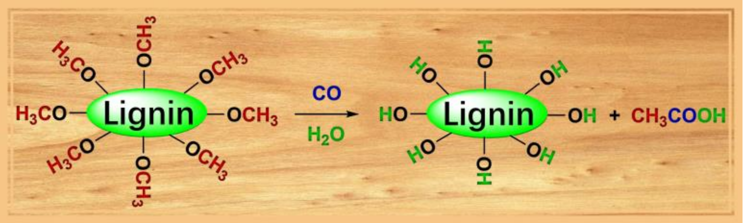

A strategy for the transformation of methoxyl group in lignin is proposed. The route to produce acetic acid by selective reaction of methoxyl group in lignin with CO and water over $RhCl_3$ is developed. The conversion of methoxyl group in the lignin can reach 87.3% with 100% selectivity to acetic acid.

Qingqing Mei, Huizhen Liu, Xiaojun Shen, Qinglei Meng, Hangyu Liu, Junfeng Xiang, Buxing Han**

Page No. – Page No.

Selective Utilization of Methoxyl Group in Lignin to Produce Acetic Acid