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Catalytic conversion of Kraft lignin into platform chemicals in supercritical ethanol over a $Mo(OCH_2CH_3)_x/NaCl$ catalyst

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ABSTRACT

A $Mo(OCH_2CH_3)_x/NaCl$ catalyst showed high efficiency in supercritical ethanol without adding H_2 in the conversion of Kraft lignin to chemicals, including C_6 alcohols, C_8-C_{10} esters, benzyl alcohols and arenes. Control experiments were done with $MoCl_5$, $NaOC_2H_5$ and the physical mixture of them. The $Mo(OCH_2CH_3)_x/NaCl$ catalyst exhibited superior activity among the samples examined. The overall yield increased as the reaction temperature increased from 260° to 300°C. The yield of aromatic compounds achieved 303 mg/g lignin over the $Mo(OCH_2CH_3)_x/NaCl$ catalyst at 300 °C for 6 h. $MoCl_5$ and $NaOC_2H_5$ forms $Mo(OCH_2CH_3)_x$ in the catalyst preparation, which behaves as the active species in Kraft lignin conversion. The primary aromatics formed from the catalytic lignin depolymerization steps may undergo secondary reactions to form the final products.

1. Introduction

Lignin is considered as the only large-volume renewable bioresource containing natural aromatic rings [1,2]. Nowadays, the catalytic lignin depolymerization (CLD) has been recognized as a promising approach to produce high valued aromatic chemicals and fuels [3,4]. Kraft lignin was considered as major pollutant of the paper and pulp industries since the beginning of the commercial application of alkaline pulp technology, and now it is mainly utilized as a low-grade fuel for balancing the process energy [5]. CLD reaction became a focus in the recent decade as a new route for aromatic chemicals such as benzene production [6]. Commodity aromatics such as benzene, toluene, xylene and styrene derivatives have been in a net short for modern society [7]. Therefore, the development of new catalytic technologies for the efficient conversion of Kraft lignin to aromatics is of crucial importance [1]. Various strategies for Kraft lignin conversion have been explored, which can be broadly classified into acid/base catalyzed depolymerization/hydrolysis [8], pyrolysis, hydrogenation, oxidation, liquid-phase reforming, gasification to syngas, as well as biodegradation [3].

The depolymerization of lignin in alcohols has been investigated in the recent decade. Barta et al. [9] examined the alcoholysis of organosolv lignin in supercritical methanol at 300 °C, using a Cu-doped porous metal oxide as the catalyst, and obtained cyclohexyl derivatives with reduced oxygen content and negligible aromatics. Huang et al. [10] investigated the depolymerization of soda lignin in supercritical ethanol over a $CuMgAlO_x$ catalyst and achieved a monomer yield of 23 wt% at 300 °C for 8 h. Ma et al. [5] reported the complete ethanolysis of Kraft lignin over an activated carbon supported α-molybdenum carbide catalyst (α-MoC_{1-x}/AC) and obtained 1.64 g/g lignin yield of identified monomers, including C_6-C_{10} esters, C_6 alcohols, arenes, phenols and benzyl alcohols, without formation of char or tar at 280 °C for 6 h.

Other Mo-based catalysts were further used in the conversion of Kraft lignin. Li and co-workers [5,11–15] reported the depolymerization of Kraft lignin in ethanol with several Mo-based catalysts. The aromatic monomer yield as high as 575 mg/g lignin was obtained at 330 °C with a MoC_{1-x}/Cu-$MgAlO_z$ catalyst. Recently, Mo-based catalysts, e.g., supported β-Mo_2C on carbon materials, $NiMo/Al_2O_3$, etc. have been shown with superior activity and selectivity for the CLD reaction [16,17]. Wang

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and co-workers reported the Mo/Sepiolite catalysts on catalytic depolymerization of Kraft lignin under supercritical ethanol [18]. A 40Mo/SEP sample showed the highest lignin conversion (98.6%) and lignin oil yield (84.3%) at 290 °C for 3 h, where the yield of petroleum ether-soluble product reached 70.8% (mainly monomers and dimers). Ma et al. [11] proposed the reaction pathways of the CLD reaction over the Mo-based catalysts in supercritical ethanol and postulated that the main active species was likely molybdenum ethoxide. Kraft lignin is first fragmented into segments in the *m/z* range of 700–1600 via a non-catalytic ethanolysis process. Meanwhile, the main active Mo(V) species dissociates from the solid catalyst into the fluid phase due to the interaction with ethanol. Then mainly the dissociative species catalyzes, with the participation of radicals, the further degradation of the segments into small molecules.

Herein, the catalytic performance of $Mo(OCH_2CH_3)_x/NaCl$ ($Mo(OEt)_x/NaCl$) in CLD reaction in supercritical ethanol without gaseous H_2 with the lignin from Kraft pulp process is reported. High yield of liquid products is obtained. This proves partly the molybdenum ethoxide mechanism proposed in references [11,14].

2. Experimental

2.1. Materials

The Kraft lignin was purchased from Sigma-Aldrich (product number 471003). The Kraft lignin contains Klason lignin, polysaccharides, extractives (fats, resin acids and terpenoids), other organics and inorganics, with contents of 45.7, 10.1, 4.0, 27.1 and 13.1 wt%, respectively [5]. Analytical reagents (AR), including anisole, were ordered from Tianjin Guangfu Technology Development Co., Ltd. and used as received. Same grade solvents, e.g., ethanol, were purchased from Tianjin Jiangtian Chemical Co., Ltd. $MoCl_5$ was obtained from Shanghai Macklir Biochemical Co., Ltd. $NaOC_2H_5$ was bought from Shanghai Meryer Chemical Technology Co., Ltd.

2.2. Catalyst preparation

0.530 g $NaOC_2H_5$ was placed in a three-neck, round bottom flask, and 100 mL ethanol was added at 50 °C under stirring in air. Afterwards, 0.425 g $MoCl_5$ was added into the solution and further stirred at 50 °C for 1 h. After the reaction, the solution was centrifuged to remove NaCl precipitate with the fixed rate of 5000 rpm for 10 min at 20 °C. Then, the solvent was removed in vacuum at 50 °C, leaving $Mo(OEt)_x/NaCl$ catalyst as a red powder.

2.3. Catalyst characterization

The X-ray powder diffraction (XRD) patterns were collected with a Bruker D8-Focus diffractometer (Cu Kα, $\lambda = 1.5406$ Å) at 40 kV and 40 mA, with scanning from 10° to 80° at a rate of 10°/min. The catalyst samples were characterized with X-ray photoelectron spectroscopy (K-Alpha+), with Al Kα as the X-ray source (1486.6 eV) under a residual pressure of 5×10^{-8} Pa. The binding energy was calibrated using C1s at 284.8 eV as the standard. ^{1}H-nuclear magnetic resonance (^{1}H NMR) and ^{13}C NMR spectra were recorded using a Varian Inova 500 MHz instrument. The catalyst was dried at 50 °C in a vacuum drying oven before dissolution with $(CD_3)_2SO$ or CD_3OD.

2.4. Catalytic Lignin depolymerization reaction

The CLD reaction was carried out in a batch reactor (Kemi Co. Ltd, 250 mL, made of Hastelloy). Typically, 1.0 g Kraft lignin, 0.25 g catalyst and 100 mL ethanol were loaded into the reactor. The reactor was sealed and purged with high-purity nitrogen for six times to remove air. The sealed reactor was then heated to the prescribed temperature and kept for prescribed time with the fixed stirring rate of 600 rpm. After the reaction, the reactor was cooled down to room temperature in air. After releasing the gas, the mixture was filtrated to separate solid residue from liquid products if exist. Internal standard anisole was added to the liquid sample before GC analysis.

2.5. Product analysis

The monomers in liquid products were identified using a gas chromatograph-mass spectrometer system (GC-MS, Agilent 6890–5973) equipped with a NIST 2.0 database. The product yield, denoted as mg/g lignin, was calculated with anisole as the internal standard using a gas chromatograph equipped with a flame ionization detector (GC-FID, Agilent 6890). The chromatograph column used for both GC-MS and GC-FID was HP-5 MS (30 m × 0.25 mm × 0.25 μm), and the temperature of the injection port was set at 280 °C. The oven temperature program for GC-FID and GC-MS was set from an initial temperature of 45 °C to a final temperature of 250 °C with the ramping of 10 °C/min, and kept at 250 °C for 7 min

The overall product yield, conversion and yield of specific product were calculated according to the following Eqs. (1), (2) and (3), respectively:

$$\text{Overall product yield (mg/g lignin)} = \frac{\text{the weight of the overall products}}{\text{the weight of input lignin}} \quad (1)$$

$$\text{Conversion (\%)} = \frac{\text{the weight of the initial monomer-the weight of the residual monomer}}{\text{the weight of the initial monomer}} \quad (2)$$

$$\text{Yield of a product (\%)} = \frac{\text{the weight of the specific product}}{\text{the weight of the initial monomer}} \quad (3)$$

3. Results

3.1. Catalyst characterizations

The XRD patterns of the $Mo(OEt)_x/NaCl$ catalyst and the precipitate obtained from the catalyst preparation are shown in Fig. 1. The counts for the pattern of $Mo(OEt)_x/NaCl$ equals to ¼ that of the NaCl for aiding to visualize the peaks. Both two samples showed the well-resolved peaks of NaCl (PDF#72–1668), which confirmed the existence of NaCl in the $Mo(OEt)_x/NaCl$ sample. However, the peak of $Mo(OEt)_x$ was not observed.

Fig. 2a presents the surface XPS spectrum of $Mo(OEt)_x/NaCl$, showing the existence of Mo^{5+} (81%) with two well-resolved peaks at binding energies of 231.7 and 234.9 eV assigned to the Mo $3d_{5/2}$ and $3d_{3/2}$ spin-orbit components, and the XPS spectrum of $Mo(OEt)_x/NaCl$ also showed the Mo(3d) energy region indeed contains Mo^{6+} (19%) with the $3d_{5/2}$ and $3d_{3/2}$ bands locating at 232.9 and 235.9 eV, respectively [19–24]. The O 1 s XPS spectrum (Fig. 2b) also showed the presence of

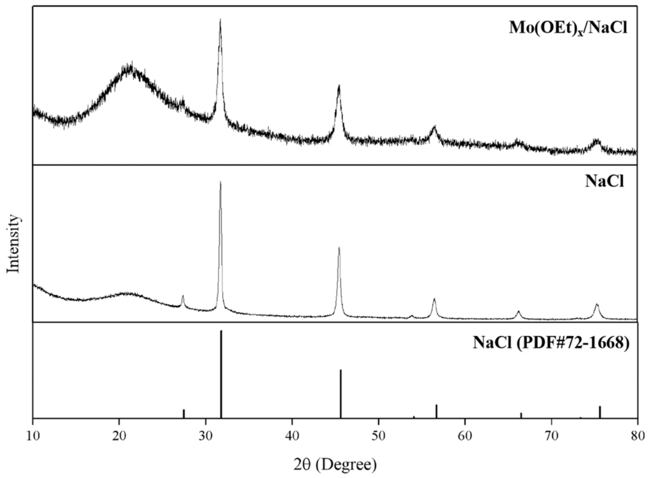


Fig. 1. XRD patterns of the Mo(OEt)$_x$/NaCl composite catalyst and NaCl.

more than one peak. In addition to the oxygen bonded to metal at 530.8 eV, the second O 1 s peak at 532.2 eV was attributed to O atoms bonded to carbon [25–27], and O 1 s peak at 535.5 eV can be assigned to the adventitious water [28].

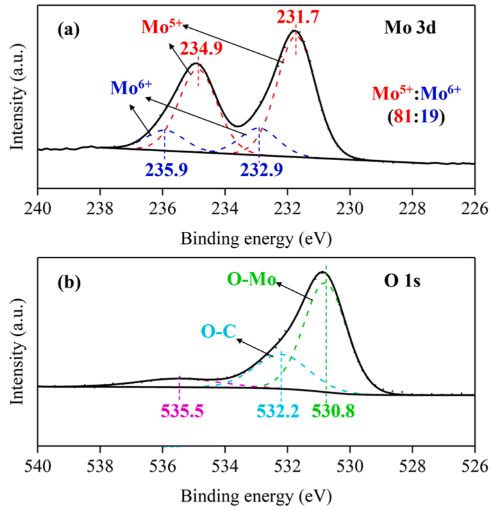


Fig. 2. XPS spectra of (a) Mo 3d and (b) O 1 s for Mo(OEt)x/NaCl catalyst.

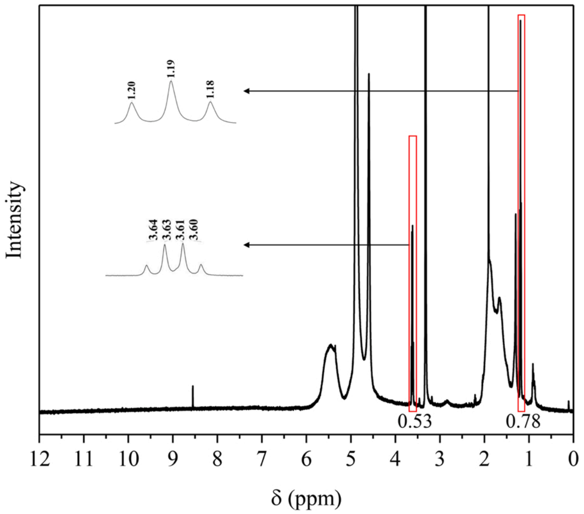


Fig. 3. ^{1}H NMR spectrum of Mo(OEt)$_x$/NaCl catalyst in CD_3OD.

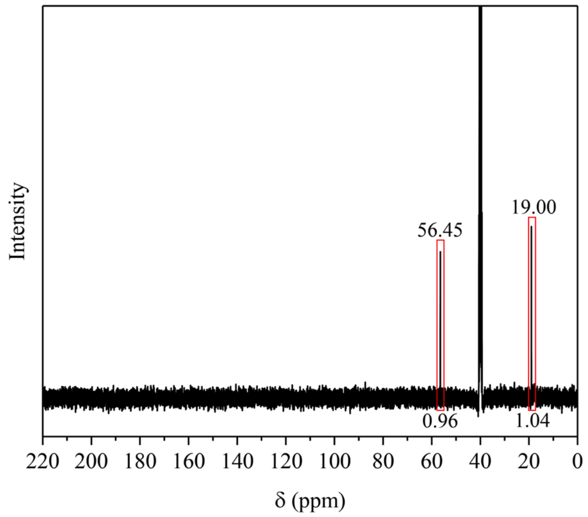


Fig. 4. ^{13}C NMR spectrum of Mo(OEt)$_x$/NaCl catalyst in $(CD_3)_2SO$.

^{1}H NMR (Fig. 3) and ^{13}C NMR (Fig. 4) were used to reveal the structure of the Mo(OEt)$_x$/NaCl catalyst. The signal assignment was based on the published works [29,30]. ^{1}H NMR spectrum showed the signals of protons in CH_2 (3.60–3.64 ppm) and CH_3 (1.18–1.20 ppm). The calculated area ratio of the total CH_2 peaks to the CH_3 was 0.53:0.78, closing to 2:3. ^{13}C NMR spectrum showed the signals of carbon in CH_3 (19.00 ppm) and CH_2 (56.45 ppm). The calculated area ratio of the total CH_2 (56.45 ppm) peaks to the CH_3 (19.00 ppm) was 0.96:1.04, closing to 1:1. The NMR spectra confirmed the existence of ethoxy (-OCH_2CH_3) in the Mo(OEt)$_x$/NaCl sample.

3.2. Catalytic lignin conversion

Fig. 5a shows the total-ion chromatogram of the liquid products obtained from the CLD of the lignin sample in ethanol over the Mo (OEt)$_x$/NaCl catalyst at 300 °C for 6 h under 0 MPa N_2 (initial gauge pressure at room temperature). The chemical structures of the identified molecules are shown in Fig. 5b. The same liquid products were also found in the previous works [11]. The liquid products mainly included C_6 alcohols, C_8-C_{10} esters, benzyl alcohols and arenes.

The blank experiment without adding lignin was also performed over the Mo(OEt)$_x$/NaCl catalyst under the same reaction conditions, and only C_6 alcohols and C_8-C_{10} esters, as shown in Fig. 6, were obtained.

The activity of $MoCl_5$, $NaOC_2H_5$ and the physical mixture of them for the CLD reaction were measured at 300 °C for 6 h under 0 MPa N_2. The results are depicted in Fig. 7 together with result of a measure without adding a catalyst. The reaction without a catalyst gave an overall yield of 483 mg/g lignin. $MoCl_5$ was almost inactive in the CLD to aromatics in ethanol, and a large amount of solid residue was obtained after the reaction. $NaOC_2H_5$ also showed low activity for the reaction, with an overall yield of small molecules of 100 mg/g lignin. The physical mixture of $MoCl_5$ and $NaOC_2H_5$ showed much better performance than both two components, with the overall yield of small molecules of 1179 mg/g lignin. The overall yield of the liquid products for Mo(OEt)$_x$/NaCl was 1407 mg/g lignin, obviously superior to that of $MoCl_5$, $NaOC_2H_5$, and physical mixture of $MoCl_5$ and $NaOC_2H_5$.

3.3. Effect of reaction temperature

Fig. 8 illustrates the effect of the reaction temperature on the yields of C_6 alcohols, C_8-C_{10} esters and aromatic compounds. All the yields of 3 types of products increased with the increase of reaction temperature. From 260–300 °C, an increase in the C_6 alcohols yield from 50 mg/g lignin to 277 mg/g lignin was observed. The yield of C_8-C_{10} esters

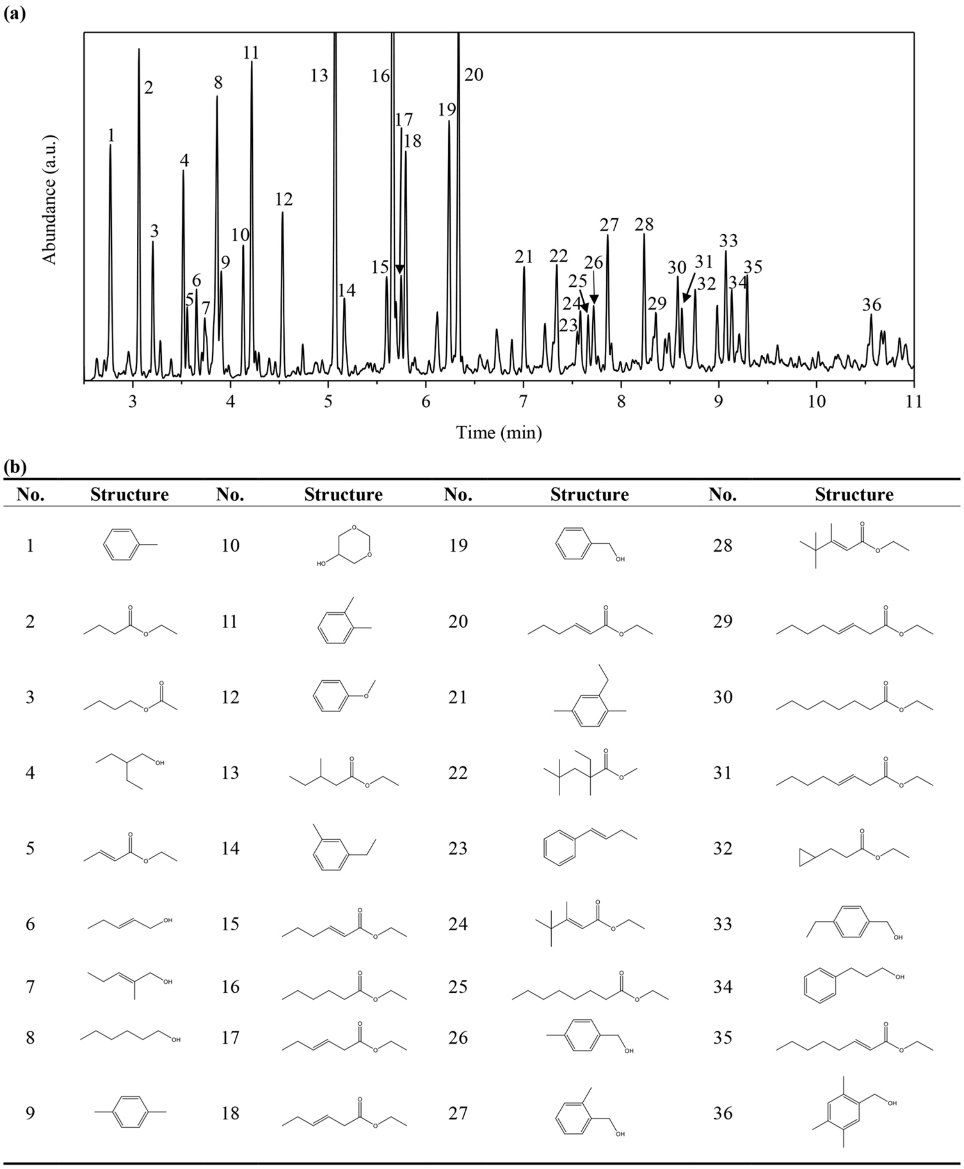


Fig. 5. (a) Total-ion chromatogram (TIC) of the liquid products obtained from CLD reaction over $Mo(OEt)_x/NaCl$ catalyst. (b) Structures of identified molecules in the liquid product. The numbers in (b) are consistent with those in (a). Anisole is the internal standard.

increased and reached 827 mg/g lignin at 300 °C. The yield of aromatics increased to 303 mg/g lignin at 300 °C.

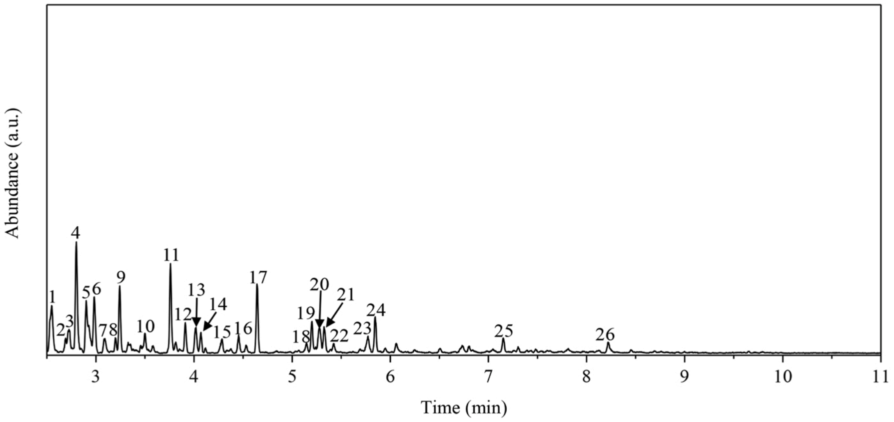
3.4. *The reaction of primary aromatics*

Benzyl alcohol, 2-methyl-benzyl alcohol and 4-methyl-benzyl alcohol were detected in the conversion of lignin. In order to reveal the reaction pathway of aromatic monomers, conversion of benzyl alcohol, 2-methyl-benzyl alcohol and 4-methyl-benzyl alcohol were examined over the $Mo(OEt)_x/NaCl$ catalyst at 300 °C for 6 h in ethanol, and the results are shown in Fig. 9. The conversion of benzyl alcohol, 2-methyl-benzyl alcohol and 4-methyl-benzyl alcohol were all up to 99%. Benzyl alcohol was converted to methylbenzene (A1) (yield 40%) and bibenzyl (A2) (yield 13%). 1,2-dimethyl-benzene (B1) was obtained from the conversion of 2-methyl-benzyl alcohol, with the yield of 47%, together with product (B2), with the yield of 22%. 4-methyl-benzyl alcohol was transformed to 1,4-dimethyl-benzene (C1) with a yield of 48% and to C2 with a yield of 20%.

4. Discussion

Much frustrating effort was devoted to synthesize molybdenum ethoxide with the reported method in patent [31]. The authors also got difficulty in purchasing pure molybdenum ethoxide chemical. Funk et al. [32] reported that $MoCl_5$ reacts with $NaOCH_3$ in methanol solution to produce $Mo(OCH_3)_5$ and NaCl. Similarly, in this work, $MoCl_5$ and $NaOC_2H_5$ indeed generated $Mo(OEt)_x$ and NaCl. Because of the NaCl impurity, this work failed to prepare pure molybdenum ethoxide and failed to quantify the NaCl in the composite catalyst. Although the peaks of $Mo(OEt)_x$ was not observed in the XRD patterns, the surface XPS spectrum and the NMR spectra confirmed the existence of $Mo(OEt)_x$. Therefore, the $Mo(OEt)_x/NaCl$ composite was used in the catalytic Kraft lignin ethanolysis reaction to verify the mechanism proposed in [11]. The reason for the low activity of the $MoCl_5$ or $NaOC_2H_5$ alone is likely due to the strong acidity of the HCl generated from $MoCl_5$ and alkaline of $NaOC_2H_5$, which causes the condensation of the lignin fragments during the CLD process. The physical mixture of $MoCl_5$ and $NaOC_2H_5$ showed much better performance than both the two components, which implies the formation of new substance from the two compounds. The Mo

(a)



(b)

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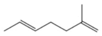
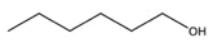
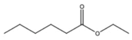
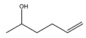
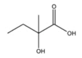
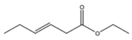
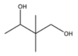
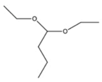
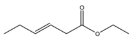
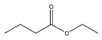
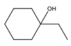
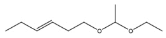
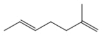
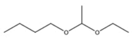
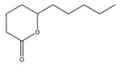
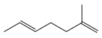
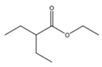
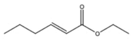
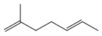
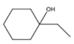
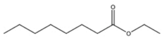
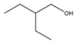
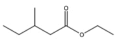
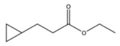
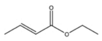
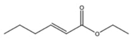
1		10		19	
2		11		20	
3		12		21	
4		13		22	
5		14		23	
6		15		24	
7		16		25	
8		17		26	
9		18			

Fig. 6. (a) TIC of the liquid products obtained from the reaction between ethanol and $Mo(OEt)_x/NaCl$ catalyst without lignin. (b) Structures of identified molecules in the liquid product. The numbers in (b) are consistent with those in (a).

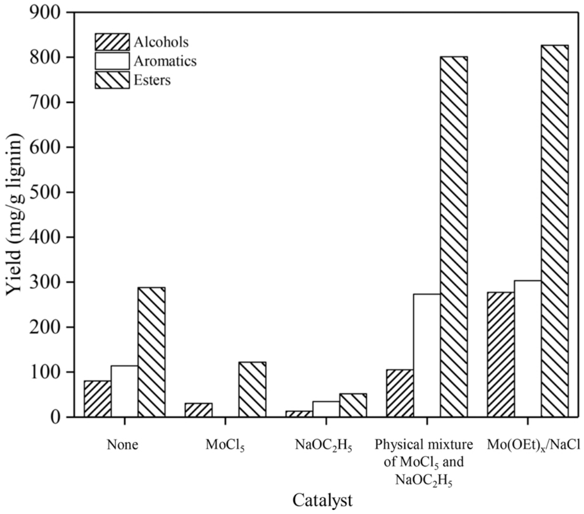


Fig. 7. The yield of C_6 alcohols, aromatics and C_8-C_{10} esters obtained from CLD reaction over different catalysts.

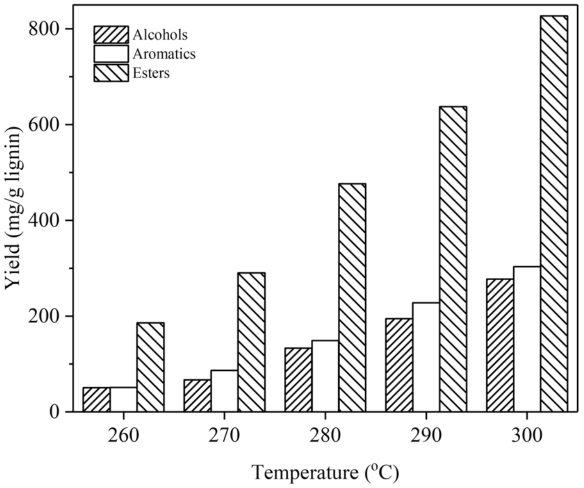


Fig. 8. The influence of temperature on the yield of C_6 alcohols, aromatics and C_8-C_{10} esters obtained from CLD reaction over $Mo(OEt)_x/NaCl$ catalyst.

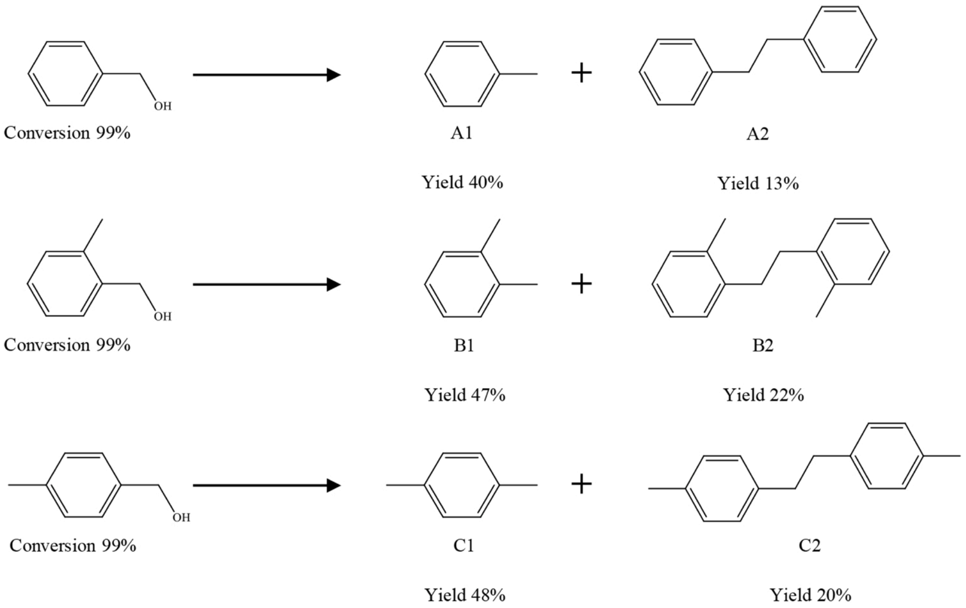


Fig. 9. The reaction pathway of the primary aromatics over the $Mo(OEt)_x/NaCl$ catalyst in ethanol.

$(OEt)_x/NaCl$ composite showed much higher activity than $MoCl_5$, $NaOC_2H_5$, and the physical mixture of $MoCl_5$ and $NaOC_2H_5$ samples under the same CLD reaction condition.

The blank experiment without Kraft lignin failed to give aromatic products, as shown in Fig. 6, indicating that aromatics were formed from CLD steps rather than those only involved ethanol. However, C_6 alcohols and C_8-C_{10} esters were detected in the product of the blank reaction without lignin but with lower yields than those in the product with the composite catalyst and lignin. C_6 alcohols and C_8-C_{10} esters can also be produced from the conversion of Kraft lignin in ethanol, which has been reported in previous works [5,11,15]. Consequently, the yield of C_6 alcohols and C_8-C_{10} esters are also listed along with that of aromatics but only the three primary aromatics are considered when discussing the reaction pathways of the primary products.

With the increase of the reaction temperature from 260° to 300°C, the overall yield increased, which is possibly ascribed to the better lignin solubility and the faster depolymerization reaction rate. This process might be facilitated by the radicals or ions produced in the supercritical ethanol. Higher temperature favors the overall yield of aromatics since it favors the formation of radicals and ions from ethanol, thus facilitates the depolymerization of lignin [15]. The amount of solid residue decreases monotonically when the reaction temperature increases, which is in consistent with the increase in the yield of liquid products.

The conversion of benzyl alcohol, 2-methyl-benzyl alcohol and 4-methyl-benzyl alcohol demonstrates that the dehydroxylation reaction occurred under the investigated conditions. Benzyl alcohol was transformed into methylbenzene. 1,2-dimethyl-benzene was obtained from the conversion of 2-methyl-benzyl alcohol. 4-methyl-benzyl alcohol was converted to 1,4-dimethyl-benzene. These aromatic products were also found in the CLD reaction, indicating that the primary monomers obtained from the CLD reaction may undergo secondary reactions to form the final liquid products.

We previously reported that supercritical ethanol itself degraded Kraft lignin into intermediate sized fragments in the *m/z* range of 700–1600 [5]. Mo-based catalysts further depolymerize the fragments into monomers [5,11,33]. Similar as proposed in [11], $Mo(OEt)_x$ is the main active species when $Mo(OEt)_x/NaCl$ is used as the catalyst. $Mo(OEt)_x$ is easy to undergo legend exchange with the lignin segments and the functional groups on the native lignin polymer chain [11]. Although we still failed to isolate $Mo(OEt)_x$ under the preparation conditions in this work, the results presented here with the composite $Mo(OEt)_x/NaCl$ catalyst partly verifies the mechanism proposed previously [11].

5. Conclusions

C_6 alcohols, C_8-C_{10} esters, benzyl alcohols and arenes were obtained in the Kraft lignin ethanolysis reaction over a $Mo(OEt)_x/NaCl$ catalyst. The XRD patterns confirm the existence of NaCl in the $Mo(OEt)_x/NaCl$ sample. The surface XPS spectrum of $Mo(OEt)_x/NaCl$ showed the existence of Mo^{5+} and Mo^{6+}. The NMR spectra confirmed the existence of ethoxy ($-OCH_2CH_3$) in the $Mo(OEt)_x/NaCl$ sample. Increase the temperature from 260 to 300 °C resulted in an increase in liquid yield from 287 to 1407 mg/g lignin over the $Mo(OEt)_x/NaCl$ catalyst in ethanol for 6 h. $MoCl_5$, $NaOC_2H_5$ and the physical mixture of them showed inferior activity to the $Mo(OEt)_x/NaCl$ catalyst. $Mo(OEt)_x$ is verified as the main active species in the conversion of Kraft lignin over different Mo-based catalysts. Benzyl alcohol, 2-methyl-benzyl alcohol and 4-methyl-benzyl alcohol were all detected in the product of the CLD reaction and were used as the reactants. The results show that their dehydroxylation reaction happened. The results presented here partly prove the Kraft lignin ethanolysis mechanism proposed in 2015. These results are useful both in finding the new and efficient composite catalyst, i.e. $Mo(OEt)_x/NaCl$, for the conversion of Kraft lignin to chemicals, and in verifying a proposed mechanism of lignin ethanolysis.

CRediT authorship contribution statement

Qingfeng Liu proposed the strategy and prepared the catalyst and also wrote the draft manuscript, Yushuai Sang joined the experiment and manuscript writing, Yunfei Bai, Kai Wu, Zewei Ma, Mengmeng Chen, and Yiming Ma joined the experiment and discussion of the idea, also polished the manuscript, Hong Chen supervised the experimental work, managed the experimental facility, revised the manuscript, and acquired funding from NSF China, Yongdan Li supervised the whole work, proposed the key points of the “hypothesis” and revised the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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