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Biomass Conversion

Catalytic Ethanolysis of Kraft Lignin into High-Value Small-Molecular Chemicals over a Nanostructured α-Molybdenum Carbide Catalyst**

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Abstract: *We report the complete ethanolysis of Kraft lignin over an α-MoC_{1-x}/AC catalyst in pure ethanol at 280°C to give high-value chemicals of low molecular weight with a maximum overall yield of the 25 most abundant liquid products (LP25) of 1.64 g per gram of lignin. The LP25 products consisted of C_6–C_{10} esters, alcohols, arenes, phenols, and benzyl alcohols with an overall heating value of 36.5 MJ kg^{-1}. C_6 alcohols and C_8 esters predominated and accounted for 82 wt% of the LP25 products. No oligomers or char were formed in the process. With our catalyst, ethanol is the only effective solvent for the reaction. Supercritical ethanol on its own degrades Kraft lignin into a mixture of small molecules and molecular fragments of intermediate size with molecular weights in the range 700–1400, differing in steps of 58 units, which is the weight of the branched-chain linkage C_3H_6O in lignin. Hydrogen was found to have a negative effect on the formation of the low-molecular-weight products.*

Lignin is one of the key components of the plant cell wall. It is responsible for the structural and mechanical integrity of plants, and is an important component of lignocellulosic biomass after harvest. Kraft lignin has been a high-volume by-product of the paper and pulp industry since the beginning of the commercial operation of alkaline pulp technology. There has been a great deal of interest in the potential use of non-edible biomass, that is, lignocellulose, as a renewable source of energy and chemicals.[1] Lignin is a polymer with a wide variability in structure. Its components depend on the biomass source, and it is most often combined with cellulose and hemicellulose. Among the various components of biomass, lignin is the least susceptible to chemical and biotransformation techniques. The lignin component therefore often becomes a low-value waste product of biomass-processing technologies, importantly, for example, in the conventional paper and pulp industry and in the modern bioethanol-fuel-production industry. In such processes, lignin is isolated on a large scale, but most of it is only utilized as a low-heating-value fuel.[1a] Over the last few years, considerable interest has developed in lignin valorization in relation to energy, chemical, and biotechnological applications. The approaches that have been investigated include hydrolysis, oxidation, and reduction, mostly under catalysis.[2–7] For example, hydrolysis can be brought about by employing base catalysts in hot water. Under these conditions, hydrolysis of C–O–C linkages occurs to produce phenol derivatives in moderate yields; however, the reaction is often accompanied by the production of tar or char.[3] A method involving oxidative cleavage of C–C and C-O–C bonds produces vanillin and its analogues but in low yields <10 wt%.[4] The oxidation of lignin also usually causes the formation of CO_x and H_2O with a corresponding loss of energy. Methods involving reduction cleave the lignin into simple monomeric compounds and defunctionalize these compounds, thus producing phenols, benzene, toluene, and/or xylene. However, the yields of these processes are also insufficient for practical significance.[5–7] Studies have also been reported on the use of capping agents or carbenium-ion scavengers, such as boric acid, phenol, and 2-naphthol, with the aim of suppressing the formation of tar and char in the aqueous solvent, and some positive effects have been observed.[3]

We report herein the results of experiments on Kraft lignin valorization and show the formation of C_6–C_{10} chemicals in remarkably high yield without any tar or char formation. The Kraft lignin underwent complete ethanolysis over an activated-carbon-supported α-molybdenum carbide catalyst (α-MoC_{1-x}/AC) in supercritical ethanol without the addition of gaseous hydrogen. Furthermore, the result was verified with a Kraft lignin originating from wheat straw and obtained by spray drying the black liquor in a local paper mill.

The nanostructured α-MoC_{1-x}/AC catalyst used was prepared by the temperature-programmed reaction of a molybdenum oxide supported on activated carbon (AC) with methane in a flowing gas mixed with hydrogen.[8] The X-ray diffraction (XRD) pattern of the catalyst showed well-resolved peaks corresponding to the α-MoC_{1-x} structure in the range 30–80° (Figure 1a). The transmission electron microscope (TEM) image of the catalyst is shown in Figure 1b. The lattice spacing marked on the micrograph for the highlighted domain is 0.239 nm and corresponds to the (111) face of α-MoC_{1-x} (JCPDS No. 15-0457). The micrograph also shows that the nanoparticles have diameters in the range

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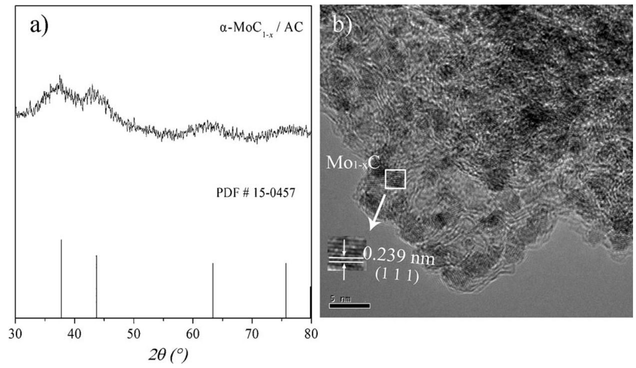
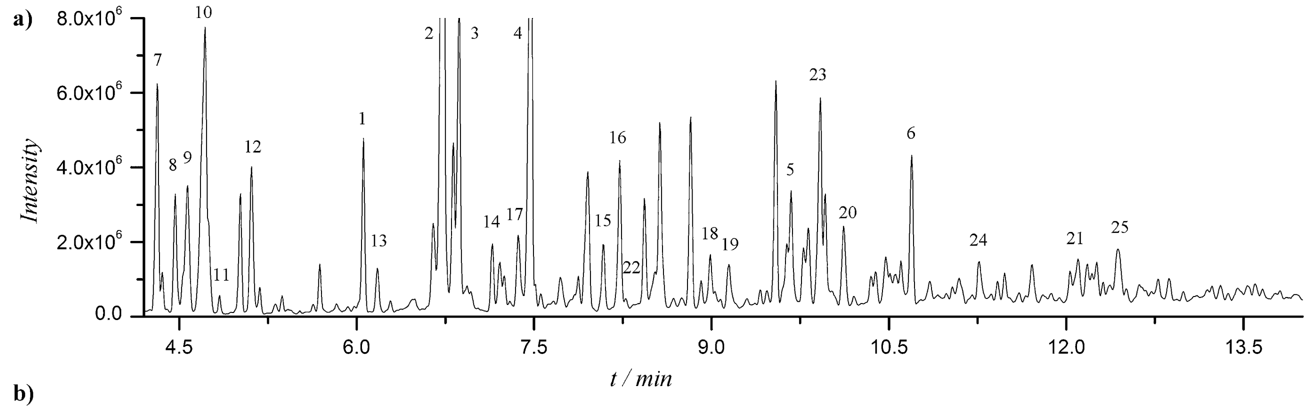


Figure 1. a) XRD pattern and b) TEM image of the α-MoC_{1-x}/AC catalyst. Scale bar: 5 nm.

2–5 nm and are well-dispersed on the surface of the activated carbon.

The ethanolysis of Kraft lignin was carried out in a batch reactor. Optimization of the reaction conditions with the α-MoC_{1-x}/AC catalyst and a lignin sample (Na and S content: 13.1 and 2.8 wt%) purchased from Sigma–Aldrich showed that the maximum yield of liquid products (LP) was obtained when the reaction was carried out at 280 °C under a pressure of 10.5 MPa for 6 h after purging with N_2 gas before sealing the reactor. The total-ion chromatogram (TIC) derived from gas chromatography–mass spectrometry (GC–MS) is shown in Figure 2 a. A total of 94 product molecules were detected in the lignin-ethanolysis system by GC–MS. The reactivity of ethanol was verified by heating ethanol and the catalyst under the same conditions (Figure 3). A total of 10 molecules, including ethyl acetate, butanol, and acetal, were detected in the product, and molecules with more than six carbon atoms were only formed to a very small extent (peaks 9 and 10 in Figure 3). The other 84 products were only obtained after the addition of lignin. Among the 84 products, the most significant 52 species were identified, 25 of which (LP25) were quantified by GC by the use of an internal standard and a flame ionization detector (FID). These products accounted for 84% of the total integrated GC peak area for all 84 detected products derived from lignin. The yields of the LP25 products are listed in Figure 2 b. These major products fall into two groups: aliphatic compounds, that is, C_6 alcohols and C_8–C_{10} esters, and aromatic compounds in the form of C_8–C_{10} arenes, phenols, and benzyl alcohols. Ethyl isopropyl sulfide was also detected in the liquid products. No dimers or oligomers were detected, and no tar or char was formed. The overall yield of the LP25 products obtained was 1.64 g per gram of lignin and was thus almost 15 times higher than the yields obtained with Ni/Al_2O_3, Ru/Al_2O_3, or Pt/AC catalysts under similar conditions.[6] The higher heating value of the LP25 products was estimated with the Dulong formula to be as high as 36.5 MJ kg^{-1}, as compared to 29.7 MJ kg^{-1} for ethanol fuel. Esters and alcohols contribute over 82 wt% of the LP25 products. As the overall yield is higher than 100 wt%, it must be concluded that ethanol is a reactant and gives rise to ethyl esters or other products through esterification or alkylation reaction routes. Both "free" lignin and lignin carbohydrate complexes exist in chemical pulp, although the structure and quantity of these materials are unclear.[9] The Sigma–Aldrich Kraft lignin used in this study contains carbohydrate derivatives, as only 45.7 wt% of



b)

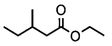
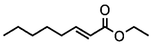
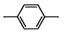
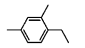
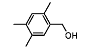
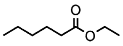
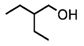
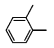
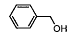
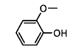
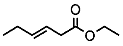
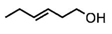
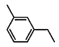
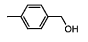
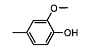
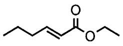
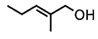
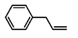
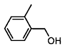
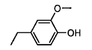
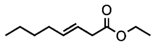
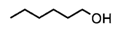
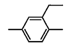
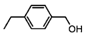
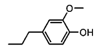
No.	Molecule	Yield	No.	Molecule	Yield	No.	Molecule	Yield	No.	Molecule	Yield	No.	Molecule	Yield
1		**56**	6		**106**	11		**3**	16		**33**	21		**10**
2		**303**	7		**96**	12		**56**	17		**13**	22		**4**
3		**197**	8		**46**	13		**12**	18		**21**	23		**35**
4		**253**	9		**79**	14		**13**	19		**14**	24		**16**
5		**32**	10		**188**	15		**14**	20		**13**	25		**23**

Figure 2. a) Total-ion chromatogram (TIC) of the liquid products. Peaks marked with numbers correspond to quantified products. b) Quantified components of the product and their mass yields (mg per gram of lignin; esters: No. 1–6; alcohols: No. 7–10; aromatic compounds: No. 11–25).

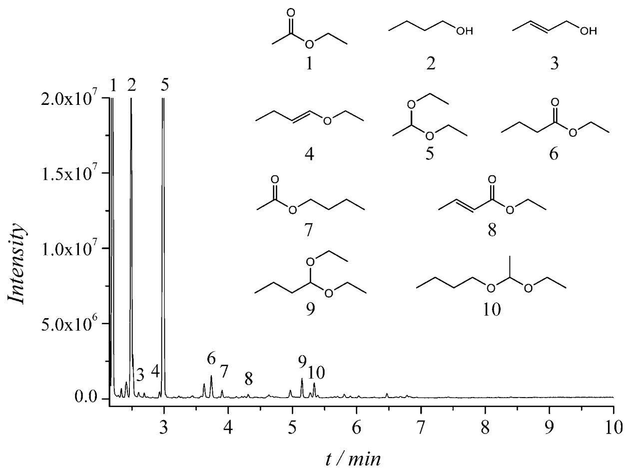


Figure 3. TIC of the liquid products of the reaction of ethanol and α-MoC$_{1-x}$/AC without lignin at 280 °C for 6 h.

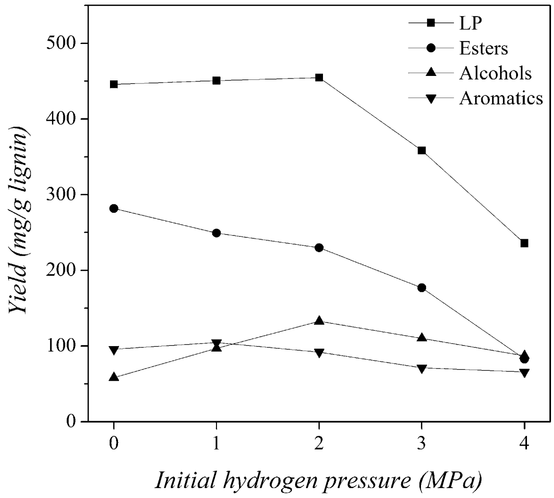


Figure 4. Effects of the initial hydrogen pressure on the LP25 yield and the yield of esters, alcohols, and aromatic compounds (reaction conditions: 280 °C, 6 h).

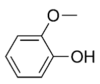
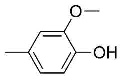
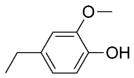
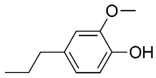
Klason lignin was isolated from it by a two-step procedure involving hydrolysis with sulfuric acid.[10] Furthermore, the overall yield of aromatic compounds produced is 61.3 wt % as based on the Klason lignin of the lignin sample, but is substantially lower than expected if the structure of lignin is assumed as drawn in a number of reports as having a dominant proportion of aromatic rings.[1,5,7a,11] The low content of hydrogen attached to aromatic rings was also confirmed by an ^{1}H NMR spectrum of the lignin. The esters identified were all ethyl esters of carboxylic acids and are generated by an esterification reaction between the ethanol solvent and lignin-derived intermediates, such as hexenuronic acid formed in Kraft pulping.[12] In previous studies, the formation of esters was observed in the catalytic hydrocracking of Kraft lignin in supercritical ethanol,[6,13] and the formation of higher alcohols and ethers (C_2–C_6) was observed in the catalytic conversion of woody biomass over a copper-doped Mg/Al mixed-oxide catalyst in supercritical methanol at 320 °C.[14] It was proposed that these alcohols are produced by the transformation of cellulosic components.[14] Furthermore, a Guerbet reaction (the transformation of primary aliphatic alcohols into the corresponding β-alkylated dimeric alcohols) between ethanol and the aliphatic fragments of Kraft lignin may also occur to produce higher alcohols. The yields of monophenols, such as 2-methoxyphenol, 4-methyl-2-methoxyphenol, 4-ethyl-2-methoxyphenol, and 4-propyl-2-methoxyphenol, were moderate. The yields of benzyl alcohols and arenes were quite high, in contrast with the results of other studies on the degradation of lignin.[5–7]

In previous studies on lignin hydrogenolysis, a high initial hydrogen pressure (IHP) was often used; however, the total yields of low-molecular-weight products were only moderate.[5,6,7b,15] The presence of a hydrogen atmosphere had no positive effect on the yield of liquid products (Figure 4). With an IHP lower than 2 MPa, the LP25 yield remained constant; with a higher IHP, the LP25 yield decreased dramatically. When the IHP was increased from 0 to 2 MPa, more alcohols and fewer esters were obtained, thus indicating that ester formation is suppressed by hydrogen. With a further increase in the IHP, the yields of both the alcohols and the esters decreased, thus indicating that hydrogen retards the formation of both types of products. As the IHP was increased in the investigated range of 0–4 MPa, the overall yield of aromatic compounds decreased. Song et al.[7c] reported that the reaction over a Ni/AC catalyst in methanol in the presence of H_2 (5 MPa) gave lower lignin conversion than that in Ar (0.1 MPa). They suggested that the conversion is lower because the release of an active hydrogen atom from CH_3OH is more facile than that from a hydrogen molecule. In this study, the inhibition effect of gas-phase hydrogen is more likely due to the suppression of the chemisorption of ethanol on the catalyst surface. In addition, the reactive intermediates perform the functions of an attacking reagent on the lignin and a capping species on the freshly formed lignin fragment.

We checked whether or not the lignin reacts to produce smaller molecules with our catalyst in another solvent (Table 1). The results show that pure ethanol is a much more effective solvent than pure water, methanol, or isopropanol. With these solvents, only small amounts of phenols were produced, with the overall phenol yield highest in water and lowest in methanol.

The treatment of lignin without a catalyst under otherwise the same conditions gave a small amount of low-molecular-weight products (Figure 5 a). Kraft lignin is insoluble in ethanol at room temperature, whereas liquid products can be obtained at 280 °C even without a catalyst (Figure 5). A matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) technique was employed to monitor the molecular weight of the lignin fragments in the experiments carried out with pure ethanol as the solvent. Figure 6 a shows the distribution pattern of the products in the *m*/*z* range of approximately 700–1400 after treatment of the Kraft lignin with pure ethanol in the absence of a catalyst. The difference in the *m*/*z* values between two large peaks is mostly 58 mass units, probably as a result of the removal of branched-chain C_3H_6O linkages. Therefore, the solid Kraft lignin can be converted into ethanol-soluble lignin

Table 1: Effects of the solvent on the yield (mg per gram of lignin) of principal products.[a]

Products	Solvent			
	ethanol	water	methanol	isopropanol
	4	14	3	17
	35	3	8	2
	16	11	5	5
	23	8	2	4
other aromatics	202	9	2	3
alcohols	409	–	–	–
esters	949	–	–	–

[a] Reactions were carried out at 280 °C for 6 h. "–" means not detected.

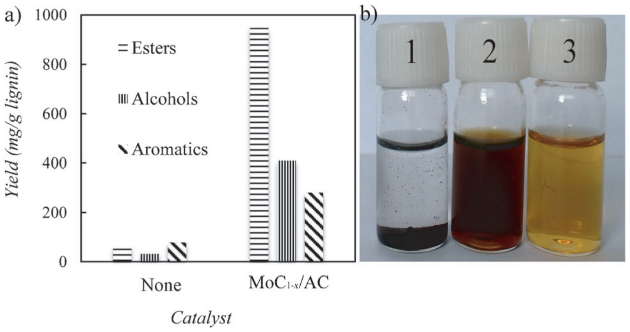


Figure 5. a) Graph showing the yields of different product types as a visual aid. The data were obtained from reactions of Kraft lignin (1 g) in ethanol (100 mL) at 280 °C for 6 h with and without the catalyst α-MoC_{1-x}/AC under a nitrogen atmosphere. b) Photographs of solutions of Kraft lignin and its liquid products: 1) Kraft lignin in ethanol at room temperature; 2) liquid products of the reaction of Kraft lignin in ethanol without a catalyst; 3) liquid products of the treatment of Kraft lignin in ethanol with α-MoC_{1-x}/AC.

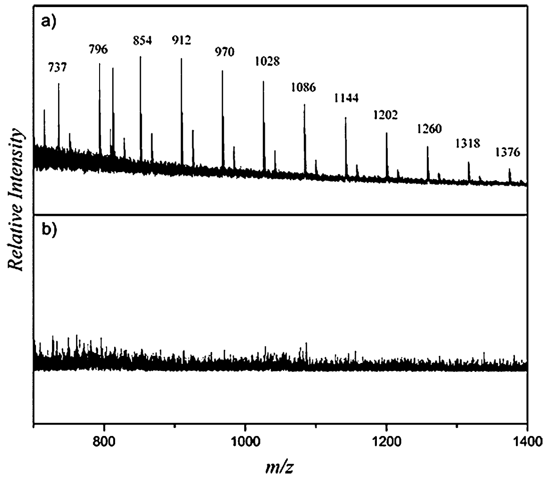
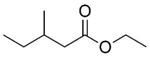
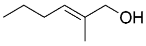
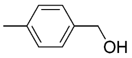
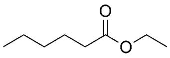
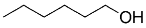
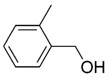
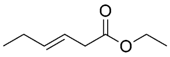
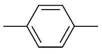
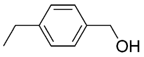
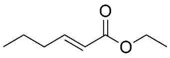
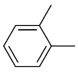
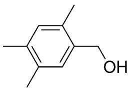
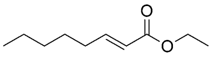
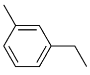
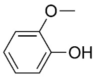
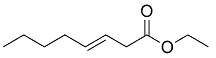
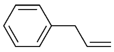
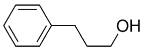
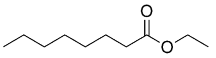
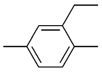
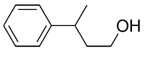
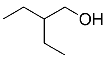
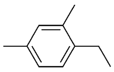
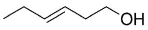
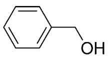


Figure 6. MALDI-TOF-MS spectrum of lignin fragments after ethanol treatment: a) without a catalyst; b) with the α-MoC_{1-x}/AC catalyst (reaction conditions: 280 °C, 6 h).

fragments under supercritical conditions without a catalyst, and the formation of most fragments occurs through a process of successive branched-chain scission. When the α-MoC_{1-x}/AC catalyst was present in the supercritical ethanol together with Kraft lignin, the fragments in the range of m/z 700–1400 disappeared (Figure 6b), and small-molecular aliphatic and aromatic compounds were obtained, as detected by GC–FID and GC–MS, thus suggesting that the short lignin chain is further converted into monomers. Cheng et al.[6] reported that the treatment of Kraft lignin in pure ethanol at 300 °C without a catalyst led to ethanol-soluble products of intermediate molecular weight (around 466–631 $g\,mol^{-1}$) in low yield (< 15 %). Nagy et al.[15a] found a pattern of molecular weight with a mass average of 1781 $g\,mol^{-1}$ when organosolv lignin in pure ethanol was heated at 200 °C with H_2 (5 MPa) without a catalyst. Song et al.[7c] claimed that fragments with molecular-weight distributions in a m/z range of approximately 1100–1600 were obtained with alcohol-soluble lignin in both ethanol and methanol. The fragmentation of several kinds of lignin in alcohols is possible; however, the molecular-weight distribution of the fragments and the fragmentation mechanism are dependent on the origin of the lignin, the kind of alcohol, and the treatment conditions. A possible reaction pathway leading to these results is that ethanol forms a complex on the surface of the catalyst which serves as the active site and facilitates the formation of reactive intermediates, such as ethyl, ethoxyl, hydroxyl, and hydrogen radicals, which then functionalize the lignin fragments formed in the supercritical ethanol phase. The introduction of the ethanol-reactive intermediates leads to the high yield of aliphatic compounds, that is, C_6 alcohols and C_8–C_{10} esters.

Wheat-straw Kraft lignin which had been extracted from the papermaking black liquor from a local paper mill by drying was employed as a feedstock in some experiments carried out under the same conditions with the α-MoC_{1-x}/AC catalyst. The product distribution (Table 2) was similar to that obtained with the Sigma–Aldrich lignin, but the overall LP yield was lower. Minor differences were also found in the product molecules. For example, ethyl caprylate (No. 7) was present in a significant quantity; this compound was not found among the LP25 products from the Sigma–Aldrich lignin because its yield was too low to be calculated (< 1 mg per gram of lignin). Four phenols were found among the LP25 products derived from the Sigma–Aldrich lignin, but only one phenol (guaiacol, No. 23) was found among the products derived from the wheat-straw lignin. Two new products, phenylpropanol (No. 24) and 3-phenyl-1-butanol (No. 25) were also found among the products derived from wheat-straw lignin. Changes in the product distributions from the lignin materials of different origin are attributed to the different source of the material and the pretreatment procedure used. Nevertheless, the feasibility of utilizing

Table 2: Quantified components obtained from the ethanolysis of wheat-straw Kraft lignin and their mass yields (mg per gram of lignin).[a]

No.	Molecule	Yield	No.	Molecule	Yield	No.	Molecule	Yield
1		42	10		88	19		41
2		192	11		171	20		108
3		184	12		22	21		23
4		210	13		74	22		50
5		14	14		8	23		3
6		36	15		10	24		32
7		29	16		12	25		22
8		47	17		35			
9		45	18		32			

[a] Reactions were carried out at 280 °C for 6 h in ethanol with the catalyst α-MoC$_{1-x}$/AC.

black-liquor lignin indicates that a potential commercial application for the technology exists, because a large volume of Kraft lignin is isolated every year all over the world.

The solids obtained from the valorization of the two substrates were collected quantitatively by filtration and then washed with ethanol, dichloromethane, and dilute HNO_3 to dissolve the alkali and alkali-earth metals, such as Na, K, and Mg. The material, which looked like black sawdust, had a weight of 490 ± 5 mg, which is approximately equal to that of the catalyst (500 mg) added to the system. Furthermore, these materials showed the same activity as the fresh catalyst after reactivation in a CH_4/H_2 gas mixture. By contrast, the solids obtained under similar conditions without a catalyst were cokelike and weighed about (615 ± 10) mg in the case of Sigma–Aldrich Kraft lignin and (680 ± 10) mg in the case of wheat-straw Kraft lignin. Thus, part of the substrate was converted into ethanol-soluble or volatile products (Figure 5b).

In summary, complete catalytic ethanolysis of Kraft lignin was achieved in supercritical ethanol over an activated-carbon-supported α-molybdenum carbide catalyst in an inert atmosphere. The products included C_6 monohydric alcohols, C_8–C_{10} esters, C_7–C_{10} monohydric phenols, C_7–C_{10} benzyl alcohols, and C_8–C_{10} aromatic hydrocarbons. The solvent and catalyst both play key roles and affect the molecular yields and product composition. The initial gas-phase composition had a significant effect on the yield of the liquid product; the reaction without hydrogen in the initial gas phase proceeded much more efficiently than that with hydrogen. Pure ethanol was the most effective solvent and reactant for the degradation of lignin in terms of the yield of liquid products. Supercritical ethanol itself can degrade Kraft lignin into small pieces; the difference in m/z between these pieces is 58, which is consistent with the branched-chain linkages, that is, C_3H_6O, in lignin. Wheat-straw Kraft lignin obtained directly from the black liquor of the pulp industry can also be used as the feed. The small organic molecules produced by this approach would fit seamlessly into the existing petrochemical infrastructure. Nevertheless, product separation and the recovery of solvent and heat are still open issues for further research.

Experimental Section

The α-molybdenum carbide catalyst was prepared by a temperature-programmed reaction procedure with 15% CH_4/H_2 (v/v) gas. Detailed synthetic procedures as well as the characterization methods are provided in the Supporting Information.

The catalytic conversion of Kraft lignin (Sigma–Aldrich) was carried out in an autoclave (Parr Instrument Company, 300 mL), typically at 280 °C for 6 h. For each experiment, Kraft lignin (1.0 g) and the catalyst (0.5 g) were put in the reactor, and the reactor was then purged with nitrogen and stirred at a rate of 400 rpm. After the desired reaction time, the solution was filtered to remove any solid residues, and each sample was injected neat into a GC–MS instrument (Agilent 6890-5973, HP-5MS; 30 m × 250 µm) for product identification and a GC–FID instrument (Agilent 6890) for quantitative analysis. The yield of liquid products was calculated from the equation: yield (mg per gram of lignin) = (weight of the product)/(weight of Kraft lignin put into the reactor).

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