

Nano WO₃-Catalyzed One-Pot Process for Mild Oxidative Depolymerization of Lignin and its Model Compounds

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Despite challenges related to the robust and irregular structure of lignin, the valorization of this aromatic biopolymer has aroused great interest. However, the current methods exhibit problems such as harsh reaction conditions, complicated operation, and difficult recovery of catalyst. Herein we present a one-pot process for the mild oxidative depolymerization of lignin and lignin model compounds catalyzed by nano WO₃, along with *tert*-butyl hydrogen peroxide (TBHP) as the oxidant and NaOH as the additive, which exhibits advantages of both homogeneous and heterogeneous catalysis. Under the optimized condition, it yielded 80.4 wt% of liquid oil from organo-

1. Introduction

With the depletion of fossil resources, the search for green and sustainable alternatives has attracted much interest increasingly.^[1-3] Non-edible lignocellulose, produced by forestry and agricultural activities worldwide and composed of 40–50% cellulose, 16–33% hemicellulose, and 15–30% lignin, could be regarded as an attractive candidate.^[4,5] In the past decades, significant advances have been achieved regarding to the utilization of cellulose and hemicellulose, while the conversion of lignin encountered difficulties owing to its robust and complexed three-dimensional amorphous structure. Lignin is the potential source of aromatic compounds,^[6] where the most common structural pattern is the alkyl-aryl ether bond (β -O-4) which makes up about 50% of all linkages and thus its cleavage is the key to depolymerize lignin.^[7–10]

A variety of distinct depolymerization methods aiming to break the ether bond have been extensively exploited, including electrocatalysis,^[11] pyrolysis,^[12,13] oxidation,^[14] and hydrogenolysis.^[15] Among them, the oxidation method is considered to be one of the most effective methods due to its mild conditions and sufficient selectivity for aromatic compounds such as phenols, aldehydes, ketones, and aromatic acids.^[16,17] It has been identified that the oxidation of C_a–O–Ar from

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 Supporting information for this article is available on the WWW under

https://doi.org/10.1002/cctc.202100670

ChemCatChem 2021, 13, 1–11 Wiley Online Library 1 These are not the final page numbers!

solv lignin with 7.6 wt% of vanillic acid as the main monomer product, accounting for 91.6 wt% monomeric selectivity. Mechanism studies on the model substrate suggest that the reaction proceeds via an oxidation of C_a —OH to C=O followed by C–O bond cleavage to afford phenol and ketone products which may undergo further oxidation to produce aromatic carboxylic acids. We have developed an operationally simple procedure for mild fragmentation of lignin and lignin model compounds with excellent yields, which provides the potential to expand the existing lignin usage from energy source to value-added commodity chemicals.

69.2 to 55.9 kcal/mol, facilitating the cleavage of the C–O bond and further the depolymerization of lignin. Although the current two-step process, selective oxidation of C_a–OH followed by reductive fragmentation^[18–20] or subsequent oxidative cracking of β -O-4^[21] has been proved efficient, it is still highly desired to develop one-step or one-pot oxidation process for the easiness and simplicity of the procedure.

Compared with homogeneous catalysts, such as Co,^[22] Cu,^[23,24] and V^[25] salts used in the oxidation of lignin and its model compounds, eco-friendly heterogeneous catalysts are promising for their robust and recyclable characteristics. A great number of heterogeneous catalysts have been successfully applied in the depolymerization of lignin including Pd/CeO₂,^[26] Co-based nanoparticles supported on nitrogen-doped carbon,^[27] CsPMoVO–Co,^[28] and Cu–Mn/ σ -Al₂O₃,^[29] etc. However, usually the degradation of lignin proceeds under harsh conditions, such as high temperature and long reaction time, necessitating the development of an efficient and mild method for oxidative depolymerization of lignin over heterogeneous catalyst.

WO₃, a semiconductor transition metal oxide, has been one of the research foci for solar-energy-driven photoelectrochemical conversion used alone or in combination with IO^{4-.[30]} However, only little attention has been paid to the application of WO₃ or other tungsten-based catalysts in the depolymerization of lignin. Recently, Mai et al.^[31] reported that enzymatic hydrolysis lignin (EHL) in supercritical ethanol over WO₃/ γ -Al₂O₃ catalyst could be converted to aliphatic and aromatic compounds with a total yield of 36.34 wt% at 320 °C for 8 h, and the overall selectivity of alkylphenols reached 67.5%. Li et al.^[32] reported a direct catalytic conversion of raw woody biomass into two groups of chemicals over Ni-W₂C/AC at 235 °C and 6 MPa H₂ for 4 h. Cellulose and hemicellulose, were converted to ethylene glycol and other diols with a total yield of up to Full Papers doi.org/10.1002/cctc.202100670



75.6% (based on the amount of cellulose & hemicellulose), while the lignin component was converted selectively into monophenols with a yield of 46.5% (based on lignin). Guo et al.^[33] further proved organosolv lignins fractionated from softwood and hardwood could be effectively converted to liquid oil with the overall yields varying from 47.3 to 55.5 wt%, affording 7.2-8.9% monophenols in the oils over W₂C/AC with an initial $\rm H_2$ pressure of 0.69 MPa at 250 $^{\circ}\rm C$ for 2 h. Ji et al. $^{\rm [34]}$ reported the deconstruction of organosolv lignin over tungsten-based bimetallic catalysts (M–W/AC, M = Ru, Pt and Pd) in hexane under 0.7 MPa H_2 at 260 °C for 10 h, resulting in 42.7 % to 66.7 wt% of aromatic liquid oil. Note that all the reports on WO₃ or W₂C were related to the hydrogenolysis or hydrogenation of lignin, and so far, no works on WO3-catalyzed oxidative depolymerization of lignin and its model compounds have been reported.

Herein, we present a one-pot process for mild oxidative depolymerization of lignin and its model compounds. With tertbutyl hydrogen peroxide (TBHP) as the oxidant and 24% NaOH as the additive, commercial nano WO₃ can efficiently catalyze the cracking of lignin model compounds into phenols, ketones and aromatic acids in good to excellent yields. When applied to organosolv lignin, the catalytic process yielded 80.4 wt% of liquid oil at 93.3 wt% conversion (based on lignin) with 7.6 wt% of vanillic acid, accounting for as high as 91.6% of selectivity in the lignin-derived monomers. Moreover, the catalyst could be recycled for 5 times without significant loss of activity. Mechanism studies show that the C_{α} -OH group in the β -O-4 models could be selectively oxidized to the corresponding ketone which then weakens the neighboring C_{β} -O-Ar bond, thus facilitating its cleavage to obtain phenols and ketones. The latter may undergo further oxidization to produce aromatic carboxylic acids.

Experimental Section

General Procedure for Oxidative Depolymerization of Lignin Model Compounds

Lignin model compound (1a-1h) (0.5 mmol), nano WO₃ (0.02 g, 0.1 mmol), 70% TBHP (540 $\mu\text{L},$ 3.9 mmol) and 24% NaOH (0.80 mL, 4.8 mmol) were placed in a 25 mL three-necked flask and stirred for a certain time at 80 °C. Thin layer chromatography (TLC) was employed to monitor the progress of the reaction. Upon completion, the reaction mixture was cooled to room temperature and acidified to pH $2 \sim 3$ with ice-cold 6 N HCl to precipitate WO₃, which was filtered, washed three times with water and ethanol, and dried under vacuum at 80°C for 10 h for recycle use. The filtrate was neutralized, extracted with ethyl acetate for three times, and then the combined organic phase was washed with saturated brine, dried over anhydrous MgSO4, and finally concentrated under reduced pressure. The resulting oil mixture was then rediluted in 2 mL of ethyl acetate, and 1 μ L of which was injected in the gas chromatography-mass spectrometry (GC-MS) for analysis with 3, 4, 5-trimethoxybenzaldehyde as internal standard (see Section 3 in the SI).

The conversion and yields of model compounds are defined as [Eqs. (1) and (2)]:

Conversion (%) =
$$(1 - \frac{W_M}{W_L}) \times 100\%$$
 (1)

Yield (%) =
$$\frac{W_I}{W_F} \times 100\%$$
 (2)

where W_L denotes the original mass of lignin model compound, W_M means the mass of unreacted lignin model compound, W_I is the actual yield of a given product, and W_F is the theoretical yield of the given product.

General Procedure for Oxidative Depolymerization of Organosolv Lignin

Organosolv lignin isolated from pinewood powder (see Section 8.1 in the SI) was subjected to the modified one-pot reaction conditions. Organosolv lignin (0.25 g), nano WO₃ (0.058 g, 0.25 mmol), 70 % TBHP (1024 $\mu\text{L},$ 7.4 mmol) and 24 % NaOH (1.6 mL, 9.6 mmol) were put in a 25 mL three-necked flask followed by the addition of 1.6 mL of 1, 4-dioxane and 90 μ L of ethylene glycol, then stirred for 4 h at 100 °C. The mixture was cooled to room temperature and acidified to pH 2~3 with 6 N HCl to precipitate unreacted lignin, which was separated by filtration, then dried and weighed (W_{R}). After standing for a period of time, WO_{3} precipitated slowly from the filtrate, then was removed by simple filtration. The remaining filtrate was neutralized, extracted with ethyl acetate for three times. The combined organic layer was concentrated under vacuum to remove the solvent, then dried to afford the liquid oil and weighed (W_D). The oil was rediluted in 2 mL of ethyl acetate, and 1 µL of which was injected in GC/MS for analysis with 3, 4, 5trimethoxybenzaldehyde as external standard to determine the monomeric yields. Also, the liquid oil was submitted to QPEOTMS analysis and the aqueous layer to a matrix-assisted laser desorption/ionization time of flight MS (MALDI-TOF MS) analysis.

The conversion and yields are calculated as follows [Eqs. (3)-(6)]:

$$Conversion(\%) = \left(1 - \frac{W_B}{W_A}\right) \times 100\%$$
(3)

$$Yield_{monomer}(\%) = \frac{\sum Wc}{W_A} \times 100\%$$
(4)

$$Yield_{liquid\ oil}(\%) = \frac{W_D}{W_A} \times 100\,\%$$
(5)

$$Selectivity_{monomer}(\%) = \frac{W_c}{\sum W_c} \times 100\%$$
(6)

where W_A is the original mass of lignin, W_B is the residual mass of lignin, W_C is the mass of a monomer, W_D is the mass of liquid oil and ΣW_C is the total mass of all the monomers.

Catalyst Recycle Experiments

After each filtration (see section 6 in SI for details), the catalyst was washed with water and ethanol for three times respectively, then dried under vacuum at $80 \,^{\circ}$ C for 10 h. The recovered catalyst was reused for the subsequent catalytic oxidation of model compound 1 a to study the reusability of the catalyst.



2. Results and Discussion

2.1. Catalyst Characterization

The X-ray diffraction (XRD) patterns in Figure 1a shows that nano WO₃ is a monoclinic phase coupled with diffraction peaks at 20 values of 23.1°, 23.7°, 24.4° and 53.6° corresponding to the (001), (020), (200) and (022) facets (JCPDS-752072), respectively. Transmission electron micrograph (TEM) and scanning electron microscope (SEM) (Figure S1) show that nano WO₃ is a sheet structure, and the particle size is in the range of 50–100 nm. The XPS spectra proves the elemental composition of the catalyst and the valence state of the elements. Figure 1b indicates the presence of W and O elements in nano WO₃, and further as shown in Figure 1c, the presence of W4f_{7/2} and W4f_{5/2} doublet at 36.0 eV and 38.2 eV in the W4f spectra is indicative of W⁶⁺ in monoclinic WO₃.

2.2. Optimization of Model Oxidative Cleavage

2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanol (1 a), a compound containing β -O-4 linkage, was selected as the lignin model compound to optimize the reaction conditions, including catalysts, oxidants, and alkaline content, etc. As shown in Table 1, a series of tungsten-based catalysts, such as WO₃, $H_{3}O_{40}PW_{12} \cdot xH_{2}O$, $Na_{2}WO_{4} \cdot 2H_{2}O$ and $H_{4}[Si(W_{3}O_{10})_{4}] \cdot xH_{2}O$, were selected to investigate the catalytic performance at 80°C with TBHP as the oxidant and NaOH as the additive. Among them, WO₃ gave as high as 98.6% conversion (entry 1) and compound 1a was efficiently cleaved into a phenol (3a, 17.2 wt%), a ketone (4a, 15.7 wt%), and an aromatic carboxylic acid (5a, 80.4 wt%), along with undetectable amounts of the oxidized ketone 2a and the dehydrated intermediate 6a in some cases. Other tungsten-based catalysts showed much lower activity than WO_3 (entries 9–11). We tried to replace WO_3 with nano WO₃ and found that 20 mol% nano WO₃ (entry 2) provided the similar conversion under the same conditions (Figure 2).



Figure 1. (a) XRD patterns of original and recycled nano WO₃. (b) XPS survey spectra of original and recycled nano WO₃. (c) W4*f* core level XPS spectra. (d) O1*s* core level XPS spectra.

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| Table 1. The oxidative cleavage of β -O-4 model compound 1 a. ^[a] | | | | | | |
|--|---|------------------------|----------------------------|------------------|-------------------|-------|
| H ₃ CO | OH OCH ₃ catalyst oxidant base | HO + H ₃ CO | о + _{Н3} СО | О Н + | H ₃ CO | |
| | 1a | 3a 4 | a | 5a | | 6a |
| Entry | Catalyst | Conversion [%] | Product yields [% |] ^[b] | | |
| | | | 3a | 4a | 5 a | 6a |
| 1 | WO ₃ | 98.6 | 17.2 | 15.7 | 80.4 | |
| 2 ^[c] | WO ₃ | 98.0 | 16.9 | 14.5 | 81.8 | |
| 3 ^[c,d] | WO ₃ | < 1.0 | trace | trace | trace | |
| 4 ^[c,e] | WO ₃ | < 1.0 | trace | trace | trace | |
| 5 ^[f] | - | 41.1 | 8.3 | 38.5 | 7.0 | |
| 6 ^[c,g] | WO ₃ | - | | | | |
| 7 ^[c,h] | WO ₃ | 2.0 | | | | < 2.0 |
| 8 ^[i] | WO ₃ | 98.9 | 13.2 | 13.2 | 80.6 | |
| 9 | $H_3O_{40}PW_{12} \cdot xH_2O$ | 59.9 | 10.9 | 47.4 | 4.8 | |
| 10 | $Na_2WO_4 \cdot 2H_2O$ | 5.1 | 2.3 | 11.3 | trace | |
| 11 | $H_4[Si(W_3O_{10})4] \cdot xH_2O$ | 20.3 | 6.1 | 15.7 | 2.0 | |

[a] Reaction conditions: **1a** (0.137 g, 0.5 mmol), catalyst (0.2 mmol), 70% TBHP (3.9 mmol), 24% NaOH (4.8 mmol), 80 °C and 2 h, [b] Yield was determined by GC-MS with 3, 4, 5-trimethoxybenzaldehyde as internal standard, [c] Nano WO₃ (0.1 mmol), [d] Oxygen instead of TBHP, [e] H₂O₂ instead of TBHP, [f] Without catalyst, [g] Without TBHP, [h] Without NaOH, [i] 1, 4-dioxane/water (1:1, v/v) as the solvent.



Figure 2. Total-ion chromatogram of fragmented lignin model compound 1 a. ^aReaction conditions: 1 a (0.5 mmol), nano WO₃ (0.1 mmol), 70 % TBHP (3.9 mmol), 24 % NaOH (4.8 mmol), 80 °C and 2 h. GC-MS spectrum was recorded with 3, 4, 5 trimethoxybenzaldehyde as internal standard (IS).

Control experiments revealed that in the absence of catalysts, the conversion was only 41.1% (entry 5), while without TBHP or NaOH, virtually no products were detected (entries 6 and 7), suggesting that an oxidant or a base was indispensable for the oxidative cleavage of 1 a. As TBHP can react with NaOH and then transfer an oxygen atom to nano WO₃ to form a metal peroxide species,^[35] the real oxidant, thereby facilitating the oxidative cleavage of model compound

1 a. However, H_2O_2 and O_2 , the most common green oxidants, were found inefficient for the reaction (**entries 3 and 4**).

Alkali was another indispensable component for this reaction. NaOH worked well and we didn't try any other alkali because NaOH is cheap and commercially available. Unexpectedly, upon the addition of NaOH, nano WO₃ gradually dissolved in it and acted like a homogeneous catalyst, thereby promoting the reaction. But when the mixture was acidified with HCl, nano



Figure 3. The depolymerization of organosolv lignin to aromatic monomers. ^aReaction conditions: organosolv lignin (25 mg), nano WO₃ (0.25 mmol), 70% TBHP (7.4 mmol), 24% NaOH (9.6 mmol), 1, 4-dioxane (1.6 mL), ethylene glycol (90 μ L), 100 °C and 4 h.





Figure 4. (a) MALDI-TOF MS spectra of organosolv lignin (b) QPEOTMS spectrum of the liquid oil resulted from lignin oxidative depolymerization^a. ^aReaction conditions: organosolv lignin (25 mg), nano WO₃ (0.25 mmol), 70% TBHP (7.4 mmol), 24% NaOH (9.6 mmol), 1, 4-dioxane (1.6 mL), ethylene glycol (90 μL), 100 °C and 4 h.

WO₃ slowly precipitated from the mixture, indicating the possibility to be recycled by filtration. Hence, nano WO₃ has the advantages of both homogeneous and heterogeneous catalysts. Besides, as shown in Tables S2 and S3, not only the amount of alkali, but also the concentration of alkali had a significant influence on the reaction. As the concentration of NaOH ranged from 3% to 18%, the conversion of 1a increased rapidly from 7% to 89.4% and the yields of guaiacol (3a), pmethoxy acetophenone (4a) and p-methoxy benzoic acid (5a) followed the similar upward trend. When the concentration of NaOH reached 24%, 98.0% conversion was achieved accompanied by improved yields of 3a (16.9%), 4a (14.5%) and 5a (81.8%). Further increase of NaOH concentration to 27% resulted in a slight increase in conversion (99.2%), but a significant decrease in the total yields of the products, implying higher alkaline content may lead to side reactions. Therefore, 24% NaOH was employed for all the following experiments. Moreover, we carried out reactions with different molar ratios of NaOH to TBHP and found that the ratio of 1:1.2 (3.9 mmol: 4.8 mmol) was optimal for this reaction (Table S3). The influences of temperature and reaction time were also investigated and found that 80 °C and reaction time of 2 h were appropriate (Table S5 and Table S6). Since water is a green and cheap solvent, no further attempt on solvents was performed. Under the optimized reaction conditions, compound 1a could be almost completely converted into guaiacol, p-methoxy acetophenone and *p*-methoxy benzoic acid.

2.3. Substrate Scope of Oxidative Cleavage

With the optimized reaction conditions in hand, we extended the scope of substrates to check the versatility of the developed protocol. Lignin model compounds with zero to three methoxy groups commonly found in natural lignin structure were synthesized and used in the mild oxidative cleavage process. As expected, the optimized conditions efficiently cleaved the C-O bond, providing the desired phenols, ketones or carboxylic acids in good to excellent yields in all cases, but whether the main product was a ketone, or an acid seemed to be related to the number of methoxy groups present on the model compounds. As shown in Table 2, For convenience, the phenyl ring adjacent to benzyl-OH was labelled A and the other ring was labelled B. In the absence of methoxy groups, 1d required 3 h to complete the conversion with benzoic acid as the main product (entry 4). As for 1b and 1c, only one methoxy group present either on ring A or on ring B, the reaction time was shortened to 2 h and the main products were the corresponding ketones (entries 2 and 3), whereas for 1a, 1e and 1h, bearing two methoxy groups in their structures, aromatic carboxylic acids were the main products (entries 1, 5 and 8). In the case of 1f and 1g, with three methoxy groups in all, the main products were the expected aromatic acids, but the reaction time was extended to 6 h to afford complete conversion (entries 6 and 7). Since oxidation is a process of losing electrons, the more electron-donating methoxy groups the substrate contains, the more favorable for the oxidation, while too many methoxy groups made the reactive center less accessible for the oxidant owing to steric hindrance, thus





Figure 5. Partial HSQC spectra of organosolv lignin (a) before and (b) after oxidative depolymerization^a. ^aReaction conditions: organosolv lignin (25 mg), nano WO₃ (0.25 mmol), 70 % TBHP (7.4 mmol), 24 % NaOH (9.6 mmol), 1, 4-dioxane (1.6 mL), ethylene glycol (90 μL), 100 °C and 4 h.

decreasing the rate of reaction. As the production of acids was a consequence of the continued oxidation of ketones, long reaction time was beneficial for the production of carboxylic acids. Note that for model compounds with methoxy groups on phenyl ring B, the yields of phenols were much lower (**entries 1**, **3**, **5 and 7**), and even for compound **1 f**, with two methoxy groups on ring B, no corresponding phenol was observed (**entry 6**). The presence of methoxy groups imparts phenyl ring





B higher electron density which makes the resulting phenols susceptible to excessive oxidation or polymerization^[36] as identified in Wang's work.^[21] Given the fact that β -O-4 model compounds containing γ -OH are difficult to be cleaved,^[37-39] the catalytic fragmentation of **1e** faces greater challenges. Fortunately, our proposed catalytic system could almost completely break compound **1e** into the desired products within 8 h under the mild condition, suggesting that the catalytic system has the potential to depolymerize natural lignin.

2.4. Plausible Mechanism Discussion

On the basis of the above experiments, the possible mechanism is proposed as shown in Scheme 1. It was observed that no oxidation occurred in the absence of NaOH or TBHP. However, upon the addition of NaOH, it readily reacted with TBHP and abstracted the hydrogen atom to produce a tertiary butyl peroxy anion, which then transferred the oxygen atom to the tungsten atom in the center of WO₃ to generate a threemembered ring peroxide A, the real oxidative species. The evidence for its formation came from the typical IR absorption peaks at 495, 640, and 950 cm⁻¹ ^[40,41]. The three-membered ring peroxide A then reacted with compound 1 a and converted the $\mathsf{C}_{\!a}\!\!-\!\!\mathsf{OH}$ to ketone form $\mathbf{2a},$ significantly reducing the bond energy of the adjacent C-O bond^[42-45] which was prone to suffer a breakage to give guaiacol and p-methoxy acetophenone. The resulting acetophenone may undergo further oxidative cleavage to give benzoic acids. In order to prove our idea, compound 2a was synthesized as the substrate and submitted to the optimized condition, giving rise to guaiacol and p-methoxy benzoic acid as 1 a did, which indicated 2 a

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Scheme 1. Possible reaction mechanism of cleaving model compound 1 a.

maybe the oxidative intermediate arising from **1a**. When the same procedure was applied to *p*-methoxy acetophenone, *p*-methoxy benzoic acids was achieved, identifying the generation of benzoic acids via continued oxidation of the corresponding ketones.

To gain insight into the low yield of guaiacol **3***a*, we also observed the behavior of guaiacol under the same conditions. The amount of guaiacol dropped off with time but no products were detected by GC-MS, accounting for the disproportionately lower yields of guaiacol and other phenols bearing methoxy groups. MALDI-TOF MS analysis (Figure S3) reveals the absence of guaiacol (m/z 124.14) and the presence of some unknown compounds in the products corresponding to m/z 332.3, m/z340.7, m/z 430.3 and m/z 509.2 respectively, indicating polymerization may occur under the alkaline medium (Figure 2).

The C_{α} -H transfer process was studied using deuterium labeled **1 a**' as the substrate and toluene as the solvent to avoid H/D exchange in an alkaline medium (see section 5.3 in SI for details). The results demonstrated that the deuterium atom on C_{α} didn't transfer to the methyl group of the ketone product, suggesting that the hydrogen atoms removed from the alcohol group did not participate in the subsequent cleavage of the ether C–O bond. Further, the kinetic isotope effect (KIE) experiments identified that the dehydrogenation of **1 a** to **2 a** is the rate-limiting step (section 5.4 in SI).

GC/MS analysis revealed **6a**, the dehydrated product of **1a**, formed in negligible amount in some cases. As we thought dehydration was just a trivial side reaction under the optimized conditions, no further study on **6a** was performed.

2.5. Recyclability of Catalyst

Experiments were also conducted to examine the reusability of nano WO_3 . Nano WO_3 readily dissolved in the alkaline medium, when acidified to pH 2~3 it precipitated from the mixture and the heterogeneous nature made it easily removed from the aqueous phase by filtration. The recyclable catalyst collected

through multiple experiments was subjected to five successive run of optimized experiments. In each cycle, nano WO3 was recovered by filtration and washed with water and ethanol for three times. Then, the recovered nano WO₃ was reused directly after drying under vacuum at 80 °C for 10 h. To our delight, there was no obvious loss of activity after five cycles with conversion of 97.9%, 97.8%, 97.4%, 97.3% and 97.0%, respectively (Figure S7). As shown in XRD and XPS (Figure 1), the recovered catalyst (the red line) shows peak absorptions at the same positions but with decreased intensities when compared with original nano WO₃ (the dark line), indicating no significant structural change occurred to the recycled catalyst under the optimized reaction conditions. The SEM image of the recycled nano WO₃ (Figure S1c) reveals the decrease of the particle size as well as the concomitant agglomeration, and the latter may be considered the main reason for the decline in the intensities in XRD and XPS. The decrease of the particle size was beneficial for the catalytic activity of nano WO₃, whereas agglomeration showed the adverse effect and counteracted the influence of the former. Overall, the catalytic performance of recycled nano WO3 was not so much affected and after five runs it still exhibited a similar activity as the original nano WO₃.

2.6. Large Scale Reaction

As described in section **7** in **SI**, the synthetic utility of the developed protocol was further demonstrated by a gram-scale reaction with 1.37 g of **1a** as the substrate and other reagents remained the same proportion. To our delight, full conversion was observed within 6 h, resulting in 17.2% guaiacol, 12.1% *p*-methoxy acetophenone and 83.4% *p*-methoxy benzoic acid, almost in the same yields as the microscale reaction.



2.7. Catalytic Oxidation of Lignin

The results obtained with the model compounds encouraged us to explore the possibility of applying the methodology to the conversion of authentic lignin feedstock. However, the organosolv lignin derived from pinewood powder could not be depolymerized at all under the optimized conditions, this being ascribed to the poor solubility of organosolv lignin in water. Therefore, organic solvents miscible with water such as tetrahydrofuran (THF), acetone, ethanol and 1, 4-dioxane, were added to the reaction mixture as the co-solvent, respectively. Among them, a 1, 4-dioxane/water (1:1, v/v) combination could dissolve the organosolv lignin and provide a homogeneous mixture which was then submitted to the same procedure but still no signals were observed by GC-MS, indicating no reaction occurred or products obtained could not be detected by GC-MS. Based on the results of model compounds, phenolic products may undergo further oxidation or polymerization under the conditions and the other main products, aromatic ketones and/or intermediates may undergo aldol condensation under higher alkaline content. Although related precedents found the use of ethylene glycol beneficial in reductive lignin depolymerization or under acidolysis conditions,^[46] we attempted to add ethylene glycol to our alkaline and oxidative medium in order to suppress the recondensation reactions. To our delight, after the addition of 90 µL of ethylene glycol, the organosolv lignin could be effectively decomposed into monomers and oligomers in 1, 4-dioxane/water (1:1, v/v) at 100 °C within 4 h, and only traces of residual lignin remained, highlighting the efficiency of our catalytic oxidative methodology. Under the optimized conditions, the catalytic process gave 93.3 wt% conversion for lignin and 80.4 wt% of liquid $oil^{\scriptscriptstyle [47]}$ with three main monomers identified as 1-(4-hydroxy-3-methoxyphenyl) ethanone (M1, 0.3 wt%), vanillic acid (M2, 7.6 wt%), and 3-hydroxy-4-methoxybenzoic acid (M3, 0.4 wt%) by GC-MS (Figure 3 and Figure S9), where the selectivity for vanillic acid accounted for 91.6% in the lignin-derived monomers. The three monomers contain typical G-type unit, indicating that the pinewood lignin comprises mainly of G units. QPEOTMS characterization of the liquid oil (Figure 4b) showed that the obtained products are mostly in the range of 100–600 μ , indicating fragmentation towards smaller oligomers and monomers. Furthermore, the clean profile suggests the breakage mainly occurred to some specific sites in organosolv lignin, thereby indicating the selectivity of this method.

To gain insight into the cleavage mechanism for real lignin, 2D-HSQC-NMR spectra of the side chain region for the organosolv lignin before and after reaction were compared (Figure 5, for complete HSQC see Figure S8). It was found that cross signals of methoxy groups and β -O-4 aryl ether bond were the dominant linkages in pinewood lignin. Besides, β -5 linkages (resinol, structure B) and β - β linkages (phenylcoumaran, structure C) were observed. After the oxidation, most of the A, B, C linkages and methoxy group disappeared in the side-chain region of the lignin residue (Figure 5, panel b vs a), suggesting that the catalytic system could effectively cleave the three major linkages of A, B, and C as well as demethoxylation.

3. Conclusion

Herein, we report a mild one-pot oxidative strategy for the depolymerization of lignin model compounds into phenols, ketones, and aromatic acids, catalyzed by nano WO₃ in combination of TBHP and NaOH at 80 $^\circ\text{C}.$ Nano WO $_3$ has dual features of both homogeneous and heterogeneous catalysts, indicating the potential of full conversion and the possibility for catalyst recycle. Upon the addition of NaOH, nano WO₃ became homogeneous and readily reacted with TBHP to produce the real oxidative species, three-membered ring peroxide, which was highly effective in oxidizing benzyl-OH to C=O and further fragmentated β -O-4 bonds in lignin model compounds to give the corresponding aromatic ketones or acids in good to excellent yields. After reaction, the mixture was acidified to precipitate WO₃, which could be recycled 5 times without significant loss of activity. When the modified protocol was applied to the depolymerization of lignin, it offered 93.3 wt% conversion and 80.4 wt% of liquid oil with 7.6 wt% of vanillic acid, accounting for 91.6% selectivity in the lignin-derived monomers. With this, the mild catalytic system with sufficient activity for lignin depolymerization are promising for the production of useful aromatics.

Acknowledgements

This work was supported by the Fundamental Research Funds for the Central Universities (China University of Mining and Technology, 2019XKQYMS49) and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: β -O-4 Cleavage · Lignin depolymerization · Nano WO₃ · Oxidative depolymerization · One-pot

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Manuscript received: May 9, 2021 Revised manuscript received: June 22, 2021 Accepted manuscript online: June 22, 2021 Version of record online:

FULL PAPERS

Catalytic oxidative depolymerization: Herein we described a one-pot process for the mild oxidative depolymerization of lignin and lignin model compounds catalyzed by commercial nano WO₃, along with *tert*-butyl hydrogen peroxide (TBHP) as the oxidant and NaOH as the additive. The catalytic system exhibits advantages of both homogeneous and heterogeneous catalysts.



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1 – 11

Nano WO₃-Catalyzed One-Pot Process for Mild Oxidative Depolymerization of Lignin and its Model Compounds