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Catalytic roles of Mo-based sites on MoS₂ for ethanolysis of enzymatic hydrolysis lignin into aromatic monomers

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ABSTRACT

The depolymerization of enzymatic hydrolysis lignin (EHL) is examined over one-step hydrothermal-synthesized MoS₂ in ethanol without hydrogen gas. Value-added aromatic molecules, mainly including alkyl-substituted phenols (A-Ps), are obtained without char or tar formation. The MoS₂ samples prepared with different Mo and S precursors have been tested and the highest aromatic monomer yield of 226.4 mg/g EHL is achieved over the MoS₂ prepared with thioacetamide and sodium molybdate as precursors (STA-MoS₂) at 320 °C for 12 h. Proper ratios of Mo⁶⁺/Mo⁵⁺ (~0.46–0.65) and (Mo⁶⁺+Mo⁵⁺)/Mo⁴⁺ (~0.47–0.62) on the surface of MoS₂ catalysts are found to be significant for the achievement of high overall aromatic monomer yield. MoO_xS_y species with Mo⁵⁺ and S₂²⁻ is proposed as the active site for the production of complex alkyl phenols *via* demethoxylation and alkylation. The carbon deposition and the exchanges of sulfur and oxygen atoms resulted from the oxidization are likely responsible for the deactivation of catalyst.

1. Introduction

Lignin is a main component of lignocellulose, accounting for 15–30 wt% in mass and 40% in energy of lignocellulose [1–3]. Lignin is mainly composed of three different hydroxylated phenylpropane units, *i.e.*, syringyl (S), guaiacyl (G) and *p*-hydroxyphenyl-propane (H), connected with C-C and C-O linkages, *e.g.*, β -5, β - β , β -1 and β -O-4 linkages. As its aromatic nature, lignin is a potential candidate to replace the existing fossil-based resources for production of aromatic-based fuels and chemicals [4–8]. Enzymatic hydrolysis lignin (EHL) is the large-volume waste of 2nd generation (2 G) bioethanol production and has not been utilized efficiently. Producing aromatic fuels and chemicals from EHL will significantly improve the economy and sustainability of 2 G bioethanol industry [7,9–11].

Mo-based catalysts have been successfully employed in Kraft lignin (KL) depolymerization. For instance, Ma et al. [12] achieved the complete depolymerization of KL over a MoC_{1-x} /activated carbon catalyst in

ethanol at 280 °C for 6 h, forming C8-C10 esters, C6 alcohols, arenes, monophenols and benzyl alcohols as main products [12]. Afterwards, similar products were also obtained from the depolymerization of KL with Mo/Al₂O₃, Mo₂N/Al₂O₃ and MoO₃ as catalysts, and Mo(OC₂H₅)₅ was proposed as the active species for KL solvolysis reaction over varied Mo-based catalysts [13]. High yield of aromatic monomers, up to 575 mg/g KL, was obtained when using $MoC_{1-x}/CuMgAlO_x$ as a catalyst at 330 °C [14]. The depolymerization of EHL was focused recently. Mai et al. [15] and Bai et al. [9] depolymerized EHL into alkylphenols, such as isopropylphenols, butylphenols and pentylphenols, which are the precursors for synthesis of surfactant and pharmaceutical chemicals. [16,17] However, both the WO₃/ γ -Al₂O₃ catalyst used by Mai et al. [15] and NiMo/y-Al2O3 catalyst used by Bai et al. [9] were significantly deactivated after 1 time use. Sang et al. [10,11] depolymerized EHL with unsupported Ni catalysts prepared via nickel formate decomposition, achieving complete EHL liquefaction with 20-30 wt% monomer yields, where H₂ was regarded as essential for formation of high yield of

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Table 1

Texture data of the commercial- and hydrothermally synthesized-MoS₂ samples.

Catalysts	$S_{BET} (m^2/g)$	Pore volume (cm ³ /g)	Pore diameter (nm)
C-MoS ₂	4	0.02	3.3
STA-MoS ₂	108	0.47	3.7
ATA-MoS ₂	57	0.19	4.3
AT-MoS ₂	112	0.41	3.7
AS-MoS ₂	6	0.04	3.5
STA-MoS2 ^a	96	0.40	3.7
STA-MoS2 ^b	15	0.04	3.8

^a used catalyst after 1 run,

^b used catalyst after 5 runs



Fig. 1. XRD patterns of fresh C-MoS $_2$ and hydrothermally synthesized MoS $_2$, and used STA-MoS $_2$ after 1 run.

monomers and elimination of char.

Transition metal sulfides such as MoS₂ [18-22], VS₂ [23,24] and mixed sulfide catalysts (e.g., sulfided CoMo and NiMo catalysts) [25-28] have already been reported as good candidates in lignin depolymerization reaction or hydrodeoxygenation of lignin model compounds. Typically, Kumar et al. [28] reported a highly efficient, solvent free approach of depolymerization of KL to aromatic monomers over a series sulfide NiMo and CoMo catalysts on various acidic and basic supports (i. e., Al₂O₃, ZSM-5 and MgO-La₂O₃). The higher total monomer yield of 26.4 wt% with 15.7 wt% alkylphenols was obtained over sulfide NiMo/MgO-La₂O₃ at 350 °C for 4 h and initial 10 MPa H₂. However, the preparation methods of those reported sulfide catalysts were cumbersome, which were generally composed of an initial wet impregnation and a subsequent high temperature vulcanization under H₂S or in-situ addition of sulfur source (i.e., dimethyldisulphide). MoS₂ can be conveniently synthesized with a hydrothermal method in a single step [22,29,30], which is not examined for lignin solvolysis reaction.

In our recent work, we reported that a one-step hydrothermally synthesized MoS₂ showed high activity for the conversion of guaiacol to alkylphenols in supercritical methanol without any gaseous hydrogen input [30]. Herein, we extended our work with hydrothermally prepared MoS₂ catalysts with different Mo and S precursors for the depolymerization of EHL in ethanol without hydrogen. Based on the

characterization of catalysts and products, the reaction pathway and roles of different Mo-based active sites were discussed. The stability of MoS_2 catalyst was also examined.

2. Materials and Methods

2.1. Chemicals

The EHL sample was obtained from Shandong Longlive Biotechnology Co., Ltd. Prior to use, the obtained sample was dried at 60 °C overnight. Nitrogen and hydrogen (99.99%) were purchased from Tianjin Liufang Gas Co., Ltd. The chemicals and solvents including sodium molybdate, ammonium molybdate, thioacetamide, thiourea, sublimed sulfur, hydrazine hydrate (85%), anisole, ammonium hydroxide and ethanol were analytical grade and procured from Tianjin Guangfu Technology Development Co., Ltd. 38 wt% concentrated hydrochloric acid was supplied by Tianjin Real & Lead Chemical Co., Ltd. The intermediates such as 4-ethylphenol, 2-ethylphenol, 4-methylguaiacol, 4ethyl guaiacol, ethyl ferulic acid and methyl p-coumarate were purchased from Heowns, Biochemistry Co., Tianjin. The deionized water was prepared with an ultrapure water purification machine (UPH-1–10). For comparison purpose, a commercial MoS₂ (C-MoS₂) was procured from Maclin Co., Shanghai.

2.2. Catalyst

2.2.1. Synthesis of the catalysts

The molybdenum sulfide catalyst samples were prepared with a hydrothermal method, as described previously [30], using different precursors of Mo and S, i.e., ammonium molybdate (NH₄)₂MoO₄), sodium molybdate (Na2MoO4)), thiourea (NH2CSNH2) and thioacetamide (CH₃CSNH₂)). The STA-MoS₂ sample was prepared with dissolving Na₂MoO₄ (~6 g) and CH₃CSNH₂ (~9.4 g) in a mixture of equal volume (15 mL) of deionized water and ethanol. After ultrasonication for 15 min, the solution was treated with few drops of concentrated hydrochloric acid (~3 mL) to form slurry, which was then transferred into a 50 mL stainless-steel autoclave and underwent a hydrothermal reaction at 200 °C for 24 h. To prepare ATA-MoS₂ sample, both (NH₄)₂MoO₄ (~0.80 g) and CH_3CSNH_2 (~1.50 g) were dissolved in 30 mL deionized water with ammonium hydroxide (6 mL). Then, the mixture was sonicated at room temperature for 30 min and transferred into the autoclave, which was kept at 200 °C for 20 h. AT-MoS2 was obtained after dissolving (NH₄)₂MoO₄ (0.18 g) and NH₂CSNH₂ (0.65 g) in 28 mL deionized water, subsequently, hydrochloric acid was added into mixture until the pH was \sim 1, and the whole mixture was transferred to the 50 mL autoclave. The autoclave was heated to 200 °C for 12 h. AS-MoS2 was synthesized with $(NH_4)_2MoO_4$ (~2.3 g), sublimed sulfur (~0.75 g) and hydrazine hydrate (~12 mL), which were initially dispersed in 60 mL deionized water followed with 20 min of ultrasonication treatment. The obtained suspension was kept at 200 °C for 24 h in 100 mL autoclave. After each hydrothermal reaction, the autoclave was cooled down to the room temperature and the precipitate was obtained via vacuum filtration. Subsequently the precipitate was washed several times with ethanol until the filtrate became neutral. Finally, the collected solid was dried in vacuum at 60 °C overnight prior to the characterization and further use.

2.2.2. Catalyst characterization

All catalyst characterization methods and their instruments were used as reported in our previous work [30]. Briefly, specific surface area (S_{BET}), pore size distribution and pore volume of the all fresh hydro-thermal MoS₂, C-MoS₂ and used STA-MoS₂ samples were analyzed using a Quantachrome Autosorb-1 measured at 196 o.C. X-ray diffraction (XRD) patterns of the freshly synthesized and used samples were tested at a scanning rate of 10°/min in the diffraction angle range (2 θ) from 10° to 90° at room temperature on Rigaku D/max 2500 v/pc.

(1)



Fig. 2. XPS spectra of (a) Mo 3d and (b) S 2p of fresh C-MoS₂, STA-MoS₂, ATA-MoS₂, AT-MoS₂ and AS-MoS₂.

Raman spectra for the used samples were collected using a LabRAM HR Evolution microscopic confocal Raman spectrometer (HORIBA Hobin Yvon S.A.S., France). All measurements were done under the 532 nm He-Ne laser-excitation.

The chemical states of the fresh and used samples were revealed by X-ray photoelectron spectroscopy (XPS). XPS spectra of those samples were recorded with a PHI 1600 ESCA system spectrometer equipped with a Mg K α X-ray source (hv = 1253.6 eV). The binding energy (BE) of C 1 s peak at 284.6 eV (C-C/C-H) was used as an internal standard.

other aromatic products (OPs)) was calculated according to Eq. (1). The selectivity (S) of complex A-Ps (isopropyl- and butyl- substituted phenols) in overall A-Ps was symbolized as S and was calculated with Eq. (2). The yield (Y/%) of products from the conversion of model compounds were calculated with Eq. (3). All the results were confirmed with triplicate experiments and the average values were taken for calculation. In the following equations, M and n represents the mass and mole of corresponding chemicals, respectively.

$$Yield(mg / g \quad EHL) = \frac{M(overall \ aromatics \ or \ individual \ grouped \ products)_{output}}{M(EHL)_{input}}$$

2.3. Catalytic reaction

The ethanolysis of EHL was carried out in a 300 mL stainless steel autoclave reactor (Kemi Co. Ltd, Hastelloy). Typically, 1.0 g of EHL, 80 mL of ethanol and 0.5 g of catalyst were introduced into the reactor. After purging the reactor with nitrogen gas for 5 times, it was heated to the desired temperature (260–330 °C) with a stirring speed of 600 rpm. After completing the reaction, the reactor was cooled down rapidly to room temperature, and the liquid products were collected by suction filtration.

In the recycle test, the used MoS_2 catalyst was collected after washing with 10 mL of ethanol. Prior the next use, the solid was dried at 60 $^\circ C$ for 2 h in vacuum.

2.4. Product analysis

With anisole as an internal standard, the liquid products were analyzed and quantified using gas chromatograph equipped with a flame ionization detector (GC-FID, Agilent Technologies, model 6890) and a HP-5 MS capillary column (Agilent, 30 m \times 0.25 mm \times 0.25 µm). The same GC and quantitative analysis methods were followed as given in our previous work [30]. The yield of overall aromatic monomers or individual grouped products (*i.e.*, alkyl-substituted phenols (A-Ps) and

$$S(\%) = \frac{M(complex \ A - Ps)_{output}}{M(overall \ A - Ps)_{output}}$$
(2)

$$Y(\%) = \frac{n(individual \ product)_{output}}{n(reactants)_{input}}$$
(3)

The FTIR spectra of the bare EHL and EHL ethanolysis products were recorded with a IRAffinity-1S FT-IR spectrophotometer of Shimadzu. Matrix assisted laser desorption/ionization time-of-light mass spectroscopy (MALDI-TOF-MS) of the liquid products were measured to identify the molecular weight distribution with an Autoflex tof/toflll of Bruker Dalton Corporation. A 15 g/L solution of 2,5-dihydroxyl benzoic acid (DHB) (Sigma) in ethanol was used as matrix. The two-dimensional heteronuclear single quantum coherence-nuclear magnetic resonance (2D-HSQC NMR) spectra were recorded on a Bruker AVAVCE III HD 400 MHz. The deuterium generation reagent was DMSO- d_6 .

3. Results and Discussion

3.1. Catalyst characterization

Although the partial characterization of C-MoS₂ and STA-MoS₂



Fig. 3. (a) TIC and the corresponding structures of the liquid products obtained from the ethanolysis of EHL over STA-MoS₂. (b) Yield of overall aromatic monomers and A-Ps obtained from EHL ethanolysis without catalyst or over different MoS₂. (Reaction conditions: 1.0 g EHL, 80 mL ethanol, 320 °C, 6 h, 0.5 g catalyst, initial 0 MPa (gauge) N₂, 600 rpm). A-Ps: alkyl substituted phenols, OPs: other aromatic products.

samples such as textural and structural properties have already been given in our previous work [30], few salient characteristic results are included in the present work as well to understand the texture-structure-activity relationships. Table 1 lists the textural data of the fresh C-MoS₂ and synthesized-MoS₂ samples. STA-MoS₂ (108 m^2/g) and AT-MoS₂ (112 m^2/g) have large specific surface areas. ATA-MoS₂ shows a moderate surface area (57 m^2/g). Nevertheless, the surface areas of C-MoS₂ and AS-MoS₂ are only 4 and 6 m^2/g , respectively. Correspondingly, the pore volumes of STA-MoS₂ (0.47 cm^3/g) and AT-MoS₂ (0.41 cm³/g) are much larger than those of ATA-MoS₂ (0.19 cm³/g), C-MoS₂ (0.02 cm³/g) and AS-MoS₂ (0.04 cm³/g). Nevertheless, different catalysts have similar pore diameters which are in the ranges of ~3.3-4.3 nm. The high surface area and pore volume of STA-MoS2 were decreased to 96 m^2/g and 0.40 cm^3/g after 1 run, respectively, and further drastically decreased into $15 \text{ m}^2/\text{g}$ and $0.04 \text{ cm}^3/\text{g}$ after 5 runs, respectively.

The XRD patterns of the fresh and used samples are given in Fig. 1. Fresh C-MoS₂ exhibits all the specific diffraction peaks of the hexagonal MoS₂ phase (PDF#17–0744). For catalyst samples prepared *via* hydrothermal route, only two broad peaks at 33° and 58.8° were recognized,

which are attributed to (101) and (110) planes of MoS₂ with the corresponding *d*-spacing of 0.271 and 0.158 nm, respectively. After 1 run, the diffraction angle of (101) and (110) lattice plane of STA-MoS₂ increased by 1.0° and 1.7° , respectively, and the *d*-spacing assigned to these two planes decreased by 0.008 and 0.004 nm, respectively.

The XPS spectra of different MoS₂ samples are illustrated in Fig. 2. Fig. 2(a) presents the XPS of Mo 3d (~228–237 eV) signals of different MoS₂ samples [18,30–32]. For C-MoS₂, only the peaks of Mo⁴⁺ (3d_{3/2} and 3d_{5/2}) were detected. Nevertheless, the XPS of fresh synthesized-MoS₂ samples can be deconvoluted into the peaks of Mo⁶⁺ (3d_{3/2} and 3d_{5/2}), Mo⁵⁺ (3d_{3/2} and 3d_{5/2}) and Mo⁴⁺ (3d_{3/2} and 3d_{5/2}) [33,34]. Meanwhile, the contents of Mo⁴⁺, Mo⁵⁺ and Mo⁶⁺ sites on different fresh synthesized-MoS₂ samples are similar, which are in the range of ~60–70%, ~20–30% and ~10–20%, respectively, except for AT-MoS₂ which has the highest content Mo⁴⁺ (69.9%) and Mo⁵⁺ (26.4%) and the lowest content of Mo⁶⁺ (3.7%). Fig. 2(b) presents the XPS of S 2p (~160–170 eV) signals of the MoS₂ samples. Only the peaks of S²⁻ (2p_{1/2} and 2p_{3/2}) in C-MoS₂ were detected, while the peaks of S²⁻ samples. The contents of SO_x, S2²⁻ and S²⁻ on STA- and AS-MoS₂ are in similar



Fig. 4. Influences of (a) temperature (6 h), and (b) reaction time (320 $^{\circ}$ C) on the yield of overall aromatic monomers and A-Ps obtained from the ethanolysis of EHL over STA-MoS₂ catalyst (Reaction conditions: 1.0 g EHL, 80 mL ethanol, 0.5 g catalyst, initial N₂ 0 MPa (gauge), 600 rpm).



Fig. 5. FTIR spectra of (a) EHL, and the bio-oils obtained from the ethanolysis of EHL (b) without catalyst, and over (c) C-MoS₂ and (d) STA-MoS₂ at 320 $^{\circ}$ C.



Fig. 6. The MALDI-TOF profiles of the bio-oils obtained from EHL ethanolysis (a) without catalyst (6 h), and over STA-MoS₂ for (b) 6 h and (c) 12 h at 320 $^{\circ}$ C.

ranges, which are 3.9–4.7%, 16–22% and 74.1–79.3%, respectively. Nevertheless, ATA-MoS₂ has highest content of SO_x (19.2%) and lowest content of S²⁻ (53.3%), and AT-MoS₂ has highest content of S₂²⁻ (29.9%) and lowest content of SO_x (3.7%).

3.2. Catalytic ethanolysis of EHL

3.2.1. Activity

The total-ion chromatogram (TIC) of the liquid products obtained from STA-MoS₂ catalyzed EHL ethanolysis at 320 °C and the corresponding structure are depicted in Fig. 3(a). Twenty-seven aromatic monomers were quantified, and, among these monomers, alkylphenols (A-Ps) are the main products. The extend GC-TIC with retention time of 8-12 min and with other MoS₂ as catalysts were also plotted along with their molecules as listed in Fig. S2 and Fig. S3, respectively. Fig. 3(b) show the yields of overall aromatic monomers and A-Ps obtained from non-catalytic reaction and catalytic reactions over different MoS₂ catalysts. Without a catalyst, EHL was converted with ethanol into 50.1 mg/ g EHL aromatic monomers, mainly including ortho-ethylphenol, orthomethylguaiacol, ortho-ethylguaiacol, ethyl ferulic acid and methyl pcoumarate (Fig. S1), with formation of a certain amount of char. When a catalyst was added, EHL was completely liquified without formation of char. ATA-MoS₂ gave the highest overall aromatic monomer yield (202.8 mg/g EHL), followed by STA-, AS-, AT- and C-MoS2 with the corresponding yield of 175.6, 142.3, 133.7 and 102.8 mg/g EHL, respectively. Furthermore, the yield of A-Ps among overall aromatic monomers can be considered as a standard to measure the activity of catalyst for EHL ethanolysis into highly value-added chemicals. The decreasing order of the A-Ps yield for different catalyst is as follows: STA-MoS₂ (111.9 mg/g EHL) > ATA-MoS₂ (103.9 mg/g EHL) > AS- MoS_2 (88.9 mg/g EHL) > AT-MoS_2 (84.2 mg/g EHL) > C-MoS_2 (41.7 mg/g EHL). Due to its relatively higher activity towards A-Ps formation, we further used STA-MoS₂ for examining the effect of the reaction conditions and recyclability test.

3.2.2. Effect of reaction conditions

Fig. 4(a) illustrates the effect of reaction temperature on the yields of overall aromatic monomers and A-Ps with STA-MoS₂ as a catalyst for 6 h. The overall aromatic monomer yield was found to be < 50 mg/g EHL at \leq 270 °C, which was increased to 102 mg/g EHL at 280 °C. As the temperature increases to 330 °C, the yield of overall aromatic monomers increased monotonically to 185.6 mg/g EHL. The A-Ps yield show similar increasing trend from 280 (68.5 mg/g EHL) to 330 °C



Fig. 7. 2D-HSQC NMR spectra of liquid products obtained from EHL ethanolysis (a) without catalyst and over (b) STA-MoS₂, (c) ATA-MoS₂, (d) AT-MoS₂ and (e) AS-MoS₂ at 320 °C for 6 h.



Fig. 8. Product distributions and corresponding yields from 2EP, 4EP, 4MG, 4EG, EFA and HMP conversion over STA-MoS₂ in ethanol at 320 °C for 6 h.

(118.6 mg/g EHL). The effect of the reaction time on yields of overall aromatic monomers and A-Ps with STA-MoS₂ as the catalyst at 320 °C was also examined, and the results are plotted in Fig. 4(b). The overall aromatic monomer and A-Ps yields were increased monotonically with increasing the reaction time and reached the highest 226.4 and 140.7 mg/g EHL respectively for 12 h.

3.3. Analysis of liquid products

3.3.1. FTIR analysis

The FTIR spectra of EHL, and the bio-oils obtained with and without catalysts are plotted in Fig. 5, and the assignments of all the bands are listed in Table S1 [21,35,36]. The bands for hydroxyl groups at $3402\ \text{cm}^{-1},\ \text{aryl groups}$ at $1595\ \text{cm}^{-1}$ and carbonyl groups at 1110 cm⁻¹ were found to be existed on both EHL and reaction products. Other typical functional group bands, i.e., methyl, methylene and methoxy, were observed in the liquid products, which reveals the existence of oxygen-containing aromatic compounds predominately. Specifically, the intensity order of alkyl groups characterized by the band at 2868–2966 cm⁻¹ is as follows: STA-MoS $_2$ > C-MoS $_2$ ~ without catalyst > EHL (Fig. 5(a-d)). Alkyl groups were dominantly released or formed during the EHL ethanolysis process, which resulted in the intensity improvement in the bio-oils obtained with or without a catalyst [37,38]. The higher yield of A-Ps obtained over STA-MoS₂ than that over C-MoS₂ or without catalyst (Fig. 3(b)) clearly indicates the higher alkylation activity, and the formed substituted aliphatic side chain in A-Ps explained the relatively stronger intensity of alkyl groups over STA--MoS₂ (Fig. 5(d)). The hydrothermally prepared MoS₂ (STA-MoS₂) has already been proved to exhibit a higher alkylation activity than C-MoS₂ in previous work [30]. The peak contributed to the aromatic C-H out-of-plane stretching (821 cm⁻¹) from EHL was slowly reduced (Fig. 5 (b-d)) over MoS₂. In more details, a very weak band at 821 cm⁻¹ clearly revealed the release of guaiacyl units from EHL over STA-MoS2 was poorer than that over the other catalysts studied [30,37].

3.3.2. MALDI-TOF-MS analysis

The MALDI-TOF-MS technique is employed to monitor the change of molecular weight of the lignin fragments after reaction. Fig. 6(a) shows the molecular weight distribution of the bio-oils with the m/z range of 331–1311 for the dissolution of EHL without catalyst at 320 °C for 6 h. In the m/z range of 331–400, the m/z difference of 14 for each adjacent peak may be due to the insertion or removal of -CH₂- functional group. Furthermore, all the obtained fragments from the conversion of EHL is soluble in ethanol [12]. As shown in Fig. 6(b), the m/z fragment was significantly reduced to 259–996 range on STA-MoS₂ catalyst, which confirms the ability to depolymerize EHL linkage in ethanol. While the higher overall aromatic yield was achieved at 12 h, the m/z peak distribution of liquid products mainly center on 367 with a broader m/z range of 259–1088 than that for 6 h (Fig. 6(c)), which may result from the dominant depolymerization reaction accompanied by the repolymerization of small molecules as the reaction time increase [13].

3.3.3. 2D-HSQC NMR analysis

2D-HSQC NMR spectra of the products obtained from EHL ethanolvsis without catalyst or over different hydrothermal MoS₂ catalysts are illustrated in Fig. 7. Three regions are presented, namely, H-C-C- correlation region ($\delta C/\delta H$: 5–40/0–3 ppm) in which C atoms are not connected to O atoms, H-C-O- correlation region ($\delta C/\delta H$: 40–65/3–5 ppm) in which C atoms are directly connected to O atoms, and aromatic C(Ar)-H correlation region ($\delta C/\delta H$: 105–140/6–8 ppm). The spectra of EHL had been reported in our previous work [11]. As shown in Table S2, the signals of -CH₃, methoxyl groups, β-O-4 alkyl ether (A''), resinol structure (B'') containing β - β and α -O- γ linkages, phenylcoumarane structure (C'') containing β -5 and α -O-4 linkages, structural units of lignin (p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S)), p-coumaric acid (CA) and ferulic acid derivatives (FA) were detected in EHL [39,40]. As shown in Fig. 7(a), the intensity of the -CH₃ signal in the H-C-C- region after EHL ethanolysis without catalyst becomes more stronger than that in EHL. The structure of β -O-4 alkyl ether disappeared after noncatalytic ethanolysis. Moreover, the C-H cross signals of alkyl side chains and ester side chains (ES), such as the C_{α} -H_{α} signals (para-methyl (PM_{α}), *para*-ethyl (PE_{α}) and ES_{α}), and the C_{β}-H_{β} signals (*para*-propyl (PP_{β})), are recognized. In the H-C-O- regions, the signals of methoxy group and C_{y} -H_y (ES_y) were detected. In the C(Ar)-H correlation region, the signals of S unit, CA and hydrogenated FA (HFA) were also detected. When the hydrothermally synthesized MoS₂ was added, the intensity of -CH₃ signals were significantly increased and contributed to the highest for AT-MoS₂. Nevertheless, the signals of methoxy groups disappeared. Meanwhile, the signals of *para*-propanol side chains ($PPol_{\alpha}$ and $PPol_{\beta}$) in the H-C-C- region, the G and H units in C(Ar)-H region appeared, which revealed the hydrothermal MoS₂ showed fine demethoxylation (DMO) activity to realize the conversion of S units into G and H units via removing methoxy groups. The highest intensity of G and H units were achieved with AT-MoS₂, which indicates that AT-MoS₂ showed highest DMO activity. In more detail, the signals of dimers containing α -O-4 (B') and $\beta\text{-}\beta$ linkages (C' $_\beta$ and C' $_\gamma$) in H-C-O- region were only identified when AT-MoS₂ was used as a catalyst. The results indicated AT-MoS₂ exhibited poorest activity of EHL depolymerization among all the hydrothermal MoS₂, which was consistent with the yield of aromatic monomers as shown in Fig. 3(b).

3.4. Conversion of intermediates

2-ethylphenol (2EP, #1 in Fig. S1), 4-ethylphenol (4EP, #2 in Fig. S1), 4-methyl guaiacol (4MG, #3 in Fig. S1), 4-ethylguaiacol (4EG, #4 in Fig. S1), methyl *p*-coumarate (HMP, #5 in Fig. S1) and ethyl ferulic acid (EFA, #6 in Fig. S1) were obtained from the non-catalytic (Fig. S1) reaction, but A-Ps are the main products in synthesized-MoS₂ catalyzed EHL ethanolysis reactions. Hence, these monomers obtained from the non-catalytic reaction may be the intermediates for the formation of A-Ps. In order to verify this hypothesis, the conversion of the



Fig. 9. The effect of (a) Mo^{6+}/Mo^{5+} and (b) $(Mo^{6+}+Mo^{5+})/Mo^{4+}$ calculated by the XPS data of different types of MoS_2 on the yield of overall aromatic monomers, (c) The effect of contents of Mo^{5+} and S_2^{-2-} species on the selectivity of complex A-Ps (iPr-Ps and Bu-Ps) in the overall A-Ps obtained from EHL ethanolysis over different types of MoS_2 , (d) Yield of G unit and its derivatives in the liquid products obtained from EHL ethanolysis over different hydrothermal MoS_2 .

Table 2

The selectivity of complex A-Ps in overall A-Ps during the EHL ethanolysis reaction with different reaction time, and the Mo^{5+} and S_2^{2-} content on the spent catalyst according to the XPS data.

Reaction time/h	S (complex A-Ps)/%	Content of species on spent STA-MoS $_2$ after reacted for corresponding time/%	
		Mo ⁵⁺	S ₂ ²⁻
0 (Fresh)	_	21.9	16
1	81.9	31.8	22.4
2	75.3	30.4	18.6
4	74.9	28.6	17
6	66.6	24.3	12.9

above-mentioned molecules over STA-MoS2 in ethanol at 320 °C for 6 h were examined. As shown in Fig. 8, 2EP and 4EP were converted mainly into isopropyl-substituted phenols (iPr-Ps) with total yield (Y/%) of 10% and 42.4% respectively. 4MG was converted into 2,6-ditert-butyl-4methyl phenol with the yield of 72%. 2,6-diisopropylphenol, 2,6ditert-butylphenol and 4-ethyl-2,6-ditert-butylphenol were obtained from the conversion of 4EG, with the yields of 10.9%, 36.8% and 27.4%, respectively. These products were also obtained from the conversion of EFA, with the yield of 10% (2,6-diisopropylphenol), 32.7% (2,6-ditertbutylphenol) and 32.4% (4-ethyl-2,6-ditert-butylphenol). Moreover, 19.5% of 2,6-diisopropylphenol and 13.1% of 2,6-ditert-butylphenol were obtained from the conversion of HMP. The ¹H NMR spectra of the liquid products obtained from the conversion of above-mentioned intermediates was shown in Fig. S4. These results indicate that STA-MoS₂ catalyzes the demethoxylation and alkylation reactions of phenolic monomers to form complex A-Ps (i.e., isopropyl- and butylphenols) which are also enriched in the products obtained from EHL ethanolysis reaction. FTIR results also revealed that methoxy groups were removed and alkyl groups were added during the STA-MoS₂ catalyzed EHL depolymerization reaction. MoS₂ had been considered as one of the optimal candidates with high performance in hydrogen evolution reaction (HER) [41,42]. Moreover, no extra gaseous hydrogen was needed in this work. Therefore, MoS₂ could be considered as an effective and potential candidate, over which a cascade reaction, including hydrogen releasing through HER from ethanol, EHL depolymerization and demethoxylation of lignin-derived intermediates into complex A-Ps, was achieved.

3.5. Active sites of MoS_2

Valencia et al. [43] discussed the active phases of Mo-based catalysts for HDO reaction of palmitic acid, and thought that the contents of Mo⁶⁺, Mo⁵⁺ and Mo⁴⁺ in the catalyst significantly influence its activity. Herein, the ratio of Mo^{6+}/Mo^{5+} and $(Mo^{6+}+Mo^{5+})/Mo^{4+}$ of different MoS₂ catalysts were calculated, based on the results of XPS, to analyze the active sites of these catalysts. As shown in Fig. 9(a) and (b) the ratio of $\mathrm{Mo}^{6+}/\mathrm{Mo}^{5+}$ is increased in an order: AT-MoS_2 (0.14) $< STA\text{-}MoS_2$ (0.46) < ATA-MoS₂ (0.65) < AS-MoS₂ (0.81), and the ratio of $({\rm Mo}^{6+}{\rm +Mo}^{5+})/{\rm Mo}^{4+}$ also increased in the same order, i.e., AT-MoS_2 $(0.43) \ < \text{STA-MoS}_2 \ (0.47) \ < \text{ATA-MoS}_2 \ (0.62) \ < \text{AS-MoS}_2 \ (0.68).$ Nevertheless, STA-MoS₂ and ATA-MoS₂ gave higher yields of overall aromatic monomer than AT-MoS2, AS-MoS2 and C-MoS2. These results indicate that the catalytic activity of MoS2 catalysts for EHL ethanolysis to aromatic monomers were first increased and then decreased with the increase of the ratios of Mo^{6+}/Mo^{5+} and $(Mo^{6+}+Mo^{5+})/Mo^{4+}$ and reach high values when the ratios of Mo^{6+}/Mo^{5+} and $(Mo^{6+}+Mo^{5+})/Mo^{4+}$ are



Fig. 10. (a) Conversion of hydrogen and ethyl radicals from ethanol to discharge electrons, (b) catalytic cycle of different Mo-based species, and (c) proposed reaction pathways for complex A-Ps formation from EHL ethanolysis over MoS₂. (*i*Pr-Ps: isopropyl substituted phenols, Bu-Ps: butyl substituted phenols. Complex A-Ps were composed of *i*Pr-Ps and Bu-Ps).



Fig. 11. Recyclability of the STA-MoS₂ catalyst on the yield of overall aromatic monomers and A-Ps during ethanolysis of EHL (Reaction conditions: 1.0 g EHL, 80 mL ethanol, 320 $^{\circ}$ C, 6 h, initial 0 MPa (gauge) N₂, 600 rpm).

in the range of 0.46-0.65 and 0.47-0.62, respectively.

Based on the XPS results, three different species were found to be existing on the surface of the hydrothermally synthesized MoS_2 catalysts, namely Mo sulfide (MoS_2 having Mo^{4+} with S^{2-} species), Mo oxysulfide (MoO_xS_y having Mo^{5+} with S_2^{2-} species) and Mo oxide (MoO_3 with Mo^{6+}) [44–47]. Nevertheless, MoO_xS_y and MoO_3 phases were not identified in the XRD patterns of the fresh hydrothermal MoS_2 samples which may be due to their amorphous structure. No MoO_xS_y phase exists on C-MoS₂ as there was complete absence of Mo^{5+} peak in XPS (Fig. 2 (a)). The complex A-Ps (*i*Pr-Ps and Bu-Ps) from EHL depolymerization

are expected in higher proportion due to their widely industrial application value, which are generally acted as important raw material for the production of oil-soluble phenolic resin, surfactant, antioxygen and flame retardant [48,49]. The relationship between the selectivity of complex A-Ps in total A-Ps yield and the content of Mo^{5+} and S_2^{2-} on MoS_2 surface is shown in Fig. 9(c). The highest selectivity of complex A-Ps was achieved with AT-MoS₂ as a catalyst (78.6%), which was followed with ATA-, AS-, STA- and C-MoS2 with the complex A-Ps selectivity of 74.6%, 72.6%, 66.6% and 5.5%, respectively. The selectivity of complex A-Ps increased with the increase of the content of Mo^{5+} and $S2^{-2}$ on MoS₂ surface, indicating that MoO_xS_y phase is the active sites for DMO and alkylation process to produce the main products of complex A-Ps. Therefore, AT-MoS₂ showed the highest DMO activity, which was also proved by the 2D-HSQC analysis as shown in Fig. 7. Moreover, the signals of S units disappeared when hydrothermal MoS2 was added (Fig. 7(a-e)), while the signals of G and H units appeared. Therefore, the yield of G units and their derivatives, which were obtained through the DMO of S units, could also show the DMO activity of hydrothermal MoS₂. As shown in Fig. 9(d), the yield of G units and their derivatives was decreased as follows: AT-MoS₂ (18.8 mg/g EHL) > ATA-MoS₂ $(16.5~mg/g~\text{EHL}) > \text{AS-MoS}_2~(15.4~mg/g~\text{EHL}) > \text{STA-MoS}_2~(13.5~mg/g~\text{EHL}) > 0.5~\text{MoS}_2~(12.5~mg/g~\text{EHL}) > 0.5~\text{MoS}_2~(12.5$ EHL), which was perfectly consistent with the decrease order of Mo⁵ and S_2^{2-} contents.

In addition, the properties of STA-MoS₂ after reaction for different time (1, 2, 4 and 6 h) was further measured to observe the change of catalyst during EHL ethanolysis. As shown in Table 2, based on the XPS data, the content of Mo^{5+} and S_2^{2-} were increased to 31.8% and 22.4% respectively after 1 hour, and further decreased with the extension of reaction time. After 6 h (used STA-MoS₂ after 1 run), the Mo^{5+} and S_2^{2-} content were deceased to 24.3% and 12.9%, which were higher and lower respectively than that of the fresh sample. The results indicated Mo^{5+} and S_2^{2-} on STA-MoS₂ was generated at the beginning of reaction in ethanol, and then gradually consumed during the reaction. Moreover,



Fig. 12. (a) XRD patterns, (b) XPS spectra of Mo 3d and S 2p, and (c) Raman analysis of used STA-MoS₂ after 5 runs. (d) Relative atomic contents of Mo, S and O on the surface of fresh and used (after 1 and 5 runs) STA-MoS₂ catalyst by XPS (Note: Only Mo, S and O are semiquantitative and the total content of Mo, S and O for each sample was round to 100%).

the selectivity of complex A-Ps in the overall A-Ps was gradually decreased from 81.9% (1 h) to 66.6% (6 h). The results further verified that Mo^{5+} and S_2^{2-} might be the actives sites on MoS_2 surface for its DMO activity in the EHL ethanolysis process, which played a significant role in the achievement of abundant complex A-Ps.

3.6. Possible mechanism of complex A-Ps formation

Ma et al. [13] proposed a radical mechanism for Kraft lignin conversion in supercritical ethanol. Hydrogen and ethyl radicals were generated from ethanol (Fig. 10(a)). Therefore, we further proposed the pathway of A-Ps formation based on the 2D-HSQC NMR (Fig. 7) and intermediates conversion results (Fig. 8). Meanwhile, referred to the published work [36], the cycles of Mo-based species in EHL ethanolysis for the reduction reaction via acceptance of electrons from the conversion of radicals (hydrogen and ethyl radicals) into cations, and the oxidation reaction via discharge of electrons was proposed in Fig. 10(b). The discharged electrons would be joined in the A-Ps formation. As shown in Fig. 10(c), β -O-4 linkage in EHL structure was broken during the non-catalytic ethanolysis of EHL to release methoxy-containing S units, which were further demethoxylated into G units over MoS₂ and then into complex A-Ps through DMO/alkylation reaction with the effect of the discharged electrons and cations (Pathway a'). On the other hand, several phenolic monomers obtained from non-catalytic ethanolysis further undergo DMO and alkylation reaction over MoS2 to form complex A-Ps (Pathway b'). In more detail, the -C-C-COO- group of HFA and CA units were removed to form acetic acid and formic esters, which are the by-products of EHL ethanolysis (Fig. S2).

3.7. Stability and deactivation of STA-MoS₂

The reusability of the STA-MoS₂ catalyst is shown in Fig. 11, the yield for overall aromatic monomers and A-Ps did not obviously change in initial 2 runs, but generally decreased to 125.4 and 80.7 mg/g EHL

respectively in the 4th run. Similar yields of overall aromatic monomers (133.3 mg/g EHL) and A-Ps (87 mg/g EHL) were further obtained in the 5th run. These results imply that STA-MoS₂ is recyclable at least for three catalytic runs.

In the XRD patterns of used STA-MoS₂ after 5 runs, the intensity of diffraction peak at 34° assigned to (101) plane decreased, and new crystalline phases of monoclinic MoO₃ (PDF#47-1081) and hexagonal MoO₂ (PDF#50-0739) appeared (Fig. 12(a)), which indicate the occurrence of oxidization for MoS_2 . Due to the oxidization, Mo^{4+} was decreased to 40.7%, and the Mo^{6+} and SO_x contents of used STA-MoS₂ after 5 runs were significantly increased to 32.3% and 13.9% respectively (Fig. 12(b)). Hence, the Mo^{6+}/Mo^{5+} and $(Mo^{6+}+Mo^{5+})/Mo^{4+}$ of the used STA-MoS₂ after 5 runs were increased to 1.51 and 2.10, respectively, exceeding the above-mentioned proper ratio range. The loss of atomic sulfur content was also observed on the used catalyst. As shown in Fig. 12(d), the sulfur content on STA-MoS₂ decreased from 74.8% to 56.6% after 1 run, and further decreased to 43.2% after 5 runs. However, the oxygen content on STA-MoS₂ gradually increased from 1.4% to 7.6% after 1 run, and further increased to 28.3% after 5 runs. These results clearly revealed the sulfur-oxygen exchange occurred gradually in EHL ethanolysis reaction. Badawi et al. [50] also reported that the produced water during hydrodeoxygenation process of oxygenated compounds over MoS₂ led to the formation of vacancies by removing sulfur atoms from the metallic edge with oxygen atoms, and the sulfur-oxygen exchanges on the surface of MoS₂ was resulted in the continuous deactivation of catalyst. In addition, Raman spectrum revealed that both amorphous and graphite carbon coexisted on the surface of used STA-MoS₂ after 5 runs as shown in Fig. 12(c). Therefore, the carbon deposition and the sulfur-oxygen exchanges which is resulted from the oxidization on MoS₂ are responsible for the deactivation of the catalyst.

4. Conclusions

Enzymatic hydrolysis lignin (EHL) was completely depolymerized in supercritical ethanol to value-added oxygen-contained aromatic monomers over MoS₂ catalyst prepared through a single-step hydrothermal method with different Mo and S precursors. Among these catalysts, the catalyst prepared with thioacetamide and sodium molybdate as precursors gave the highest aromatic monomer yield, *i.e.*, 226.4 mg/g EHL, at 320 °C for 12 h. MoS₂ catalysts with proper ratios of Mo⁶⁺/Mo⁵⁺ (~0.46–0.65) and (Mo⁶⁺+Mo⁵⁺)/Mo⁴⁺ (~0.47–0.62) exhibited higher activity for EHL depolymerization into aromatic monomers, and MoO_xS_y species having Mo⁵⁺ with S₂²⁻ acted as the main active sites for the production of complex alkyl phenols *via* demethoxylation and alkylation reaction. The carbon deposition and the sulfur-oxygen exchanges resulted from the oxidization are responsible for the deactivation of the catalyst.

CRediT authorship contribution statement

Kai Wu did the major part of the experiment and made the first draft of the manuscript. Yushuai Sang and Saravanan Kasipandi polished the manuscript and discussed the details with great improvement. Yiming Ma, Hairui Jiao and Qingfeng Liu did the experiments together with Kai Wu and discussed all the details of the work as well as the manuscript. Hong Chen provided a part of the funding and guided the experimental work. Yongdan Li initiate the project and supervised the work.

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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2022.03.014.

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