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Selective catalytic conversion of guaiacol to phenols over a molybdenum carbide catalyst†

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An activated carbon supported α-molybdenum carbide catalyst (α-MoC$_{1-x}$/AC) showed remarkable activity in the selective deoxygenation of guaiacol to substituted mono-phenols in low carbon number alcohol solvents. Combined selectivities of up to 85% for phenol and alkylphenols were obtained at 340 °C for α-MoC$_{1-x}$/AC at 87% conversion in supercritical ethanol. The reaction occurs *via* consecutive demethylation followed by a dehydroxylation route instead of a direct demethoxygenation pathway.
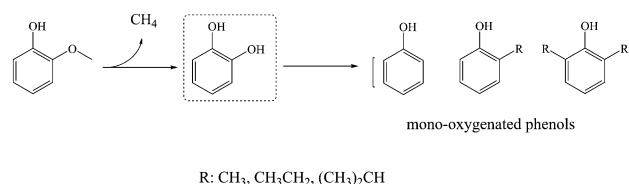
Lignin is becoming an important renewable feedstock for the sustainable production of fuels and value-added chemicals and has received considerable attention in the last decade.[1] We recently reported that Kraft lignin can be completely ethanolysed to small molecules in supercritical ethanol over an α-MoC$_{1-x}$/AC catalyst in an inert atmosphere.[2] However, the reaction pathways in the ethanolysis are complex and difficult to follow. Furthermore, in the utilization of lignin derived compounds, the high oxygen content and poor chemical stability are often the limiting factors.[2,3] Therefore, obtaining information from the reactions of model compounds is often meaningful to the utilization of the lignin derived compounds.[4]

Guaiacol, which contains simultaneously hydroxyl and methoxyl functional groups, has been typically used as a model compound in the study of lignin valorization.[5–8] Early studies indicated that sulfided CoMo and NiMo catalysts and supported metal hydrogenation catalysts (Ni, Ru, Pt and Pd) have activity in the hydrodeoxygenation (HDO) of guaiacol under high H$_2$ pressure and temperature.[5,6] However, aromatic ring hydrogenation occurred simultaneously and the employment of the noble metal-based catalysts could significantly raise the cost. For the sulfided catalysts, continuous addition of sulfur is required in the reactant stream.[5]

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Recently, molybdenum-based hydrotreating catalysts *e.g.*, Mo$_2$C, Mo$_2$N, MoS$_2$, MoO$_3$ *etc.* have shown good activity and selectivity in the HDO of guaiacol.[7–10] Jongerius and coworkers obtained phenol and methylated phenols from guaiacol over a supported Mo$_2$C catalyst, with a total selectivity of 69% phenolics.[8] However, the hydrogenation of the aromatic ring also occurred. Similarly, Prasomsri *et al.* showed that MoO$_3$ is active and selective for a direct C–O bond cleavage of guaiacol in a vapour-phase over a packed-bed flow reactor, producing phenol and hydrocarbons with selectivities of 29.3% and 53.5%, respectively, at 320 °C. The stability of their catalyst was poor at further higher temperatures *i.e.* >350 °C.[9a] Veryasov *et al.* reported that a novel urchin-like crystalline MoS$_2$ showed a high activity on the HDO of the liquefied wood sample, where the oxygen content decreased from 43.3% to 8.2% at 300 °C under 8.0 MPa H$_2$ pressure.[10]

Here, we report the catalytic deoxygenation of guaiacol to mono-oxygenated phenols over the α-MoC$_{1-x}$/AC catalyst with high selectivity in popular solvents without the hydrogenation of benzene rings (Scheme 1).
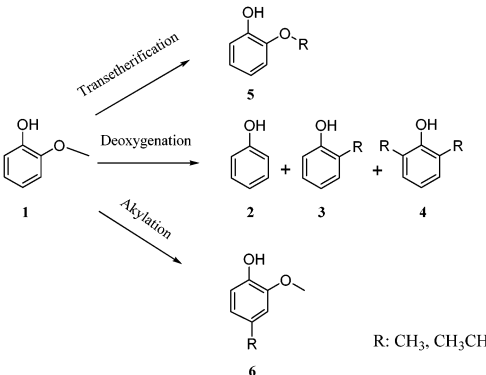
The catalyst used in this work has a Mo content of 30 wt%, a BET-specific surface area of 749 m^2 g^{-1}, micropore and mesopore volumes of 0.12 and 0.59 cm^3 g^{-1}, respectively, and a mean pore diameter of 7.9 nm. The XRD and TEM analysis data were presented in our previous work.[2] The catalytic performance of the α-MoC$_{1-x}$/AC catalyst was examined in a number of solvents, *i.e.* methanol, ethanol, isopropanol, tetralin, *n*-hexane and water at 340 °C under 0 MPa N$_2$ (gauge and being the initial pressure at room temperature) (Table 1). In the organic solvents, *i.e.* methanol, ethanol, isopropanol, tetralin and *n*-hexane, mono-oxygenated

R: CH$_3$, CH$_3$CH$_2$, (CH$_3$)$_2$CH

Scheme 1 Reaction pathway for the deoxygenation of guaiacol.

Table 1 Deoxygenation of guaiacol (**1**) in different solvents^a

R: CH₃, CH₃CH₂, (CH₃)₂CH ^{b}

Entry	Solvent	T/°C	t/h	M^c/%	C^d/%	S^e/%				
						2	3	4	5	6
1	Methanol	340	4	91	85	16	32	36	0	7
2	Isopropanol	340	4	96	84	15	34	38	2	7
3	Tetralin	340	4	95	53	84	5	0	0	6
4	n-Hexane	340	4	90	43	31	55	0	0	4
5	Water	340	4	98	36	5	0	0	94^f	0
6^g	Water	340	4	97	33	5	0	0	93^f	0
7	Ethanol	340	4	92	87	15	32	38	3	4
8	Ethanol	320	4	91	56	12	29	41	3	6
9	Ethanol	300	4	88	35	10	26	38	5	9
10	Ethanol	280	4	82	22	7	22	34	7	12
11	Ethanol	340	5	93	89	14	33	39	3	4
12	Ethanol	340	3	93	71	14	32	38	4	5
13	Ethanol	340	2	95	44	14	30	37	6	8
14	Ethanol	340	1	97	36	12	28	40	7	10
15^h	Ethanol	340	4	87	86	15	31	35	3	3
16^i	Ethanol	340	4	90	84	17	30	37	2	4
17^j	Ethanol	340	4	91	85	14	32	39	3	3

^{a} Reaction conditions: guaiacol (2.0 g), catalyst (0.5 g), solvent (60 ml), initial N₂ pressure at room temperature 0 MPa (gauge), 340 °C, 4 h, stirred at 400 rpm, the yields were calculated by mole. ^{b} For methanol, tetralin, n-hexane solvent, R = CH₃; for ethanol, R = CH₃CH₂, for isopropanol, R = (CH₃)₂CH. ^{c} M: mass balance. ^{d} C: conversion of **1**. ^{e} S: selectivity. ^{f} R:H. ^{g} The catalyst used in entry 6 was MoO₂/AC. ^{h} First reuse. ^{i} Second reuse. ^{j} Third reuse.

products such as phenol (**2**), alkyl phenol (**3**) and dialkyl phenol (**4**) were obtained as the major products with a high selectivity, while small amounts of transetherification products (**5**) and alkyl guaiacols (**6**) were also measured in the product. The substituent group in the *o*-position of the phenolic hydroxyl group depends on the solvent, *viz.* CH₃ for methanol, tetralin and *n*-hexane, CH₂CH₃ for ethanol and (CH₃)₂CH for isopropanol. Neither full deoxygenation products (benzene, toluene) nor ring-hydrogenation products (cyclohexane, cyclohexene, cyclohexanone, *etc.*) were observed in this work, indicating that the α-MoC₁₋ₓ/AC catalyst has excellent selectivity to partially deoxygenated compounds. Besides, ESI-MS analysis of the reaction mixture obtained from entry 7 revealed some peaks of higher molecular weight in the product mixtures (Fig. S2, ESI†), but these products could not be identified. These results showed great difference from those reported in the literature, where fully deoxygenated products and hydrogenation products were obtained over conventional HDO catalysts (CoMo, NiMo catalysts *etc.*) and the transetherification products were produced as the main products with γ-Al₂O₃ as the catalyst.[5–9,11]

Interestingly, α-MoC₁₋ₓ/AC performs high conversions of molecule **1** in alcohol solvents (methanol, ethanol, and isopropanol) due to the similar nature of the hydrogen donor and the high diffusivity of the molecules under the supercritical conditions.[12] For example, guaiacol was converted to phenolic compounds with a conversion of 87% at 340 °C for 4 h in ethanol, while it afforded a lower conversion of 53% in tetralin[13] (entry 3 Table 1), which was also widely used as a hydrogen-donor solvent. This may be due to the weak polarity of tetralin compared to the ethanol solvent. For the alkane solvent, *i.e. n*-hexane (entry 4), a conversion of only 43% was achieved. Meanwhile, the selectivity of alkyl phenols obtained in the organic solvents shows a trend of: in alcohols (methanol, ethanol, isopropanol) > in *n*-hexane > in tetralin. In sharp contrast, catechol, which was not detected in the products with organic solvents, was formed with a selectivity of 94% in water (entry 5). The structural transformation of Mo₁₋ₓC into MoO₂ in the high temperature water may contribute to this result (Fig. S1, ESI†). To verify this assumption, a control experiment was carried out using MoO₂/AC as the catalyst (entry 6). It turned out that the product distribution is similar to that achieved with MoC₁₋ₓ/AC (entry 5).

The reaction temperature has a profound effect on the conversion and product distribution. In the investigated temperature range (280–340 °C), an increase in the reaction temperature results in an improvement of the conversion of **1** from 22% to 87% and a higher selectivity towards the total phenolic compounds (**2**, **3**, **4**) from 63% to 85% in ethanol solvent, which was much higher than that typically obtained with CoMo/Al₂O₃, Mo₂C/CNF and Mo₂N/AC as catalysts in a similar solvent and at a similar temperature but with hydrogen in the atmosphere.[7,8] In those cases, ring-hydrogenation occurred as an important side reaction. Furthermore, with the increase of temperature from 280 to 320 °C, the **4**'s selectivity slightly rises from 34% to 41%. However, the further increase of reaction temperature leads to a slight decrease of 4's selectivity.

Data in entry 11 to entry 14 showed the effect of reaction time on the reaction. The conversion increases with the increase of the reaction time and the highest conversion reached 89% after 5 h, while the selectivity towards the total phenolic compounds (**2**, **3**, **4**) showed a slight increase from 80% to 86%. Compared to the slight change of the selectivity of phenolic compounds, the selectivities of **5** and **6** decreased obviously with the increase of the reaction time.

The reusability of the catalyst was tested for the reaction at 340 °C for 4 h in the ethanol solvent (Table 1, entries 15–17). After each run, the catalyst was recovered using a centrifugation technique and used directly in the next run without any treatment. The recovery of each catalyst after every run was close to 100% while the particle size of the recovered catalyst decreased slightly (Table S1, ESI†). It is obvious that similar conversion and selectivity towards the products were achieved in the three cycles. The XRD patterns of the recovered Mo₁₋ₓC catalysts showed that the Mo₁₋ₓC nanoparticles still retained their small sizes (<5 nm, calculated by the Scherrer equation) (Fig. S1, ESI†), thus indicating that the catalysts can be reused at least 3 times without noticeable loss of activity.

In addition to guaiacol, the reactions with catechol, phenol and anisole as reactants were examined with ethanol as the solvent.
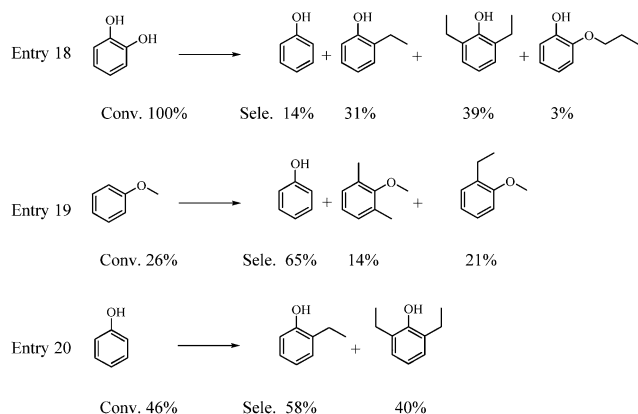
Scheme 2 Deoxygenation of lignin-derived model compounds on the α-MoC$_{1-x}$/AC catalyst in ethanol (reaction conditions: see entry 7 in Table 1).

As shown in Scheme 2, full conversion of catechol was achieved after 4 h at 340 °C over the catalyst (entry 18). Phenol, ethyl phenol, and diethyl phenol were formed as the major products with selectivities of 14%, 31% and 39%, respectively. This result is in accordance with that obtained from guaiacol as the reactant under the same conditions (Table 1, entry 7). This indicates that catechol was formed as an intermediate in guaiacol deoxygenation (Scheme 1). In contrast, the reaction with anisole as the reactant (Scheme 2, entry 19) under the same conditions only showed a conversion of 26% with phenol as the major product with 65% selectivity. In the reaction with phenol as the reactant (Scheme 2, entry 20), ethyl phenol and diethyl phenol were found as the major products with selectivities of 58% and 40%, respectively, but the conversion was only 46%. The product distribution from the phenol conversion was very different from that with guaiacol as the feedstock, indicating that phenol should not be the intermediate in the deoxygenation of guaiacol. Furthermore, methanol, which was considered as one of the products of the demethoxygenation of guaiacol,[5] was not detected in the deoxygenation of guaiacol. Moreover, gas products of the guaiacol conversion were identified using a gas mass spectrometer and methane was indeed produced. Therefore, it can be deduced that the reaction pathway of guaiacol is that catechol is a primary product followed by the hydroxyl group removal to form phenol (Scheme 1). However, it was reported that direct demethoxygenation to phenol was the reaction pathway of the guaiacol conversion over the Mo$_2$C catalyst because no catechol was detected.[8] A reasonable explanation is that the absence of catechol may be attributed to a full conversion of consecutive reactions (entry 18).

In summary, the α-MoC$_{1-x}$/AC catalyst is an effective catalyst for the deoxygenation of guaiacol to phenols in alcohol solvents under an inert atmosphere. Higher temperature favours the conversion to and the selectivity for phenols. The reactions take place via demethylation at the methoxy group followed by deoxygenation and transalkylation. Compared to the hydrogenation catalysts, no complete deoxygenation and benzene ring-hydrogenation products are produced, which make it an excellent catalyst for the production of phenolic compounds from the lignin depolymerization stream.

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12 The maximum reaction pressures are 16.8 MPa, 13.9 MPa, and 14.7 MPa for methanol, ethanol, and isopropanol at 340 °C, respectively, which are beyond their critical point.
13 The reaction pressure is 0.8 MPa for tetralin at 340 °C.