Mo$_2$C catalyzed vapor phase hydrodeoxygenation of lignin-derived phenolic compound mixtures to aromatics under ambient pressure

Cha-Jung Chen, Wen-Sheng Lee,[†] and Aditya Bhan*

Department of Chemical Engineering and Materials Science

University of Minnesota - Twin Cities

421 Washington Avenue SE

Minneapolis, Minnesota 55455

USA

E-mail addresses: chenx990@umn.edu (C.-J. Chen), wlee5@dow.com (W.-S. Lee), and abhan@umn.edu (A. Bhan)

*Corresponding author

[†]Current address: Core R&D, The Dow Chemical Company, 2030 Dow Center, Midland, Michigan, 48674, USA

Abstract

High aromatics yield (>90%, benzene and toluene) was obtained from vapor phase hydrodeoxygenation (HDO) of phenolic compound mixtures containing m-cresol, anisole, 1,2-dimethoxybenzene, and guaiacol over molybdenum carbide catalysts (Mo_2C) under atmospheric pressure at 533–553 K, even with H_2 to phenolic compound molar ratios ~3,300. Toluene selectivity increased proportionately (4%–66%) to m-cresol content in HDO of phenolic compound mixtures (molar composition: 0%–70%) at quantitative conversion. Phenol selectivity increased with decreasing conversion, implying that the aryl-methoxyl bond in guaiacol is cleaved first, before the aryl-hydroxyl bond. Low selectivity to cyclohexane and methylcyclohexane (<10%) across the conversions investigated (18–94%) demonstrates that undesired successive hydrogenation reactions of aromatics over Mo_2C were inhibited, presumably due to in situ oxygen modification, as inferred from titration studies of aromatic hydrogenation reactions using methanol and water as titrants.

1. Introduction

Direct upgrade of pyrolysis vapors from depolymerized lignocellulosic biomass can be a sustainable process to produce aromatics [1-3] such as benzene, toluene, and xylenes, because phenolic monomeric compounds in vapor phase pyrolyzates can recombine and form oligomeric compounds after condensation, resulting in corrosive and viscous bio-oil [4, 5]. Catalytic hydrodeoxygenation (HDO) can upgrade pyrolysis vapors by selectively removing oxygen heteroatoms in phenolic compounds as water. Selective cleavage of aryl-oxygen bonds in lignin-derived phenolic compounds, i.e. Ar-OH or Ar-OR, however, is challenging because the bond dissociation energies of aryl-oxygen bonds (422–468 kJ mol^{-1}) are 80–130 kJ mol^{-1} higher than that of aliphatic-oxygen (R-OR) bonds [6]. High H_2 pressure (~1–5 MPa) and/or high temperature (~473–723 K) reaction conditions, therefore, are commonly employed for HDO of phenolic compounds [7, 8], which can promote successive hydrogenation of aromatic rings, resulting in low yield of aromatics.

Low yield of benzene and/or toluene (<30%) was obtained from vapor phase HDO of single phenolic model compounds, such as m-cresol or guaiacol, over alumina supported Pt catalysts [9, 10], carbon-supported bimetallic Pt-Sn catalyst [11], gallium-modified H-BEA zeolite [12] and silica-supported transition metal [1]/ metal phosphide catalysts [13] at temperatures from 523–723 K under atmospheric H_2 pressure as a result of incomplete deoxygenation, significant concurrent hydrogenation, transalkylation, and/or demethylation reactions.

High yield of benzene and/or toluene (~80%) could be achieved from liquid phase anisole HDO over bimetallic FeMo phosphide catalysts at 673 K, however, high hydrogen pressures (2.1 MPa) were required to achieve this yield [14]. Zhao et al. [15]

3

reported >50% benzene selectivity from vapor phase HDO of guaiacol over transition metal phosphides, specifically, Ni_2P/SiO_2 and Co_2P/SiO_2, at 573 K under atmospheric pressure. High benzene selectivity (99%) for vapor phase phenol HDO over 20.3 wt% Ni/SiO_2 at 573 K and ambient pressure has been demonstrated by Shin et al. [16]. Prasomsri et al. [17] also reported high benzene and toluene selectivity in vapor phase HDO of anisole (~75%), m-cresol (~99%) over MoO_3, however, low benzene and toluene selectivity was found in guaiacol HDO (~45%) at ~1 bar of H_2 pressure and 593–623 K [17].

Zhao and co-workers [18] showed that liquid phase upgrade of a phenolic monomer mixture containing 4-n-propylphenol, 2-methoxy-4-n-propylphenol, 4-hydroxy-3-methoxyphenylacetone, and 4-allyl-2,6-dimethoxyphenol could be achieved on carbon-supported palladium with H_3PO_4 acting as a dual-functional catalyst at 523 K and 5 MPa H_2. At nearly quantitative conversion, ~80% selectivity to alkanes, and ~8% methanol selectivity were observed [18]. Kinetic studies of single phenolic compounds, such as anisole, catechol, and guaiacol, suggest that multistep reactions including hydrogenation, hydrolysis, and dehydration are involved in HDO of the phenolic mixture [19]. Zhao and co-workers [19] further demonstrated that n-hexane-extracted bio-oil, which contains C_5– C_6 furans, ketones, aldehydes, and C_6–C_9 phenolic compounds, could be quantitatively converted to the corresponding C_5–C_9 hydrocarbons with ~85% selectivity to C_6–C_9 cycloalkanes with and/or without C_1–C_3 alkyl groups using a Ni/H-ZSM-5 catalyst at 523 K and 5 MPa H_2 in the aqueous phase.

HDO of model pyrolysis vapor, containing guaiacol, H_2, CO, CO_2, and H_2O, over silica supported iron catalysts under atmospheric pressure was investigated by Olcese et

al. [20] at 673 K and atmospheric pressure, in which ~40% yield to benzene and toluene was observed, however, severe catalyst deactivation (100% to ~20% in 6 h) concurrently occurred. An integrated process which combines fast-hydropyrolysis of biomass with downstream vapor phase HDO to produce liquid fuels (H_2Bioil) has recently been proposed by Agrawal et al. [3]. HDO of fast-hydropyrolysis vapor of poplar (~23 wt% of lignin) over 5 wt% Pt–2.5 wt% Mo supported on multiwalled carbon nanotubes at 25 bar H_2 pressure and 573 K resulted in ~54% total hydrocarbon yield, of which ~20% were C_6–C_8^+ hydrocarbons including cyclic alkanes [3]. Efforts to directly treat pyrolysis vapor from oak and switch grass pyrolysis using a 5 wt% Ru/TiO_2 catalyst at 673 K and atmospheric pressure (H_2 ~0.58 atm) by Wan et al. [2] resulted in phenol as the dominant product from HDO of the pyrolyzates derived from oak or switch grass, suggesting that deoxygenation was incomplete and hydrogenation of the ring was negligible [2]. These reports demonstrate the challenges of direct HDO of phenolic mixtures to aromatics even with the expense of noble metal catalysts.

Molybdenum carbide, nitride, phosphide and oxide supported on titania have been shown to selectively catalyze gas phase HDO of phenol with >85% selectivity to benzene at 723 and 773 K, however, high H_2 pressure (25 bar) was employed [21]. The site time yield for vapor phase phenol HDO products on 15 wt% Mo_2C/TiO_2 catalyst was found to be ~3 times higher than that on 15 wt% MoO_3/TiO_2 and 6.8 wt% Mo_2N/TiO_2 [21], demonstrating that molybdenum carbide catalysts are more active than molybdenum oxides and/or nitride catalysts for HDO of phenolic compounds. Our recent study showed that β-Mo_2C is stable for vapor phase anisole HDO and can preferentially cleave the Ar-O bond, resulting in >90% selectivity to benzene (C_6^+ basis) at ambient pressure and 423

K [22]. Metallic sites were suggested to be involved in vapor phase anisole HDO as benzene rates normalized by the number of exposed metallic sites measured by ex situ CO chemisorption were invariant ($3.4 \pm 1.0 \times 10^{-4}$ mol s^{-1} mol$_{CO\ site}$$^{-1}$) [22]. In situ CO titration studies for anisole HDO at 423 K ($1.1 \pm 0.3 \times 10^{-3}$ mol s^{-1} mol$_{CO\ site}$$^{-1}$) demonstrated that only a fraction of CO chemisorption sites are active for HDO catalysis [23].

Herein, mixtures of lignin-derived phenolic model compounds containing characteristic bonds, i.e., Ar-OH and Ar-OCH$_3$, such as m-cresol, anisole, 1,2-dimethoxybenzene (DMB), and guaiacol (GUA), were chosen to simulate pyrolysis vapor from lignin depolymerization. The lignin-derived phenolic compounds were selectively converted to the corresponding completely deoxygenated aromatics, benzene and toluene, with >90% yield at quantitative conversion, under mild reaction temperatures (533–553 K), and ambient pressure. Kinetic studies suggest that (i) direct hydrodeoxygenation of m-cresol was the dominant pathway for toluene synthesis, and (ii) the methoxyl group in guaiacol was removed prior to the cleavage of the hydroxyl bond. Low alkylbenzene selectivity (<4%) in HDO of the phenolic mixtures suggests that transalkylation and/or demethylation reactions are insignificant. High H$_2$ efficiency with <10% selectivity for subsequent hydrogenation products was, presumably, due to in situ modification of the catalyst surface by oxygenate reactants, as inferred from in situ methanol and water chemical titration of benzene/toluene hydrogenation reactions on Mo$_2$C.

2. Materials and Methods

2.1. Catalyst synthesis and characterization

Mo$_2$C catalysts were prepared based on a prior report [22]. A tubular quartz reactor (I.D. 10 mm) loaded with 1.2 g of ammonium molybdate tetrahydrate (sieved, 177–400 μm, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, Sigma, 99.98%, trace metal basis) was housed in a tube furnace (Applied Test System, Series 3210) equipped with a Watlow Temperature Controller (96 series) where the reaction temperature was monitored by a thermocouple attached to an outer thermowell of the reactor and heated in a gas mixture (total flow rate of ~2.75 cm^3 s^{-1}), comprising 15/85 vol% of CH$_4$ (Matheson, 99.97%) and H$_2$ (Minneapolis Oxygen, 99.999%) at ~623 K for 5 h with a ramping rate of ~0.06 K s^{-1} from room temperature (RT). The reactor was subsequently heated from ~623 K to ~863 K (~0.047 K s^{-1}) and held at ~863 K for 3 h. The resulting material was cooled to RT in the CH$_4$/H$_2$ gas mixture and subsequently treated in a flow (~1.67 cm^3 s^{-1}) of 1% O$_2$/He (Matheson, Certified Standard Purity) for ~2 h to passivate the carbidic surface before being removed from the reactor.

The bulk structures of both fresh and spent samples were determined using X-ray diffraction (XRD, Bruker D8 Discover, 2D X-ray diffractometer with a two-dimensional VÅNTEC-500 detector). Cu Kα X-ray radiation with a graphite monochromator and a 0.8 mm point collimator measured in two or three measurement frames at 2θ = 25°, 55°, and/or 85° with a 900 s frame/dwell were used to collect two-dimensional images which were then converted to one-dimensional intensity vs. 2θ for analysis.

CO (Matheson, 99.5%) chemisorption for Mo$_2$C formulations was measured at 323 K using a Micromeritics ASAP 2020 instrument following the protocols reported previously [22]. Briefly, the catalyst (~0.14 g) was first evacuated at 383 K (~2 μmHg) for 0.5 h, and then treated in H$_2$ at 723 K for 1 h, followed by degassing (~2 μmHg) at

723 K for 2 h. Two adsorption isotherm measurements (between 100 and 450 mmHg) were taken at 323 K. The cell was degassed (~2 μmHg) to remove weakly adsorbed species before the second isotherm. The amount of irreversibly adsorbed species was obtained by the difference between the two isotherms extrapolated to zero pressure.

The BET surface area was measured using N_2 adsorption/desorption isotherms (Micromeritics ASAP 2020). The sample was degassed (<10 μmHg) at 523 K for at least 4 h before N_2 adsorption.

2.2.   Vapor phase HDO of phenolic compound mixtures on Mo_2C

Molybdenum carbide catalysts (1.9–18.5 mg) diluted in ~0.3 g quartz sand in a tubular quartz reactor (I.D. 10 mm) were treated in pure H_2 (~1.67 cm^3 s^{-1}) at 723 K (0.125 K s^{-1}) for 1 h and cooled down to the reaction temperature before introducing reactants (~3.67 cm^3 s^{-1}) consisting of 0.03/91/balance (vol%) of oxygenates/H_2/He, in which the oxygenates represent the sum of the phenolic compound mixtures. Phenolic compound mixtures of anisole (Sigma, ReagentPlus, 99%), m-cresol (Sigma, ≥98%), guaiacol (GUA, SAFC, natural, ≥98%), and 1,2-dimethoxybenzene (DMB, Sigma, ReagentPlus, 99%) were added using a syringe pump (KD Scientific, Model 100) and the reactor effluents were analyzed by an online gas chromatograph (GC, Agilent 7890) equipped with a methyl-siloxane capillary column (HP-1, 50 m × 320μm × 0.52 μm) connected to a flame ionization detector. All lines were heated to at least 398 K via resistive heating to prevent condensation of the compounds in the lines. The equations used to calculate conversion, selectivity, and toluene or benzene ratio are shown below.

$$Total\ conversion\ of\ phenolic\ mixture =$$

$$\frac{(sum\ of\ C\ in\ phenolic\ reactants)_{in} - (sum\ of\ C\ in\ phenolic\ reactants)_{out}}{(sum\ of\ C\ in\ phenolic\ reactants)_{in}} \times 100\% \ (1)$$

$$C_6^+ \text{ product selectivity} = \frac{\text{moles of } C_{6+} \text{ product } i}{\text{moles of } C_{6+} \text{ products}} \times 100\% \quad (2)$$

$$\text{Toluene or benzene ratio} = \frac{\text{moles of toluene or benzene}}{\text{moles of } (\text{toluene} + \text{benzene})} \times 100\% \quad (3)$$

$$\text{Individual conversion} =$$

$$\frac{(\text{moles of } C \text{ in phenolic reactant } i)_{in} - (\text{moles of } C \text{ in phenolic reactant } i)_{out}}{(\text{moles of } C \text{ in phenolic reactant } i)_{in}} \quad (4)$$

Small amounts of catalyst (1.9–18.5 mg) diluted in ~0.3 g of quartz sand were employed to achieve <100% conversion for HDO of phenolic compounds at 553 K. We confirmed that high conversions reported here (82 and 94%) are reproducible as the conversions measured using catalysts that were regenerated in H_2 flow (~1.67 cm^3 s^{-1} at 723 K for 1 h) were found to be consistent (<±2%) with those of the original runs.

2.3. In situ titration for hydrogenation reactions

Vapor phase hydrogenation reactions of a benzene/toluene (molar ratio = 1/1) mixture (1.2/4.9/balance (vol%) of (benzene and toluene)/He/H_2; total flow rate of ~3.4 cm^3 s^{-1}) were carried out using ~0.34 g Mo$_2$C (~200 μmol g$_{cat}^{-1}$ CO chemisorption sites) at ~353 K and ambient pressure, in which Mo$_2$C was pretreated in H_2 (~1.67 cm^3 s^{-1}) at 723 K for 1 h before hydrogenation reactions. A lower temperature (~353 K) than that for HDO reactions (533–553 K) was chosen to allow for kinetic measurements of in situ titration experiments at differential conversion (<10%). After steady state rates of cyclohexane and methylcyclohexane were observed, a co-feed of methanol or water in argon (methanol or water/Ar of 11.5 or 24.5/balance (vol%) at a total flow rate of ~0.17 cm^3 s^{-1}) was introduced, while simultaneously removing He to maintain the same total flow rate. The transient responses of the titrant, Ar, cyclohexane, and methylcyclohexane

were tracked using an online mass spectrometer (MKS Cirrus 200 Quadrupole mass spectrometer system). The concentrations of reactants and products were quantified by GC before and after the titration.

3. Results and Discussion

3.1. Materials characterization

β-Mo_2C was identified as the major carbidic phase for a passivated Mo_2C catalyst based on the observed diffraction peaks shown in Figure 1, consistent with previous reports [22, 24, 25]. We note that the passivated Mo_2C catalyst was aged in a vial under ambient conditions for ~1 month prior to the XRD analysis.

The BET surface area (Sa) for the same catalyst but aged for ~2.5 months was ~116 m^2 g_{cat}^{-1}, in which the sample was treated in pure H_2 (~1.67 cm^3 s^{-1}) at 723 K for 1 h, passivated in 1% O_2 in He, and immediately loaded in a cell for BET measurement, however, the surface area for the same sample, directly loaded for BET measurement without H_2 pretreatment, was found to be ~23 m^2 g_{cat}^{-1}. The amount of irreversibly chemisorbed CO at ~323 K of the same Mo_2C sample, aged for ~2.5 months, was 108 μmol g_{cat}^{-1} (STP). Porous features of the fresh Mo_2C catalysts and TEM analysis were reported in our previous work [22, 25].

The crystallite size of the fresh but passivated Mo_2C was ~7.3 nm, which was estimated using the Scherrer equation for the 2θ peak at ~52°. This is comparable to both our previous report (~3.3nm) [22] and the Mo_2C catalysts reported by Boudart and coworkers (~5.8 and 11.5 nm) [26]. The particle size of a typical fresh but passivated

sample is ~70 nm, which was estimated using the equation $D_P = ~6 \times (\rho \times Sa)$, where ρ is taken as 770 kg m^{-3} [27]. These results suggest that the catalyst is polycrystalline.

Lee et al. [24] reported a significant loss in chemisorbed CO uptake (~250 to ~130 μmol g$_{cat}$$^{-1}$) and BET surface area (~125 to ~25 m^2 g$_{cat}$$^{-1}$) measured on samples that were not pretreated in H$_2$ over an initial ~10 day period; no significant change in surface area or CO adsorption capacity was noted over a subsequent aging time of ~4 months. The number of times that the sample was exposed to air, instead of the shelf life was attributed to be a more relevant descriptor for the loss in both CO uptake and BET surface area [24]. Chemisorbed CO uptake for the samples used in this study were, therefore, measured within 7 days before each reaction; the BET surface area (~106 m^2 g$_{cat}$$^{-1}$) used specifically for calculating the number of surface Mo atoms on molybdenum carbide catalysts in the titration experiments (Section 3.4) was an average value taken from two independent BET measurements of two batches of Mo$_2$C, each aged for ~2.5 months and ~1.5 months, with a H$_2$ pretreatment (~1.67 cm^3 s^{-1}) at 723 K as discussed above.

3.2. Vapor phase HDO of phenolic compound mixtures on Mo$_2$C

Figure 2 shows product selectivity and conversion for vapor phase HDO of a phenolic compound mixture comprised of m-cresol, anisole, DMB, and GUA (molar ratio = 1: 0.96: 0.95: 0.98) over ~0.02 g Mo$_2$C at 553 K under ambient pressure. Concurrent high conversion (95%), and high selectivity to benzene and toluene, at a level of ~95%, were achieved with low selectivity (<10% on a molar basis) to sequential hydrogenated products. No indication of catalyst deactivation over the course of 6 h was observed, which distinguishes Mo$_2$C catalysts from alumina supported Pt catalysts [10] and silica-

supported nickel phosphide catalysts [13] that deactivated ~15% in 4 h at 523 K and ~40% in 10 h at 573 K, respectively for m-cresol and guaiacol HDO reactions.

A comparison of specific benzene and toluene yield from vapor phase HDO of guaiacol/phenolic compounds mixture on different catalysts is shown in Table 1. We note, however, that the tabulated values were reported from HDO reactions (i) using different phenolic compounds as reactants, and (ii) at varying reaction temperatures and conversions.

Figure 3 shows the molar ratios of toluene and benzene, defined as specified in Equation 3, for vapor phase HDO of phenolic compound mixtures with different compositions over Mo_2C at 533–553 K and quantitative conversion (~100%). Toluene molar ratio was found to increase with the m-cresol content in the mixture, suggesting that toluene synthesis was dominated by direct HDO of m-cresol. The predicted molar ratios of toluene to benzene (Figure 3), assuming that toluene and benzene were produced from complete HDO of m-cresol, and from complete HDO of anisole, DMB, and GUA, respectively, were found to be consistent (<±10%) with the ratios measured experimentally from the reactor effluents, which confirms that (i) molybdenum carbide catalysts can exclusively and quantitatively cleave the aryl-oxygen bonds in phenolic compounds, and (ii) the extent of transalkylation was insignificant under the given reaction conditions, as quantitative synthesis of the corresponding aromatics was observed. The low selectivity to transalkylation products (~3% selectivity to toluene from mixture M1 at quantitative conversion) during HDO of phenolic compound mixtures on Mo_2C contrasts vapor phase HDO of phenolic model compounds such as m-cresol, guaiacol, and anisole on bimetallic Ni-Fe [28], monolithic Pt-Sn [11], MoO_3 [17], and

carbon-supported Pd-Fe [29] catalysts, in which the selectivity to transalkylation products was found to be ~12%–50%.

The molar ratio of the C_1 product, CH_4, to benzene and cyclohexane was found to be of unity for HDO of mixtures M1 and M4 at 553 K, providing additional evidence for negligible transalkylation reactions during HDO of phenolic compound mixtures. The molar ratio of C_1 to benzene and cyclohexane for HDO of mixtures M2 and M3 at 533 K was ~0.8, which may be due to a slightly higher propensity for carbon deposition at a lower reaction temperature and/or due to the higher mixture to H_2 molar ratios in the feed (3 and 6 times higher than mixture M1 and M4).

3.3. Reaction pathways for lignin-derived phenolic compounds on Mo_2C

The selectivity to phenol (Figure 4) decreased from 9% to 0.3% as the total conversion of the phenolic mixture (molar ratio of m-cresol, anisole, DMB, and GUA = 1: 0.96: 0.95: 0.98) increased from 18% to 94%, suggesting that the $Ar-OCH_3$ bond in GUA was preferentially cleaved before the Ar-OH bond. Negative conversion of anisole, calculated using Equation 4, was observed at 18% total conversion (Figure S1), indicating that the $Ar-OCH_3$ bond in DMB was first cleaved to form anisole, before it was further deoxygenated to form benzene (Scheme 1). These experimental observations are in line with recent computational chemistry calculations of bond dissociation energies (BDE) of GUA [17], showing that the Ar-OH bond (~456 kJ mol^{-1}) is stronger than the $Ar-OCH_3$ bond (~376 kJ mol^{-1}). Molar ratios of C_1 products, including CH_4 and CH_3OH, to benzene are ~1 (Figure 4); C_6^+ product selectivity and conversion were stable over 6 h time-on-stream (TOS) at all conversions (18–94%) investigated (Figure 2 and Figure S2). We note that unidentified C_6^+ compounds were observed (collectively denoted as

"Others" in Figure 4 and Figure S2) and were quantified using benzene, anisole, or m-cresol, depending on the retention time of the species in the GC chromatogram.

3.4. Oxygen modified surface for selective HDO on Mo_2C

The catalytic activity of freshly prepared bulk or supported molybdenum carbide catalysts in benzene hydrogenation reactions has been reported to be comparable to noble metal catalysts such as Ru/Al_2O_3 or Pt/Al_2O_3 [30, 31]. Choi et al. [30] reported that site time yield (STY, normalized by ex situ CO chemisorption sites) of benzene hydrogenation at room temperature was 0.09 s^{-1} on Mo_2C catalysts, and 0.35 s^{-1} on a commercial Ru/Al_2O_3 sample. Similarly, bulk molybdenum carbide catalysts have also been shown to be active for toluene hydrogenation at 423–598 K and ~3 MPa H_2 pressure, in which 100% toluene conversion was achieved at 473 K [32, 33].

Low selectivity to cyclohexane and methylcyclohexane (<10% at <100% conversion) observed in HDO of phenolic mixtures, as shown in Figure 2, suggests that successive hydrogenation reactions of the corresponding HDO products, toluene and benzene, on Mo_2C were significantly suppressed even at temperatures (533–553 K) much higher than RT, and high hydrogen to oxygenate molar ratio (~3,300). Hydrogenation reactions of an equimolar mixture of benzene and toluene on the molybdenum carbide catalyst were, therefore, investigated. In situ titration via oxygen-containing compounds, specifically, methanol and water, was implemented to probe the hydrogenation functionality, and to assess hydrogenation turnover frequency of benzene and toluene on Mo_2C at 353 K. Methanol or water was co-fed to the system after steady state rates of cyclohexane and methylcyclohexane synthesis were obtained (<10% conversion). Figure 5 shows the mass spectrometric signals of cyclohexane, methylcyclohexane, methanol or

water, and Ar normalized to their corresponding values at steady state, as a function of time during the titration experiments. The signals of cyclohexane and methylcyclohexane dropped to <1% of their steady state values in presence of the titrants, showing that hydrogenation rates of benzene and toluene were almost completely inhibited by methanol or water, and not recovered upon the removal of titrants at 353 K. These experimental results suggest that the introduction of oxygen-containing compounds, such as lignin-derived phenolic compounds, CO and water, which are typically observed in pyrolysis vapor [34, 35], to Mo_2C under HDO reaction conditions (533–553 K) can irreversibly and significantly inhibit hydrogenation of aromatic rings, resulting in high product selectivity to aromatics in HDO reactions of phenolic compound mixtures.

The activity of benzene/toluene hydrogenation reactions on molybdenum carbide catalysts was evaluated in terms of turnover frequency (TOF). The TOF of benzene and toluene hydrogenation was obtained by normalizing the synthesis rates of cyclohexane and methylcyclohexane at steady state to the number of the adsorption sites occupied by the titrant. The latter can be assessed by calculating the area between normalized mass spectrometric signals of Ar and the titrant, as shown in Figure 5, and multiplying it by a known titrant flow rate (2.2×10^{-4} mol of H_2O; 2.8×10^{-4} mol of CH_3OH) [36]. Alternatively, the number of active sites could be evaluated using the time that is required to bring the signals of cyclohexane and methylcyclohexane to zero (Figure 5), and multiplying it by a known titrant flow rate (2.2×10^{-4} mol of H_2O; 2.8×10^{-4} mol of CH_3OH). Both methods gave similar number of adsorption sites (±5%, Table S1). The resulting TOF for benzene and toluene hydrogenation at 353 K is ~2.5×10^{-4}–6×10^{-4} s^{-1}. The effective site density for benzene and toluene hydrogenation reactions prior to the in

situ titration was, therefore, $\sim 7 \times 10^2 \, \mu mol \, g_{cat}^{-1}$, which corresponds to $\sim$40% of surface Mo atoms, using a surface area of $\sim$106 m^2 g_{cat}^{-1} for a typical aged sample after pretreatment in H$_2$ ($\sim$1.67 cm^3 s^{-1}) at 723 K and Mo atom density of 1×10^{15} cm^{-2} [30].

The reported TOF for benzene/toluene hydrogenation at $\sim$353 K is about two orders of magnitude lower than that reported by Choi et al. [30] at room temperature. One possible reason for the lower TOF is that the molybdenum carbide sample used in the current study had been previously passivated using 1% O$_2$/He before being reactivated in H$_2$ at 723 K, whereas Choi et al. [30] used freshly prepared catalysts (without exposure to air) for benzene hydrogenation. In an independent study, Choi et al. [37] noted that a passivated Mo$_2$C sample treated in H$_2$ at 773 K showed only 1% conversion in benzene hydrogenation, as compared to $\sim$100% conversion measured from a freshly prepared formulation, consistent with our experimental observation that Mo$_2$C was completely inactive for hydrogenation reactions of toluene and benzene after being exposed to methanol or water.

High selectivity to the direct HDO product, 2-methylfuran ($\sim$60%), but low selectivity to the furfural hydrogenation product, furfural alcohol ($\sim$7%), has been reported by Xiong et al. [38, 39] in furfural HDO on molybdenum carbide catalysts. The high deoxygenation selectivity of furfural HDO on Mo$_2$C was attributed to the strong interaction between the C=O group in furfural, the favored binding configuration, and the Mo$_2$C surface, as adduced by density functional theory (DFT) calculations where the binding energy (BE) of furfural on a close-packed Mo$_2$C(0001) (3.54 eV) surface was found to be higher than that on a Pt(111) (0.66 eV) surface [39]. High-resolution electron energy loss spectroscopy (HREELS) measurements of furfural, furfural alcohol, and 2-

methylfuran on Mo_2C suggested that the selective C=O scission is likely to proceed through an $\eta^2(C,O)$ bonding configuration [39], and the conjugation between the five-membered aromatic ring and the C=O bond could be disrupted, increasing the propensity for the molecule to undergo deoxygenation rather than hydrogenation/dehydrogenation [38]. By analogy, we suggest that high selectivity to benzene and toluene (>90%) in HDO of phenolic compound mixtures on Mo_2C may be a consequence of the phenolic reactants binding/adsorbing in a configuration that is favorable for preferential cleavage of the stronger $Ar-OCH_3$ bond relative to the weaker $ArO-CH_3$ bond, i.e., the Ar-O bond of the phenolic compounds interacts strongly with the Mo_2C surface, and the aromatic ring helps weaken the Ar-O bond [40].

The slow increase in benzene and toluene selectivity with time-on-stream (90% to 95%) is noted to be at the expense of cyclohexanes selectivity with TOS (10% to 5%), as shown in Figure 2, which arises presumably due to a gradual and continuous modification of the catalyst surface by the oxygen-containing phenolic reactants during HDO. The total conversion of the phenolic compound mixture, however, was nearly invariant within the course of the reaction as cyclohexane selectivity decreased from 10% to 5%, suggesting that modification of the Mo_2C surface from the phenolic compounds has little or no effect on the catalytic sites for aryl-oxygen bond cleavage.

The observed inhibition of aromatic hydrogenation functionality on Mo_2C during HDO reactions was found to be correlated with in situ oxygen-modification as discussed above, however, the X-ray diffraction (XRD) pattern of the spent catalyst used for in situ methanol titration shows no peaks assigned to MoO_2, and/or MoO_3, suggesting that bulk oxidation of the molybdenum carbide did not occur. β-Mo_2C phase was identified in the

17

spent catalyst (Joint Committee on Powder Diffraction Standards, no. 35-0787, 2θ peaks at ~34.355° (100), 37.979° (002), 39.393° (101), 52.124° (102), 61.529° (110), 69.567° (103)), which evidenced that the bulk phase of the catalyst remained as Mo_2C (Figure S3) and that the oxygen modification occurred only in the surface and/or subsurface region.

4. Conclusion

Lignin-derived phenolic compound mixtures (anisole, m-cresol, guaiacol, and 1,2-dimethoxybenzene) can be selectively converted to the corresponding completely deoxygenated aromatics (benzene and toluene) with high yield (>90%) and high hydrogen efficiency (<10% selectivity for unwanted sequential hydrogenation products) via vapor phase HDO over molybdenum carbide catalysts at mild reaction temperatures (~533–553 K) and ambient pressure. The methoxyl group in guaiacol was preferentially cleaved prior to the removal of the hydroxyl group, which is in line with the higher bond dissociation energy of Ar-OH (~456 kJ mol^{-1}) relative to Ar-OCH$_3$ (~376 kJ mol^{-1}) in lignin-derived phenolic compounds based on computational chemistry calculations [17]. In situ methanol and/or water titration of benzene/toluene hydrogenation reactions suggest that the inhibition of aromatic hydrogenation functionality on Mo_2C during HDO reactions is a result of in situ modification of the catalyst surface by oxygenates. These experimental results demonstrate a feasible approach to directly upgrade pyrolysis vapor without the expense of noble metal catalysts and the use of severe reaction conditions (high H$_2$ pressure and/or high temperatures).

References

[1]   R.N. Olcese, J. Francois, M.M. Bettahar, D. Petitjean, A. Dufour, Energy & Fuels 27 (2013) 975-984.

[2]   S. Wan, T. Pham, S. Zhang, L. Lobban, D. Resasco, R. Mallinson, AIChE Journal 59 (2013) 2275-2285.

[3]   V.K. Venkatakrishnan, W.N. Delgass, F.H. Ribeiro, R. Agrawal, Green Chemistry 17 (2015) 178-183.

[4]   K.L. Deutsch, B.H. Shanks, Applied Catalysis A: General 447 (2012) 144-150.

[5]   R.J. Evans, T.A. Milne, Energy & Fuels 1 (1987) 123-137.

[6]   E. Furimsky, Applied Catalysis A: General 199 (2000) 147-190.

[7]   H. Wang, J. Male, Y. Wang, ACS Catalysis 3 (2013) 1047-1070.

[8]   M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B.C. Gates, M.R. Rahimpour, Energy & Environmental Science 7 (2014) 103-129.

[9]   T. Nimmanwudipong, R.C. Runnebaum, D.E. Block, B.C. Gates, Energy & Fuels 25 (2011) 3417-3427.

[10] P.T.M. Do, A.J. Foster, J.G. Chen, R.F. Lobo, Green Chemistry 14 (2012) 1388-1397.

[11] M.A. Gonzalez-Borja, D.E. Resasco, Energy & Fuels 25 (2011) 4155-4162.

[12] A. Ausavasukhi, Y. Huang, A.T. To, T. Sooknoi, D.E. Resasco, Journal of Catalysis 290 (2012) 90-100.

[13] S.K. Wu, P.C. Lai, Y.C. Lin, Catalysis Letters 144 (2014) 878-889.

[14] D.J. Rensel, S. Rouvimov, M.E. Gin, J.C. Hicks, Journal of Catalysis 305 (2013) 256-263.

[15] H.Y. Zhao, D. Li, P. Bui, S.T. Oyama, Applied Catalysis A: General 391 (2011) 305-310.

[16] E.-J. Shin, M.A. Keane, Industrial & Engineering Chemistry Research 39 (2000) 883-892.

[17] T. Prasomsri, M. Shetty, K. Murugappan, Y. Roman-Leshkov, Energy & Environmental Science 7 (2014) 2660-2669.

[18] C. Zhao, Y. Kou, A.A. Lemonidou, X. Li, J.A. Lercher, Angewandte Chemie International Edition 48 (2009) 3987-3990.

[19]C. Zhao, J. He, A.A. Lemonidou, X. Li, J.A. Lercher, Journal of Catalysis 280 (2011) 8-16.

[20] R. Olcese, M.M. Bettahar, B. Malaman, J. Ghanbaja, L. Tibavizco, D. Petitjean, A. Dufour, Applied Catalysis B: Environmental 129 (2013) 528-538.

[21] S. Boullosa-Eiras, R. Lødeng, H. Bergem, M. Stöcker, L. Hannevold, E.A. Blekkan, Catalysis Today 223 (2014) 44-53.

[22] W.-S. Lee, Z. Wang, R.J. Wu, A. Bhan, Journal of Catalysis 319 (2014) 44-53.

[23] W.-S. Lee, A. Kumar, Z. Wang, A. Bhan, ACS Catalysis 5 (2015) 4104-4114.

[24] W.-S. Lee, Z. Wang, W. Zheng, D.G. Vlachos, A. Bhan, Catalysis Science & Technology 4 (2014) 2340-2352.

[25] M.M. Sullivan, J.T. Held, A. Bhan, Journal of Catalysis 326 (2015) 82-91.

[26] J.S. Lee, S.T. Oyama, M. Boudart, Journal of Catalysis 106 (1987) 125-133.

[27] E.A. Blekkan, C. Pham-Huu, M.J. Ledoux, J. Guille, Industrial & Engineering Chemistry Research 33 (1994) 1657-1664.

[28] L. Nie, P.M. de Souza, F.B. Noronha, W. An, T. Sooknoi, D.E. Resasco, Journal of Molecular Catalysis A: Chemical 388–389 (2014) 47-55.

[29] J.M. Sun, A.M. Karim, H. Zhang, L. Kovarik, X.H.S. Li, A.J. Hensley, J.S. McEwen, Y. Wang, Journal of Catalysis 306 (2013) 47-57.

[30] J.S. Choi, G. Bugli, G. Djega-Mariadassou, Journal of Catalysis 193 (2000) 238-247.

[31] J.S. Lee, M.H. Yeom, K.Y. Park, I.-S. Nam, J.S. Chung, Y.G. Kim, S.H. Moon, Journal of Catalysis 128 (1991) 126-136.

[32] M.L. Frauwallner, F. Lopez-Linares, J. Lara-Romero, C.E. Scott, V. Ali, E. Hernandez, P. Pereira-Almao, Applied Catalysis A: General 394 (2011) 62-70.

[33] A.S. Mamède, J.M. Giraudon, A. Löfberg, L. Leclercq, G. Leclercq, Applied Catalysis A: General 227 (2002) 73-82.

[34] D. Mohan, C.U. Pittman, P.H. Steele, Energy & Fuels 20 (2006) 848-889.

[35] H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Fuel 86 (2007) 1781-1788.

[36] S.L. Shannon, J.G. Goodwin, Chemical Reviews 95 (1995) 677-695.

[37] J.-S. Choi, G. Bugli, G. Djéga-Mariadassou, in: F.V.M.S.M. Avelino Corma, G.F. José Luis (Eds.), Studies in Surface Science and Catalysis, Elsevier, 2000, pp. 2885-2890.

[38] K. Xiong, W. Yu, J.G. Chen, Applied Surface Science 323 (2014) 88-95.

[39] K. Xiong, W.S. Lee, A. Bhan, J.G. Chen, ChemSusChem 7 (2014) 2146-2149.

[40] S.H. Pang, J.W. Medlin, ACS Catalysis 1 (2011) 1272-1283.

List of Schemes

Scheme 1. Reaction pathways for hydrodeoxygenation of lignin-derived phenolic compound mixtures comprising m-cresol, anisole, 1,2-dimethoxybenzene, and guaiacol on molybdenum carbide catalysts.

List of Tables

Table 1. Specific yield of benzene and toluene from vapor phase HDO of guaiacol/anisole/phenolic compound mixtures at 1 bar.
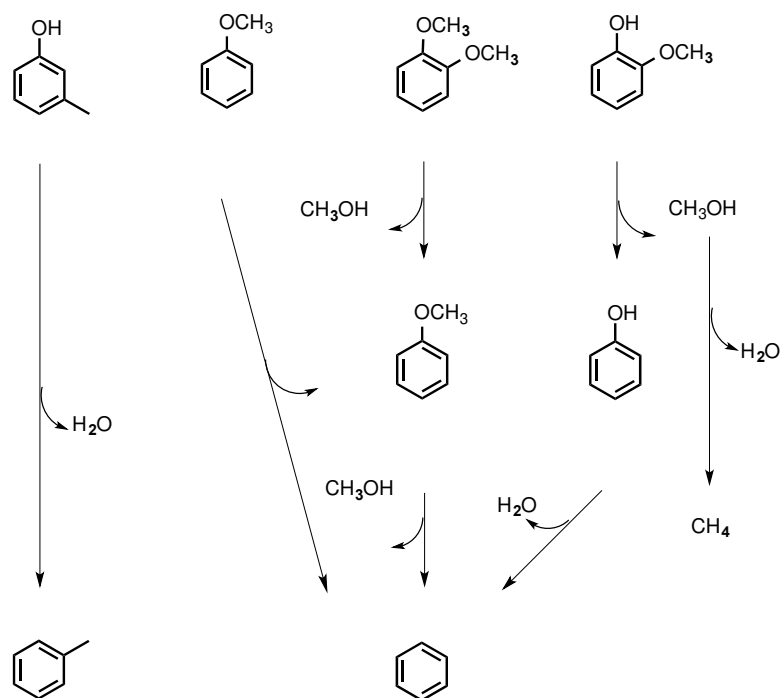
List of Figures

Figure 1. X-ray diffraction pattern of a Mo_2C catalyst. The sample was treated in a flow of 1% O_2/He mixture (~1.67 cm^3 s^{-1}) for ~2 h at RT and was aged for ~1 month in a vial under ambient conditions prior to XRD analysis.

Figure 2. Conversion and product selectivity for HDO of a phenolic compound mixture over ~0.02 g Mo_2C. Molar ratio of m-cresol: anisole: DMB: GUA = 1: 0.96: 0.95: 0.98; Feed = phenolic mixture (0.03)/ H_2 (91)/ He balance (vol%) at 114 kPa total pressure and at 553 K; space velocity 198 cm^3 s^{-1} g_{cat}^{-1}; ex situ CO uptake = 124 μmol g_{cat}^{-1}; Cyclohexanes contains methylcyclohexane and cyclohexane.

Figure 3. Ratio of toluene (■) and benzene (☐), defined as molar flow rate of (toluene or benzene)/ (toluene + benzene) × 100%, from reactor effluents of HDO reactions at different mixture compositions at quantitative (100%) conversion on 0.1 g Mo_2C under ambient pressure at 533 K for M2 and M3 (ex situ CO uptake = 224 μmol g_{cat}^{-1}), and 553 K for M1 and M4 (ex situ CO uptake = 135 μmol g_{cat}^{-1}); (•) predicted toluene ratios from the compositions of mixtures, assuming that m-cresol was completely deoxygenated to toluene, while anisole, DMB, and GUA were deoxygenated to benzene. Molar compositions of phenolic compound mixtures [m-cresol: anisole: DMB: GUA] = 0: 0.35: 0.35: 0.3 (M1); 1: 0.96: 0.95: 0.82 (M2); 1: 0: 0.95: 0 (M3); 1: 0.16: 0.16: 0.13 (M4). Feed (M1 and M4) = phenolic mixture (0.03)/ H_2 (91)/ He balance (vol%) at 114 kPa total pressure; space velocity ~36.6 cm^3 s^{-1} g_{cat}^{-1}. Feed (M2 and M3) = phenolic mixture (0.07 and 0.15)/ H_2 (77)/ He balance (vol%) at 108 kPa total pressure; space velocity ~19.0 cm^3 s^{-1} g_{cat}^{-1}.

Figure 4. Selectivity for HDO of phenolic compound mixtures and molar ratio of C_1 products (methane and methanol) to benzene at different conversions (18–94%). Molar ratio of m-cresol: anisole: DMB: GUA = 1: 0.96: 0.95: 0.98; Feed = phenolic mixture (0.03)/ H_2 (91)/ He balance (vol%) at 114 kPa total pressure and at 553 K; Selectivity reported is an average value taken between ~3.6–21 ks time-on-stream; Different conversions were achieved by using different mass of catalyst (1.9–18.5 mg, ex situ CO uptake ~124 μmol g_{cat}^{-1}); space velocities 198–1.9 × 10^3 cm^3 s^{-1} g_{cat}^{-1}; Cyclohexanes contains methylcyclohexane and cyclohexane; Others contains unidentified C_6^+ hydrocarbons, which were quantified using benzene, anisole, or m-cresol, depending on the retention time of the species in the GC chromatogram.

Figure 5. Mass spectrometric signals of methylcyclohexane and cyclohexane normalized to the signals at steady state as a function of time with a titrant co-feed consisting of (a) methanol/ argon (11.5/balance, vol%) and (b) water/ argon (24.5/balance, vol%) gas mixture (total flow rate ~0.17 cm^3 s^{-1}), in which Ar was used as an internal standard. Hydrogenation reaction conditions: equimolar mixture of (benzene and toluene)/He/H_2 (vol%) = 1.2/4.9/balance, with ~0.34 g_{cat} (ex situ CO uptake ~200 μmol g_{cat}^{-1}) and space velocity of ~10 cm^3 s^{-1} g_{cat}^{-1} at ~353 K under ambient pressure.

Scheme 1. Reaction pathways for hydrodeoxygenation of lignin-derived phenolic compound mixtures comprising m-cresol, anisole, 1,2-dimethoxybenzene, and guaiacol on molybdenum carbide catalysts.

Table 1. Specific yield of benzene and toluene from vapor phase HDO of guaiacol/anisole/phenolic compound mixtures at 1 bar.

Catalyst	Reaction Temperature (K)	Space Velocity ($g_{phenolic\ compound}\ g_{cat}^{-1}\ h^{-1}$)	Conversion (%)	Phenolic Compound	Yield of benzene and toluene ($\times 10^{-7}$ mol $g_{cat}^{-1}\ s^{-1}$)
15 wt% Fe/SiO$_2$[20]	673	0.13	100	Guaiacol	1.2
Ni$_2$P/SiO$_2$[15]	573	0.06	80	Guaiacol	0.6
Co$_2$P/SiO$_2$[15]	573	0.02	70	Guaiacol	0.1
MoO$_3$[17]	593	3.5	73	Guaiacol	16
Mo$_2$C[22]	553	2.6	-	Anisole	40[a]
Mo$_2$C	553	5.5	95	Phenolic mixture[b]	14

[a] The specific yield of benzene at 553 K is extrapolated from benzene turnover rate at 423 K using apparent activation energy (~70 kJ mol^{-1}) reported by Lee et al. [22].

[b] Molar ratio of m-cresol: anisole: DMB: GUA = 1: 0.96: 0.95: 0.98; Feed = phenolic mixture (0.03)/ H$_2$ (91)/ He balance (vol%); space velocity 198 cm^3 s^{-1} g$_{cat}^{-1}$.
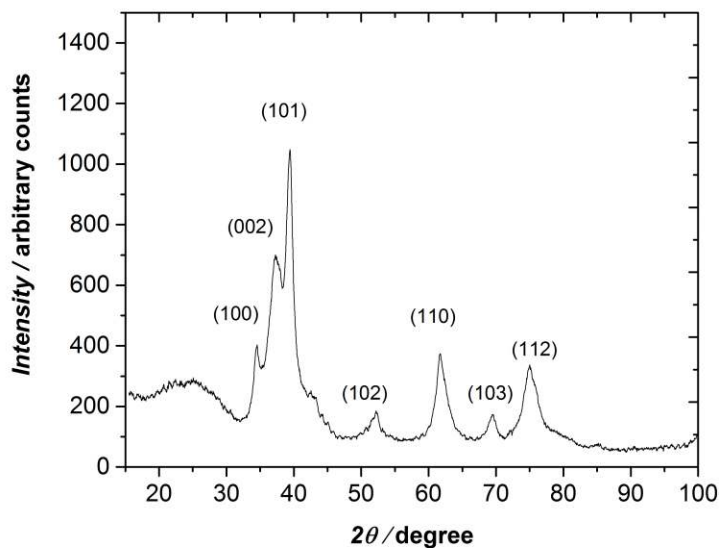
Figure 1. X-ray diffraction pattern of a Mo₂C catalyst. The sample was treated in a flow of 1% O_2/He mixture (~1.67 cm^3 s^{-1}) for ~2 h at RT and was aged for ~1 month in a vial under ambient conditions prior to XRD analysis.
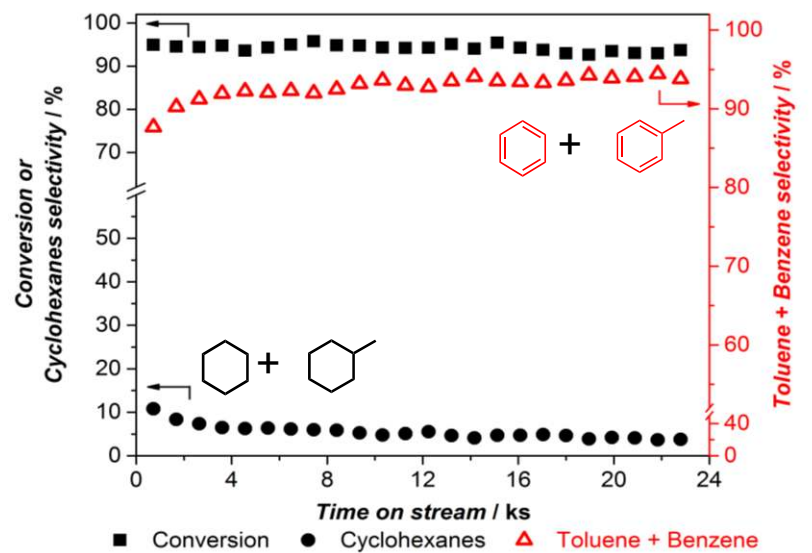

Figure 2. Conversion and product selectivity for HDO of a phenolic compound mixture over ~0.02 g Mo₂C. Molar ratio of m-cresol: anisole: DMB: GUA = 1: 0.96: 0.95: 0.98; Feed = phenolic mixture (0.03)/ H_2 (91)/ He balance (vol%) at 114 kPa total pressure and at 553 K; space velocity 198 cm^3 s^{-1} g$_{cat}^{-1}$; ex situ CO uptake = 124 μmol g$_{cat}^{-1}$; Cyclohexanes contains methylcyclohexane and cyclohexane.
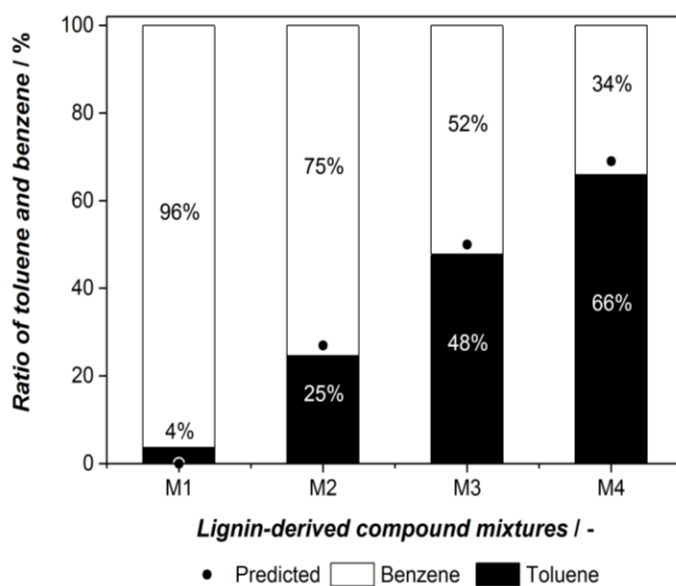
Figure 3. Ratio of toluene (■) and benzene (▢), defined as molar flow rate of (toluene or benzene)/ (toluene + benzene) × 100%, from reactor effluents of HDO reactions at different mixture compositions at quantitative (100%) conversion on 0.1 g Mo_2C under ambient pressure at 533 K for M2 and M3 (ex situ CO uptake = 224 μmol g_{cat}^{-1}), and 553 K for M1 and M4 (ex situ CO uptake = 135 μmol g_{cat}^{-1}); (•) predicted toluene ratios from the compositions of mixtures, assuming that m-cresol was completely deoxygenated to toluene, while anisole, DMB, and GUA were deoxygenated to benzene. Molar compositions of phenolic compound mixtures [m-cresol: anisole: DMB: GUA] = 0: 0.35: 0.35: 0.3 (M1); 1: 0.96: 0.95: 0.82 (M2); 1: 0: 0.95: 0 (M3); 1: 0.16: 0.16: 0.13 (M4). Feed (M1 and M4) = phenolic mixture (0.03)/ H_2 (91)/ He balance (vol%) at 114 kPa total pressure; space velocity ~36.6 cm^3 s^{-1} g_{cat}^{-1}. Feed (M2 and M3) = phenolic mixture (0.07 and 0.15)/ H_2 (77)/ He balance (vol%) at 108 kPa total pressure; space velocity ~19.0 cm^3 s^{-1} g_{cat}^{-1}.
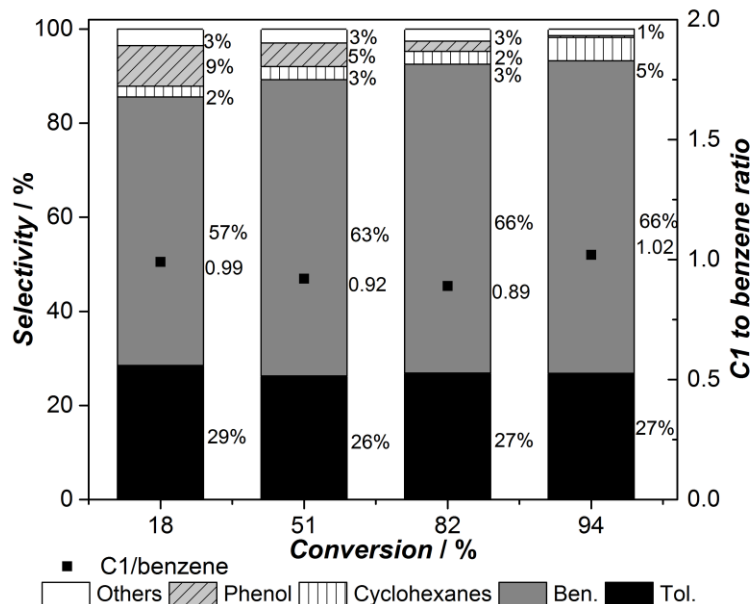
27

Figure 4. Selectivity for HDO of phenolic compound mixtures and molar ratio of C_1 products (methane and methanol) to benzene at different conversions (18–94%). Molar ratio of m-cresol: anisole: DMB: GUA = 1: 0.96: 0.95: 0.98; Feed = phenolic mixture (0.03)/ H_2 (91)/ He balance (vol%) at 114 kPa total pressure and at 553 K; Selectivity reported is an average value taken between ~3.6–21 ks time-on-stream; Different conversions were achieved by using different mass of catalyst (1.9–18.5 mg, ex situ CO uptake ~124 μmol g_{cat}^{-1}); space velocities 198–1.9 × 10^3 cm^3 s^{-1} g_{cat}^{-1}; Cyclohexanes contains methylcyclohexane and cyclohexane; Others contains unidentified C_6^+ hydrocarbons, which were quantified using benzene, anisole, or m-cresol, depending on the retention time of the species in the GC chromatogram.
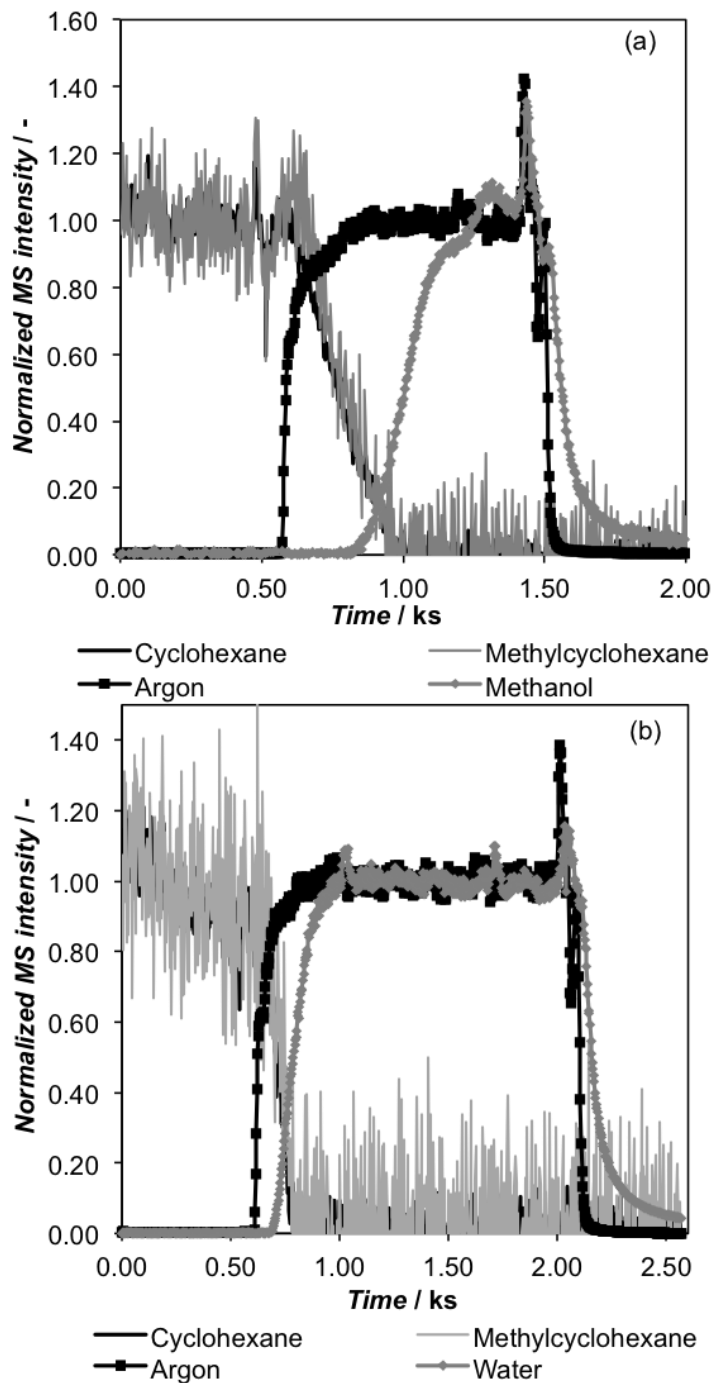
Figure 5. Mass spectrometric signals of methylcyclohexane and cyclohexane normalized to the signals at steady state as a function of time with a titrant co-feed consisting of (a) methanol/ argon (11.5/balance, vol%) and (b) water/ argon (24.5/balance, vol%) gas mixture (total flow rate ~0.17 cm^3 s^{-1}), in which Ar was used as an internal standard. Hydrogenation reaction conditions: equimolar mixture of (benzene and toluene)/He/H$_2$

(vol%) = 1.2/4.9/balance, with ~0.34 g_{cat} (ex situ CO uptake ~200 μmol g_{cat}^{-1}) and space velocity of ~10 cm^3 s^{-1} g_{cat}^{-1} at ~353 K under ambient pressure.

Table of Contents Figure