

HYDRODEOXYGENATION OF LIGNIN-DERIVED PHENOLIC COMPOUNDS ON MOLYBDENUM CARBIDES AT AMBIENT PRESSURE AND LOW TEMPERATURES

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Abstract

We report that high yields of benzene and toluene (>90% C₆⁺) can be obtained from selective hydrodeoxygenation (HDO) of lignin-derived phenolic model compounds, including anisole, m-cresol, 1,2-dimethoxybenzene, and guaiacol, on Mo₂C under ambient H₂ pressure and low temperatures (420–553 K). The low selectivity to sequentially hydrogenated aromatics (<10%), cyclohexane and methylcyclohexane, was a result of in situ modification of the oxophilic Mo₂C by oxygenates during HDO reactions, as inferred from in situ chemical titration studies of aromatic hydrogenation reactions using methanol and water. Selectivity to benzene and phenol in anisole HDO on Mo₂C formulations can be tuned by systematically incorporating oxygen in the as-synthesized Mo₂C (O/Mo_{bulk} = 0.076 to 0.276), which resulted in a decrease in benzene (97% to 18%), and an increase in phenol (0.2% to 81%) selectivity.

Keywords

Lignin upgrading, Hydrodeoxygenation, Aromatics, Molybdenum carbide.

Introduction

Lignin is a sustainable source to produce aromatics such as benzene, toluene, and xylenes (BTX). Vapor phase hydrodeoxygenation (HDO) of depolymerized lignin monomers can directly upgrade pyrolysis vapor without processing corrosive and viscous bio-oil (Venkatakrisnan et al., 2015). Selective cleavage of Ar–O bonds, however, is challenging because Ar–O bonds are strong (422–468 kJ mol⁻¹). Severe reaction conditions of high H₂ pressure (~1–5 MPa) and high temperatures (~473–723 K) thus limit the yields of BTX from HDO of lignin pyrolyzates by successive hydrogenation of the aromatic ring or direct hydrogenolysis of C–C bonds. In this work, we show that lignin-derived phenolic compound mixtures (anisole, m-cresol, guaiacol, 1,2-dimethoxybenzene) can be selectively converted to the corresponding completely deoxygenated aromatics (>90% yield) without hydrogenating the

aromatic double bonds. We report the kinetics, mechanism and site requirements for selective HDO on molybdenum carbide catalysts and demonstrate that product selectivity of anisole HDO, i.e. benzene and phenol, can be tuned in a controlled manner by systematic oxygen modifications to molybdenum carbide catalysts.

Materials and Methods

Mo₂C catalysts were prepared using ~0.6–1.2 g ammonium molybdate tetrahydrate (sieved, 177–400 μm) in a tubular quartz reactor under 15/85 vol% of CH₄ and H₂ at ~2.75 cm³ s⁻¹; the reactor was heated to ~623 K at ~0.06 K s⁻¹ and held for 5 h, which was subsequently heated at ~0.047 K s⁻¹ to ~863 K and held for 3 h. The resulting material was passivated in flowing 1% O₂/He

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mixture at $\sim 1.67\text{--}3.33\text{ cm}^3\text{ s}^{-1}$ for ~ 2 h at ambient temperature. Oxygen-modified Mo_2C formulations were synthesized by flowing 1% O_2/He over the as-synthesized catalysts at $1.5\text{ cm}^3\text{ s}^{-1}$ at temperatures ranging from 300–423 K. Mo_2C (0.5–140 mg) catalysts were treated in pure H_2 ($\sim 1.67\text{ cm}^3\text{ s}^{-1}$) at ~ 723 K for 1 h before introducing the reactant mixture ($\sim 1.67\text{--}3.67\text{ cm}^3\text{ s}^{-1}$) consisting of $\sim 0.03\text{--}0.14 / 91$ vol% of anisole, or a mixture of phenolic monomers and H_2 at reaction temperature (423–553 K).

Results and Discussion

Figure 1 shows the conversion and product selectivity of vapor phase HDO of an equimolar mixture, containing m-cresol, anisole, guaiacol, and 1,2-dimethoxybenzene, on Mo_2C at 553 K and ambient H_2 pressure. High selectivity to the completely deoxygenated aromatics ($>90\%$), benzene and toluene, but low to cyclohexane and methylcyclohexane ($<9\%$) implies that HDO of phenolic monomers on Mo_2C is hydrogen efficient.

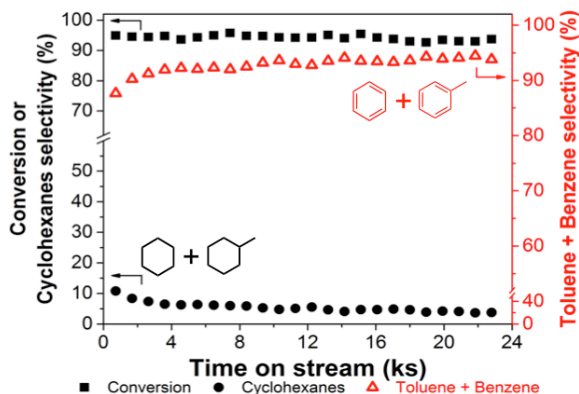


Figure 1. HDO of an equimolar mixture of lignin-derived oxygenates (anisole, m-cresol, guaiacol, 1,2-dimethoxybenzene) on Mo_2C at ambient H_2 pressure and 553 K.

In situ titration via oxygen-containing compounds, methanol and water, was used to probe hydrogenation functionality on Mo_2C . Hydrogenation rates of benzene and toluene were completely inhibited in presence of methanol or water co-feed, suggesting that the introduction of oxygen-containing compounds to molybdenum carbide formulations, including lignin-derived phenolic monomers, can irreversibly inhibit the metallic hydrogenation function (Chen et al., 2016).

Figure 2 shows the C_6^+ selectivity in anisole HDO as a function of oxygen content in oxygen-modified Mo_2C . Benzene selectivity decreased from 97% to 18%, while phenol selectivity increased from 0.2% to 81%, when the oxygen content in bulk molybdenum carbide catalysts ($\text{O}/\text{Mo}_{\text{bulk}}$) increased from 0.076 to 0.276, demonstrating that the C_6^+ product selectivity for anisole HDO can be tuned by incorporating systematic oxygen modifications to the catalysts. Benzene turnover rates measured by in situ CO titration were invariant across the four oxygen-modified catalysts, whereas benzene synthesis rates

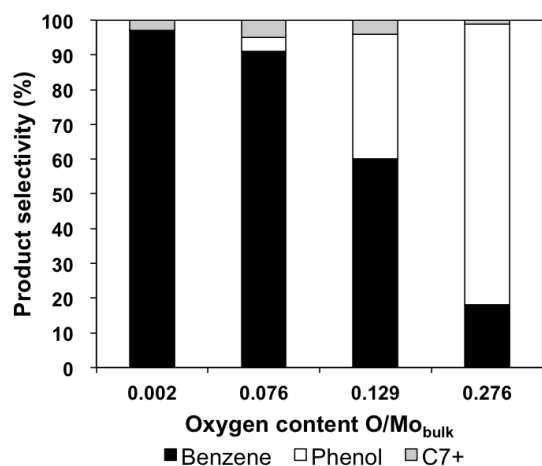


Figure 2. Product selectivity for anisole HDO on the as-synthesized fresh and oxygen modified Mo_2C formulations at 423 K and ambient pressure.

decreased from 6.89×10^{-8} to $0.17 \times 10^{-8}\text{ mol s}^{-1}\text{ g}_{\text{cat}}^{-1}$, demonstrating that oxygen chemisorption on Mo_2C formulations alters the number, not the identity, of the active sites for benzene synthesis (Lee et al. 2015).

Conclusions

Molybdenum carbide catalysts are highly selective for vapor phase HDO of lignin-derived phenolics to form aromatics. In situ oxygen modification of the surface prevents successive hydrogenation reactions. Product selectivity and anisole HDO rates can be manipulated by oxidative treatments of the catalysts.

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