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Introduction

Ex situ catalytic preconditioning of biomass pyrolysis vapors (partial deoxygenation) has the potential for both reducing the oxygen content and beneficially influencing the oxygen speciation of condensed bio-oils for enhancement of downstream condensed phase upgrading processes. Here, condensed phase upgrading processes may refer to both coprocessing and hydroprocessing with vacuum gas-oil (VGO). Reduction of oxygen content to produce bio-oils with greater hydrophobicity can enhance VGO-solubility while tailoring of oxygen speciation by removal of reactive carbonyls (e.g., acetic acid) can lessen catalytic deactivation via coking reactions.^{1,2} Furthermore, enhanced VGO-solubility and reduced coking leads to greater biogenic carbon incorporation in end-products from condensed phase upgrading processes. By leveraging the hydrodeoxygenation and alkylation activity of a titania-supported molybdenum-heteropolyacid (Mo-HPA/TiO₂) catalyst, pyrolysis vapors and resulting condensed bio-oils were effectively preconditioned for downstream upgrading.³ Data regarding the use of Mo-HPA/TiO₂ for pyrolysis vapor preconditioning will be presented on, including method of employment, catalyst characterization, and impacts on bio-oil in relation to downstream condensed phase upgrading processes. Our approach is to:

- Compare Mo-HPA/TiO₂ product distribution to HZSM-5.
- Investigate Mo-HPA/TiO₂ regeneration and characterize changes in acid site character.
- Assess product differences in terms of enhanced VGO-solubility.

Materials & Methods

- Used lab scale pulsed-flow catalyst screening equipment (Figure 1) to assess catalyst activity.
- Pyrolysis and upgrading conducted at 500°C and 400°C, respectively, using Loblolly pine biomass in He or H₂/He mixtures (30 mg BM/pulse; vapor WHSV of 2 h⁻¹).
- Compared acid catalysts: HZSM-5 (A) & Mo-HPA/TiO₂ (B).
- Utilized molecular beam mass spectrometry (MBMS) for real-time analysis of products.
- Mo-HPA/TiO₂ regeneration methods:
 - Mild Oxidative, 5 vol% O₂ in He, 425°C, 0.5 h
 - Severe Oxidative, 21 vol% O₂ in He, 550°C, 4 h
 - Reductive, 100 vol% H₂, 400°C, 5 h
- Acid site characterization via pyridine adsorption diffuse reflectance Fourier transform infrared spectroscopy (py-DRIFTS).

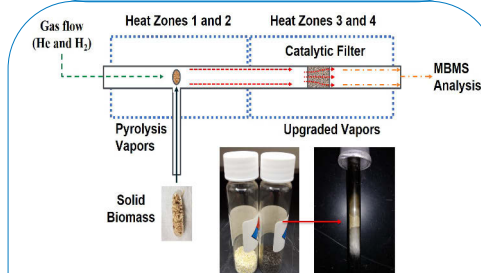


Figure 1. Lab scale pulsed-flow experimental setup showing the horizontal quartz reactor system (upper left) coupled to a molecular beam mass spectrometer (MBMS, right) for real-time analysis of products. Catalyst is shown pre- and post-reaction (cooked).

Results & Discussion

- Lab scale pulsed-flow experiments (Figure 2):
 - Catalyst A produced VGO-soluble BTX and naphthalenes without the need for added H₂.
 - Catalyst B produced polyalkyl benzenes/anthracenes in addition to BTX and naphthalenes under reducing conditions (with H₂) → increased non-polarity may enhance VGO-solubility and biogenic carbon incorporation for coprocessing
 - Catalyst B partially regenerated via mild oxidative and reductive conditions; severe oxidative treatment significantly reduced catalyst activity.
- Catalyst B, py-DRIFTS acid site characterization (Figure 3 and Table 1):
 - Addition of Mo-HPA to TiO₂ adds Brønsted acidity
 - Acidity partially retained after regeneration → B/L of ~0.2-0.3 retained post mild regeneration

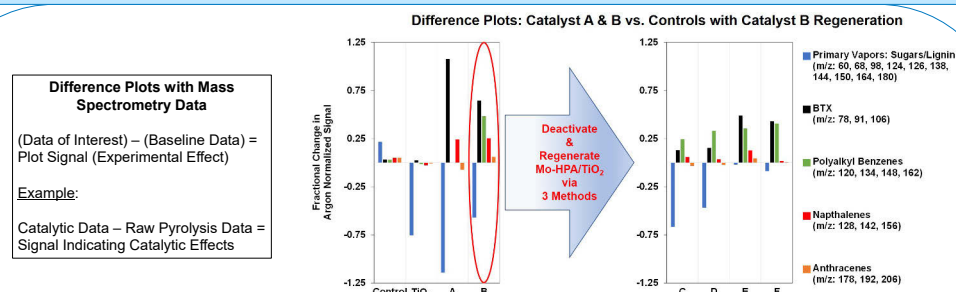


Figure 2. Mass spectral data showing pine pyrolysis upgrading using: Control hydrogen (H₂; i.e., hydrolysis), TiO₂ (titania), A HZSM-5 (without H₂), B molybdenum heteropolyacid on titania (Mo-HPA/TiO₂), C deactivated Mo-HPA/TiO₂, D severe oxidatively regenerated Mo-HPA/TiO₂, E mild oxidatively regenerated Mo-HPA/TiO₂, and F reductively regenerated Mo-HPA/TiO₂.

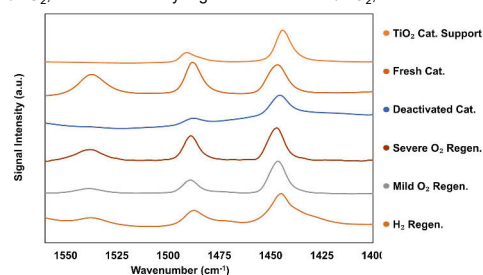


Figure 3. Acid site stability as a function of reaction via pyridine adsorption diffuse reflectance Fourier transform infrared spectroscopy (py-DRIFTS) for pulsed-flow conditions. Modes at ~1447 cm⁻¹ and ~1537 cm⁻¹ are attributed to pyridine coordination with Lewis and Brønsted acid sites, respectively. Mode at ~1490 cm⁻¹ is indicative of both Lewis and Brønsted acid sites.⁴

Table 1: py-DRIFTS Data – Brønsted and Lewis acidity ratios for TiO₂ and Mo-HPA/TiO₂ pre- and post-regeneration.

Conditions	Brønsted Acidity/Lewis Acidity Ratio (B/L)
TiO ₂	-
Fresh Mo-HPA/TiO ₂	1.27
Deactivated Mo-HPA/TiO ₂	0.05
Mild Oxidative Regeneration for Mo-HPA/TiO ₂	0.28
Severe Oxidative Regeneration for Mo-HPA/TiO ₂	0.80
Reductive Regeneration for Mo-HPA/TiO ₂	0.19

Literature Cited & Acknowledgements

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Conclusions & Future Work

- Mo-HPA/TiO₂ selective towards polyalkyl benzenes/anthracenes for potential VGO-solubility enhancement.
- Mo-HPA/TiO₂ regenerable under reductive and mild oxidative conditions.
- Future work – compare VGO-solubility of products and product speciation for HZSM-5 and Mo-HPA/TiO₂; assess preconditioned product speciation on coprocessing and/or hydroprocessing.