



Performance of mesoporous ZSM-5 in deoxygenation of straw derived pyrolysis vapors

Eschenbacher, Andreas; Jensen, Peter Arendt; Henriksen, Ulrik Birk; Ahrenfeldt, Jesper; Mentzel, Uffe V.; Jensen, Anker Degn

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Eschenbacher, A., Jensen, P. A., Henriksen, U. B., Ahrenfeldt, J., Mentzel, U. V., & Jensen, A. D. (2018). Performance of mesoporous ZSM-5 in deoxygenation of straw derived pyrolysis vapors. Abstract from Thermal & Catalytic Sciences Symposium (TCS 2018), Auburn, United States.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Performance of mesoporous ZSM-5 in deoxygenation of straw derived pyrolysis vapors

Andreas Eschenbacher¹, Peter A. Jensen¹, Ulrik B. Henriksen¹, Jesper Ahrenfeldt¹, Uffe V. Mentzel², Anker D. Jensen^{1*}

¹DTU Chemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, DK-2800, Denmark

²Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark

*Corresponding author: aj@kt.dtu.dk

1. Introduction

In order to allow processing of biomass derived fast pyrolysis oils in oil refineries, reduction of the oil's oxygen content and acid number is required [1]. Deoxygenation can be obtained by direct upgrading of the pyrolysis vapors over solid acid catalysts. A close coupled process operating at temperature and pressure conditions close to those for optimum liquid yields in pyrolysis units offers potential economic advantages over high pressure hydrotreating [2]. To date, the medium pore size ZSM-5 zeolite provides a high aromatic yield and the least amount of coke in upgrading of pyrolysis vapors [3]. However, the coke caused by reactive pyrolysis vapors causes a rapid decay in site accessibility and requires frequent regeneration to recover activity. In addition, irreversible dealumination can be caused by steam from the pyrolysis process, the dehydration reactions during upgrading and the steam produced during oxidative regeneration. We address the reversible deactivation due to coke by introducing an auxiliary mesopores network to improve the accessibility and prolong the zeolite's active time on stream. In order to reduce the irreversible deactivation, the zeolites acid site strength and density have been balanced with modifications by phosphorous stabilization.

2. Experimental

The screening of the parent, mesoporous, and phosphorous modified ZSM-5 zeolites was performed with 20 -150 g of catalyst in a fixed bed reactor downstream an ablative type pyrolysis unit. Prior to upgrading the zeolite was steamed to achieve accelerated dealumination. Crushed wheat straw pellets were used as feedstock at a feeding rate of ~2g/min. By varying the runtime and amount of catalyst, a wide range of biomass feed to catalyst (B:C) ratios was covered and upgraded liquid product was collected at an optimized condensation train, followed by detailed analysis of the liquids in terms of moisture, elemental analysis, size exclusion chromatography (SEC) and quantification of ~200 components by GC-MS/FID. Catalyst characterization was performed with ICP/XRF, NH₃-TPD, N₂ and Ar-physisorption, TEM and XRD.

3. Results and discussion

Mass and energy balances > 90 % were obtained. Towards higher B:C values, the obtained oils consist both of fully upgraded products when the catalyst was fresh and products from the breakthrough of primary pyrolysis vapors. In order to unravel the change in oil-quality with increased B:C ratio, a series of successive biomass conversion steps was performed. Towards higher B:C values, a decreasing yield of monoaromatics is accompanied by a decreased selectivity to BTX products (Fig. 1a). At 500°C, all zeolites clearly reduced the oxygen content of the oil with respect to oil obtained from passing the vapors over a silicon carbide bed (Fig. 1b). The benefit of an auxiliary mesopore network becomes apparent for oils collected at higher B:C ratios: While the microporous ZSM-5 rapidly loses its deoxygenation ability (see CBV30 for Σ B:C 0.6 to 2.6), the mesoporous ZSM-5 maintains a similar degree of deoxygenation for almost four times higher B:C ratio (see CBV30 for Σ B:C 4 to 10.2). While phosphorous stabilized mesoporous CBV55 achieves less deoxygenation at the low B:C range, their deoxygenation performance at higher B:C of ~9 is still comparable to the microporous counterpart at lower B:C of ~6. We further find that the introduction of mesopores results in higher coke formation, which can be mitigated by the addition of phosphorous.

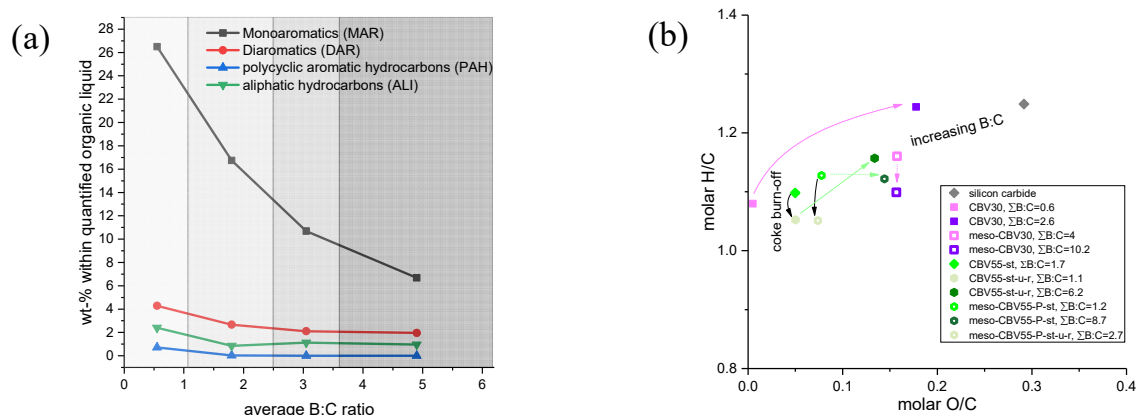


Figure 1: (a) Change of deoxygenated liquid products with increasing catalyst deactivation by coke, here shown for steamed CBV55 (b) Performance of micro and mesoporous ZSM-5 at operating temperature of 500°C based on molar H/C and O/C ratio; “P”, “st”, “u”, and “r” refers to phosphorous modification, steaming, use, and oxidative regeneration, respectively

References

- [1] G. W. Huber, “Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels: Hydrocarbon Biorefineries,” *Am. Chem. Soc.*, pp. 1–177, 2007.
- [2] A. V Bridgwater, “Production of high grade fuels and chemicals from catalytic pyrolysis of biomass,” *Catal. Today*, vol. 29, no. 1–4, pp. 285–295, 1996.
- [3] J. Jae *et al.*, “Investigation into the shape selectivity of zeolite catalysts for biomass conversion,” *J. Catal.*, vol. 279, no. 2, pp. 257–268, 2011.