

Enhanced Bio-Oil Upgrading: Mesoporous and Zeolitic Catalysts for Polyaromatic Hydrocarbon Conversion

<u>Luke HARVEY</u>, Thoams DOYLE, Rahim KAMARI, Eric KENNEDY, Michael STOCKENHUBER The University of Newcastle, Chemical Engineering, University Drive, Callaghan, Australia *Luke.Harvey@newcastle.edu.au

Significance and Relevance

The sustainable transformation of biomass-derived bio-oils into fuels and platform chemicals is central to reducing reliance on fossil hydrocarbons. This work addresses a critical limitation in bio-oil upgrading: the efficient conversion of bulky polycyclic aromatic hydrocarbons (PAHs), which constitute a major fraction of bio-oil carbon, into valuable products. We present the synthesis and application of mesoporous catalysts tailored to enhance PAH conversion, coupled with zeolitic materials for selective cracking, offering a promising pathway for advanced biomass valorization.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion Preferred presentation: Oral only

Introduction and Motivations

Global energy security increasingly relies on sustainable alternatives to crude oil derivatives and hydrocarbons. This research advances catalytic technologies to convert biocrude, derived from waste and biomass sources (e.g., lignocellulose), into fuels and high-value platform chemicals. A primary challenge in bio-oil upgrading is reducing oxygen content, which impacts stability and usability¹. Recent studies show that zeolite-based catalysts are highly effective in hydrodeoxygenation, offering control over selectivity for products such as BTEX, through structural and acidic site modifications². The micropores found in most common zeolitic materials, however are not easily accessible to bulkier compounds (PAHs) which comprise a high proportion of the carbon in bio oils. It is therefore preferable to select mesoporous catalyst supports. By optimizing catalyst properties including acid site strength and concentration, pore size and structure and catalytic metal loading, we have shown that PAH conversion is significantly increased, and selectivity may be directed toward either hydrogenated kerosene products, or single-ring aromatics and derivatives.

Materials and Methods

The mesoporous support was synthesized by mixing the required amounts of aluminum isopropoxide and tetraethyl orthosilicate together with P123 as a structure directing agent under acidic conditions. The resulting gel was aged in a PTFE-lined autoclave at 110°C for 48 hours. Aluminium-free mesoporous silica was prepared using the same method but omitting the aluminum source. Loading of the nickel was performed by wetness impregnation, followed calcination at 500°C.

Catalyst textural properties were measured using nitrogen sorption at liquid nitrogen temperature. Acid site strength and concentration was measured using ammonia temperature-programmed desorption (TPD) with a mass spectrometer.

The reaction was carried out in a vertical fixed bed plug flow reactor at elevated hydrogen pressure. A simulated bio-oil feed containing phenanthrene as a surrogate for the three-member polyaromatic hydrocarbons which constitute the largest and most challenging family of compounds comprising bio-oil, dissolved in 3-pentanone was introduced using a high pressure syringe pump.

Feed and product streams were analyzed by gas chromatography, using MSD, FID, TCD and methanizer-FID detectors.



Results and Discussion

Catalyst Characterization: The pore size distribution of the mesoporous aluminosilicate was relatively narrow and centered on

79 Å, slightly larger than the aluminum-free SBA-15 at 66 Å. The addition of nickel reduced the effective pore diameter of the Al-ABA-15 and SBA-15 by approximately 10 Å. This was not the case for zeolite BEA, with H-BEA and Ni-H-BEA having pore diameters of 7.1 and 7.0 Å respectively.



Figure 1: NH₄-TPD profiles for Al-SBA-15 and Ni-Al-SBA-15. Zeolite BEA for reference

The TPD measurements (Figure 1) demonstrate that substantial Brønsted acidity, comparable to H-BEA was engendered into the SBA-15 support through the addition aluminum into of the framework. Adding nickel at 20 wt% however, decreased the population of strong acid sites substantially, with weak acid sites dominant. We believe that this may be due to a decrease in the ratio of Brønsted to Lewis acid sites, and to a lesser extent the relaxation of the Si-O(H)-Al bond angle, known to occur readily in amorphous materials³.

Reaction Data: The nickel-free Al-SBA-15 does not exhibit high activity in either hydrogenation or cracking of the phenanthrene PAH. This is to be expected, as the metallic Ni site is active for hydrogenation and cracking does not occur to a great extent on resonance-stabilized structures, namely aromatic rings. To the extent that the phenanthrene is converted (25%), the primary product is methane. The Nickel-BEA catalyst exhibits significantly higher phenanthrene conversion (86%), with the primary products being phenanthrene hydrogenates of varying degrees, propene and ethylene. The greatest phenanthrene conversion for a single catalyst was exhibited by Ni-Al-SBA-15 (96%), with the primary products being hydrogenated phenanthrene analogues and some cracking products such as 1,2-dicyclohexylethane. An experiment with two catalyst beds (Ni-Al-SBA-15, then Ni-BEA) in equal proportion and overall quantity as the previous experiments yielded the highest phenanthrene conversion, at 98%. The primary products in this experiment were one and two-ring cyclic alkanes with various C 1-4 alkane substituents, and a high proportion of propene in the gas product stream. This demonstrates that polyaromatics may be effectively hydrogenated and cracked by the mesoporous catalyst, followed by further cracking and shape selectivity by the zeolite BEA.

References

(m/z = 16).

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