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Effects of metal impregnation on ZSM-5 for catalytic upgrading of biofuel intermediates

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INTRODUCTION

Q: How are biofuels made?

FIG. 1. *Flow diagram explaining biofuel processing*. Biomass undergoes pyrolysis in the absence of O_2 to make vapors, which are then condensed to form raw bio-oil.

Q: Why does my car not run on biofuels now?

Pyrolysis introduces oxygenates and other undesirable compounds that compromise the quality and stability of the final biofuel product.

Q: How can this be resolved?

Catalytic upgrading removes oxygen from biofuel intermediates (reducing acidity) and adds hydrogen (improving energy content).It can occur through either:
1) vapor phase upgrading (VPU) of pyrolysis vapors; or
2) hydrodeoxygenation (HDO) of raw bio-oil.

Q: What is the catch?

Carbon deposits called coke deactivate the catalyst by blocking acid sites during catalytic upgrading. Deactivation can be reduced by modifying the physicochemical features of the catalyst. Metal impregnation is one such modification under investigation.

Q: Why ZSM-5?

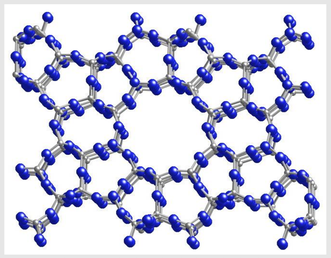


Photo: https://engineering.purdue.edu/~thomsonk/projects.html

FIG. 2. *Molecular structure of ZSM-5*.

ZSM-5 belongs to a class of silica-alumina catalysts called zeolites. Zeolites are ideal because of their:
- defined pore structure;
- high acidity; and
- product selectivity toward aromatics.

However, ZSM-5 is unstable as a catalyst due to its rapid deactivation.

RESEARCH QUESTIONS

- *Can we improve deoxygenation activity and catalyst stability of ZSM-5 through the addition of metals?*
- *What effects does metal impregnation have on the catalytic activity and physicochemical properties of ZSM-5?*

EXPERIMENTAL APPROACH

Catalyst synthesis: Metals were added to ZSM-5 via incipient wetness impregnation at a constant molar ratio of 1:2 metal-to-aluminum.

From left to right: ZSM-5, Ga/ZSM-5, Co/ZSM-5, Ni/ZSM-5, Pt/ZSM-5, Cu/ZSM-5

Catalyst characterization:

Laboratory Technique	Abbreviation	Characteristic Evaluated
Ammonia Temperature-Programmed Desorption	NH_3-TPD	Acidity
X-ray Diffraction	XRD	Crystalline structure
Nitrogen-Chemisorption	N_2-sorption	Surface area/ pore volume
Thermogravimetric Analysis	TGA	Coke formation (post-VPU)

Catalytic activity tests via VPU with pine:

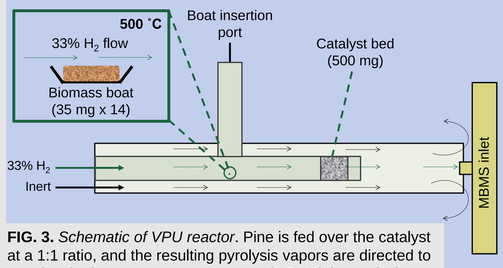
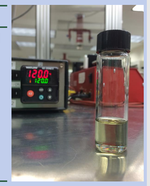


FIG. 3. *Schematic of VPU reactor*. Pine is fed over the catalyst at a 1:1 ratio, and the resulting pyrolysis vapors are directed to a molecular beam mass spectrometer (MBMS) for analysis.

Catalytic activity tests via HDO with anisole:

Table 1: Experimental conditions summary

Condition	Measurement
Reactor type	Vertical, fixed-bed
Model compound flowrate (cc/min)	0.1
H_2 gas flowrate (cc/min)	150
Inert gas flowrate (cc/min)	50
Catalyst mass (mg)	100
Reaction runtime (min)	60
Temperature (˚C)	500



Why anisole? Anisole ($C_6H_5O\text{-}CH_3$) was selected as a model compound for our study because it represents a sample of the oxygenated aromatics found in biofuel intermediates.

RESULTS & DISCUSSION

CHARACTERIZATION

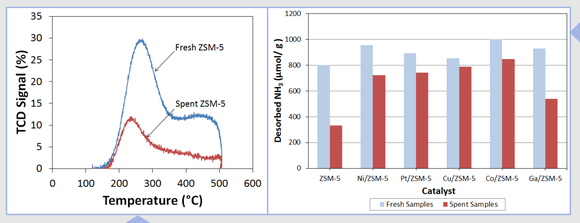


FIG. 4. *NH_3-TPD profiles of fresh and spent ZSM-5.* The peaks at ~280 ˚C and 460 ˚C are due to NH_3 desorption from weak and strong acid sites, respectively.

FIG. 5. *Desorbed NH_3 from fresh and spent samples.*

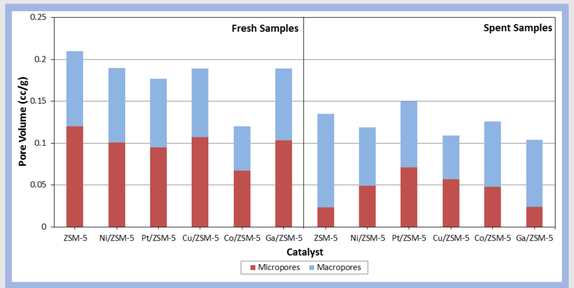


FIG. 6. *Pore volume obtained via N_2-sorption.* The loss of pore volume between fresh and spent samples can be attributed to coke filling the pores.

Table 2: Acid site retention and coke formation post-VPU

Catalyst	Acid sites retained (%)	Coke (wt%)
ZSM-5	41	10.0
Ni/ZSM-5	76	4.8
Pt/ZSM-5	83	2.5
Cu/ZSM-5	92	6.4
Co/ZSM-5	85	7.6
Ga/ZSM-5	58	9.2

Q: What can I observe from this data?

Compared to metal-added ZSM-5, unmodified ZSM-5…
- … contains the *least number of acid sites* [Figure 5]
- … *loses the most number of acid sites* post-VPU [Figure 5/ Table 2].
- … experiences the *most coke formation* [Table 2].
- … has the *largest total pore volume* [Figure 6].
- … *loses the most micropore volume* post-VPU [Figure 6].

Q: What are the implications?

Adding metals to ZSM-5 creates more acid sites and improves resistance to coke formation.

RESULTS & DISCUSSION

ACTIVITY TESTS

VPU with pine:

- Reactions with unmodified ZSM-5 had greater initial aromatic yields.
- However, ZSM-5 deactivated more rapidly due to coke formation.
- Metal-added ZSM-5 catalysts had lower initial aromatic yields, but showed more stable activity.

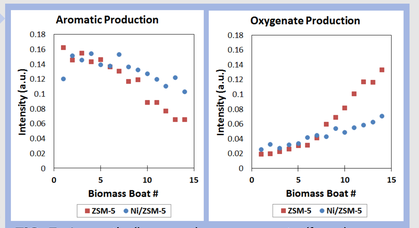


FIG. 7. *Aromatic (benzene) vs. oxygenate (furan) production during VPU.* Intensity was normalized to Ar.

HDO with anisole:

- Unmodified ZSM-5 had the least anisole conversion (7%) with the lowest hydrocarbon (HC) product selectivity (50%).
- Within the oxygenate yields, all catalysts had similar product selectivity to phenolic species.
- Benzene (m/z=78) was the only observed BTX hydrocarbon.
- Prominent oxygenate species:
  - Phenol (m/z=94)
  - Methyl-phenol (m/z=108)
  - Methyl-anisole (m/z=122)

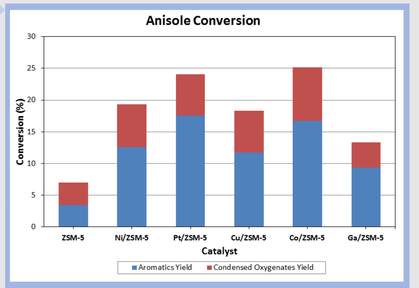


FIG. 8. *Anisole conversion with aromatic (blue) vs. oxygenate (red) yields.* ZSM-5 had 50% HC selectivity.

Q: What are the implications?

Metal-added ZSM-5 catalysts show better deoxygenation activity and catalyst stability than unmodified ZSM-5. This suggests that the physical and chemical properties of metal-added ZSM-5 are more ideal for use in catalytic upgrading of biofuel intermediates.

FUTURE WORK

Some considerations for future work include:
- **optimizing catalysts during synthesis**;
  Which metal-to-aluminum molar ratio is optimizes performance?
- **examining the effects of different operation parameters**;
  How does varying upgrading temperature, residence time, and/or catalyst-to-feed ratio affect catalytic activity?
- **evaluating the role of model compounds on deactivation**.
  Does our choice of model compound affect catalyst deactivation?

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