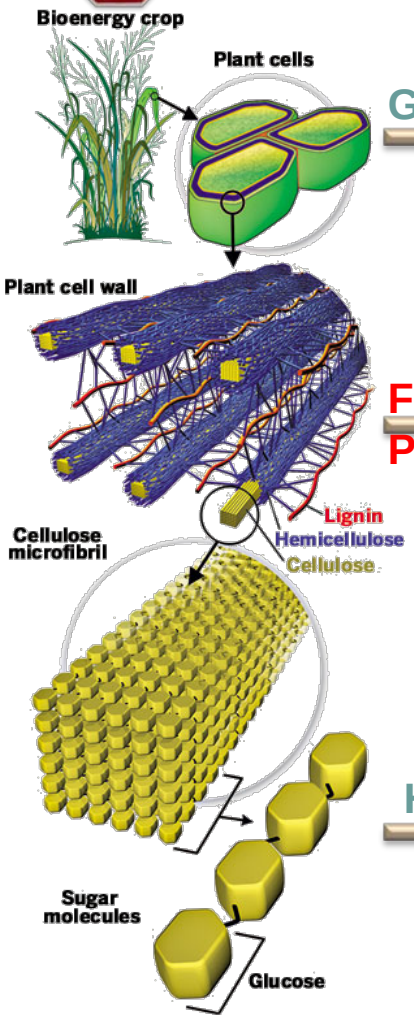
The Role of Bifunctional Catalysts on the Upgrading of Biomass Pyrolysis Oil Vapors

EPSCoR BIOFUELS RESEARCH TELECONFERENCE
2/15/12

Steven Crossley

Utilization of Biomass



Gasification → $CO + H_2$

- Methanol Synthesis → Methanol
- Fisher-Tropsch → Alkanes

Fast Pyrolysis → Bio-oils

Furanics, Light Oxygenates, Phenolics

- Hydrodeoxygenation
- Zeolite Upgrading
- Emulsification

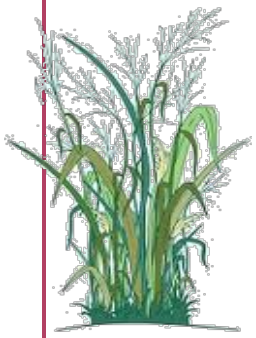
→ Hydrocarbons

Hydrolysis

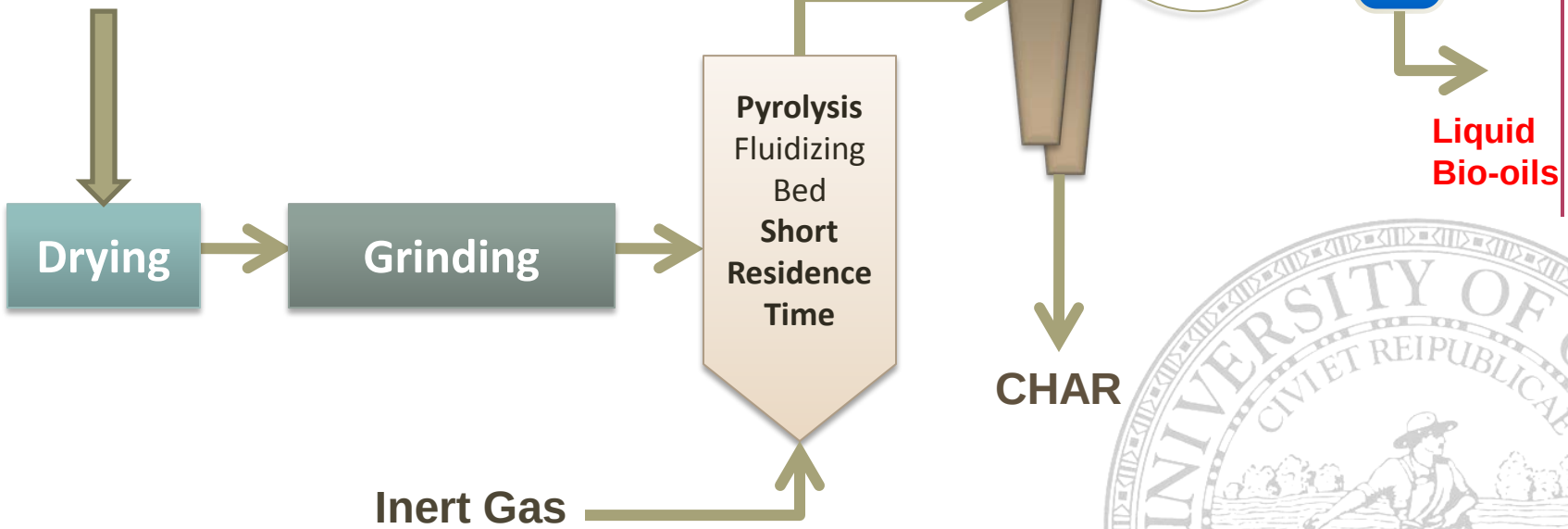
- C5-Sugars → Dehydration, Condensation, Hydrogenation → Furans, Alkanes, Alcohols
- C6-Sugars → Fermentation → Ethanol,Butanol

OBJECTIVES

Increase Liquid Yield
Remove Oxygen
Minimize Deactivation



BIOMASS
Switch grass
Sawdust, Pine
Torrefied-biomass

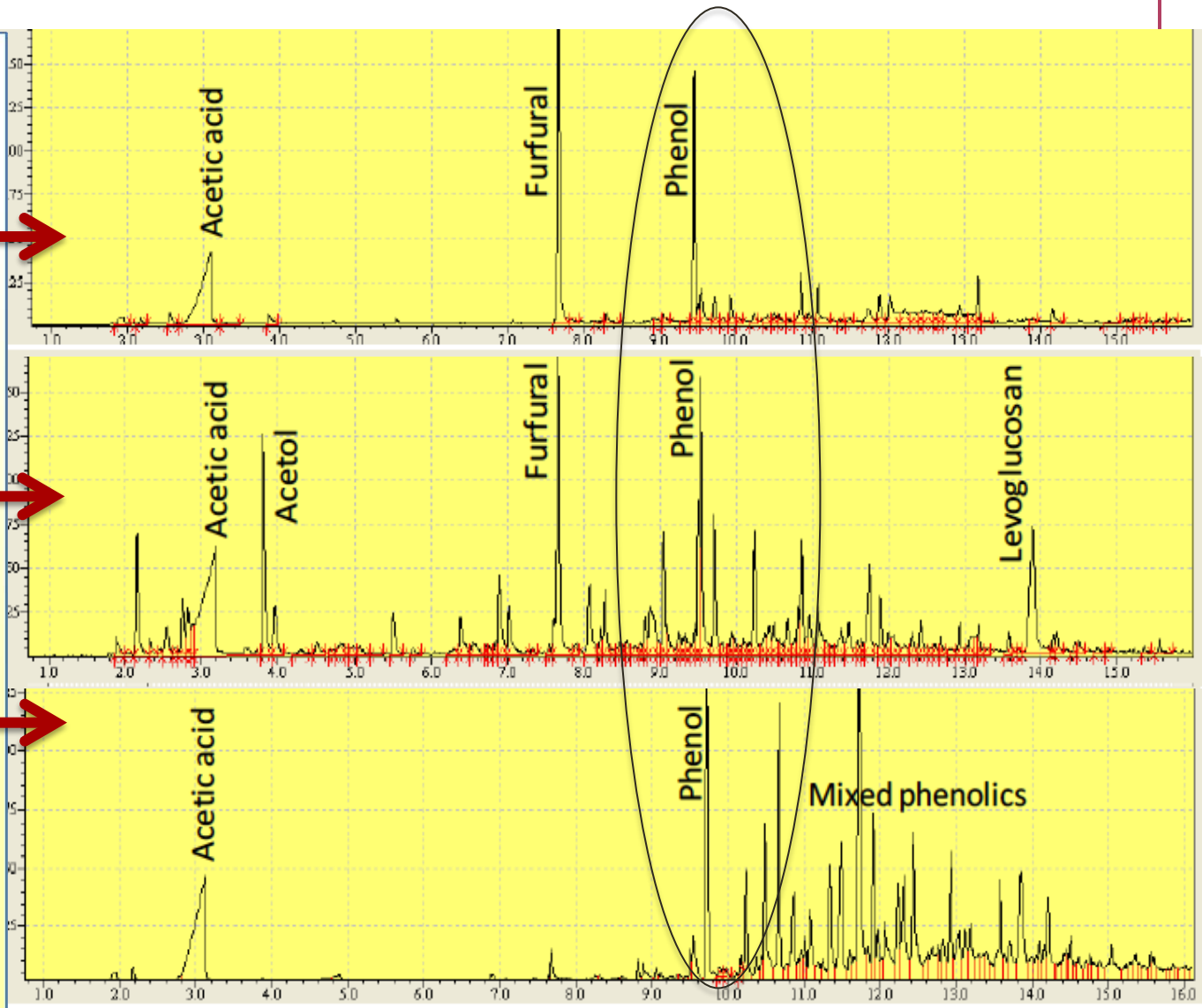


Staged Upgrading

250-275°C

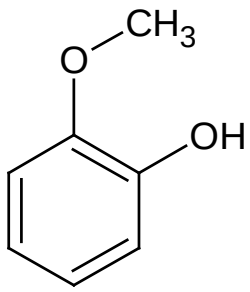
300-350°C

550-600°C

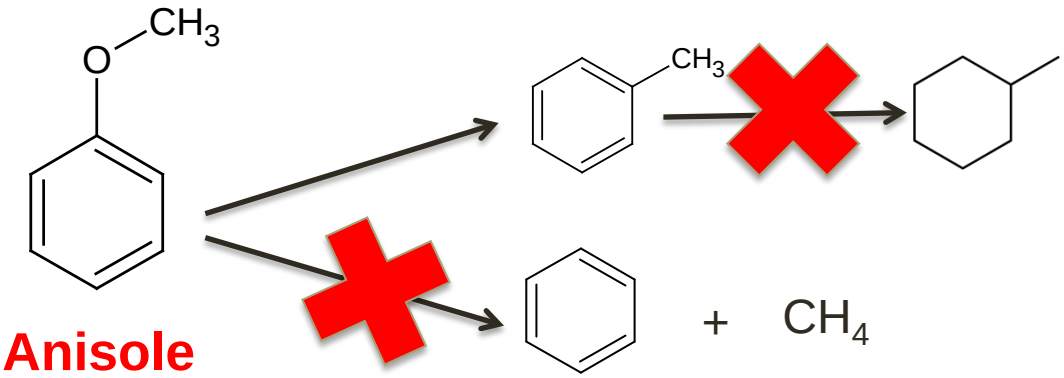


Strategy

- gas phase
- low pressure
- remove oxygen
- preserve C on ring
- minimize hydrogen consumption



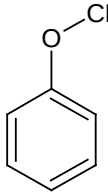
Guaiacol



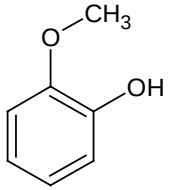
Anisole

Amorphous Silica-Alumina

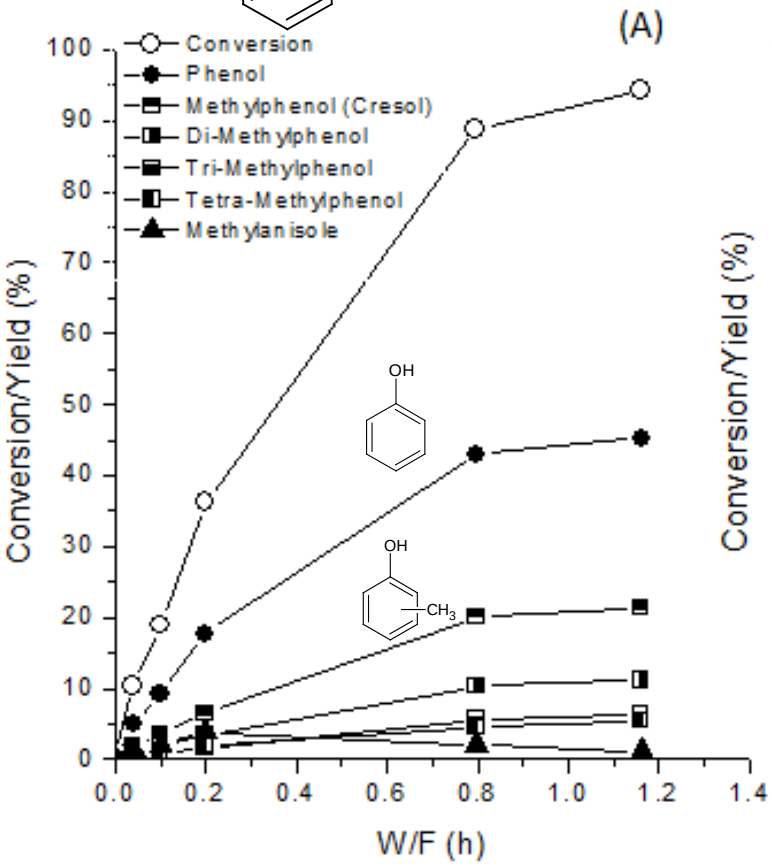
Anisole

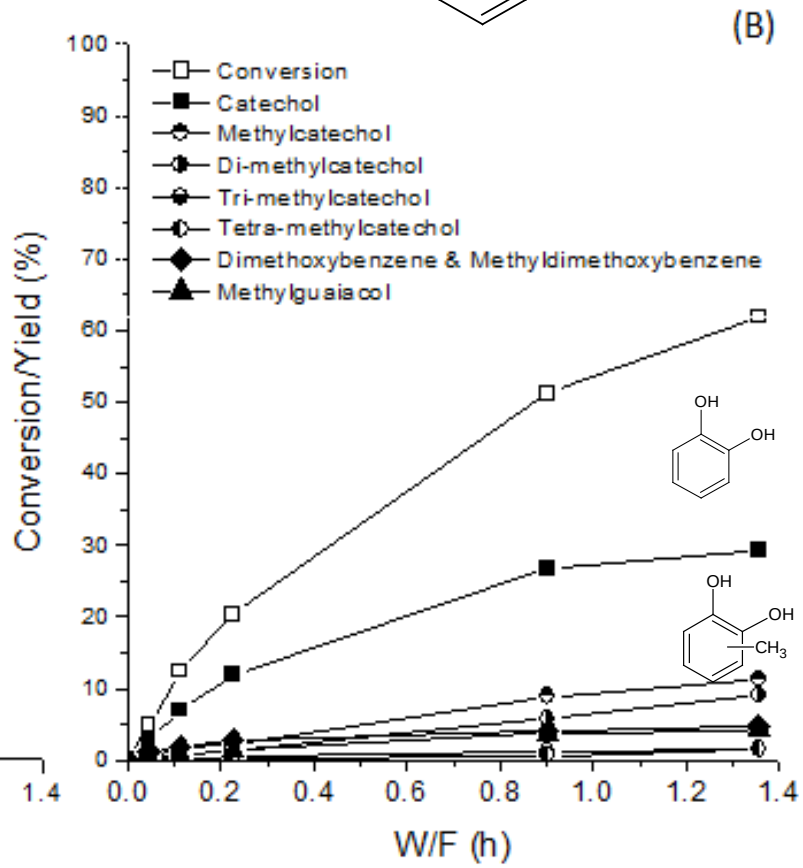


Guaiacol



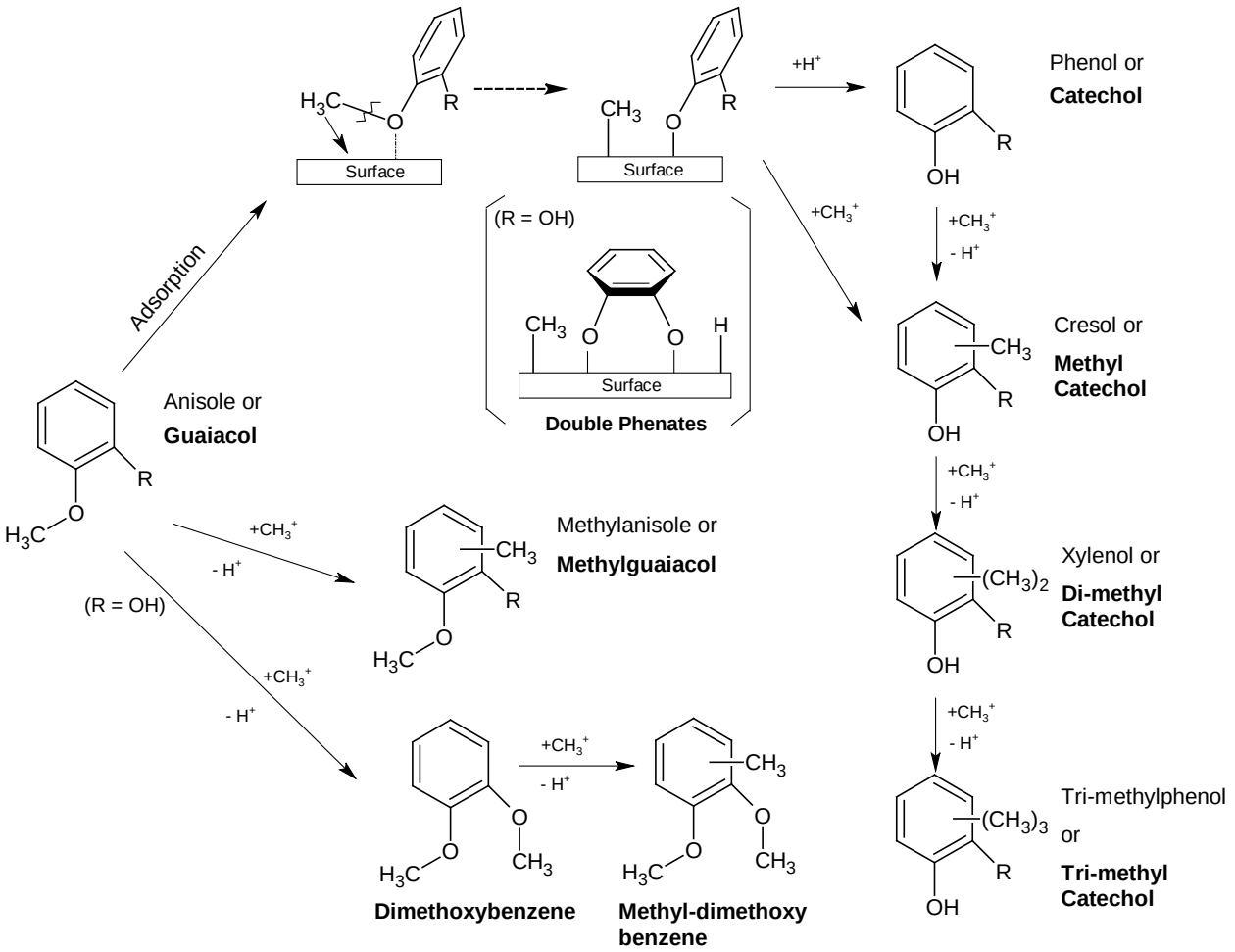
85% of CH_3 is conserved



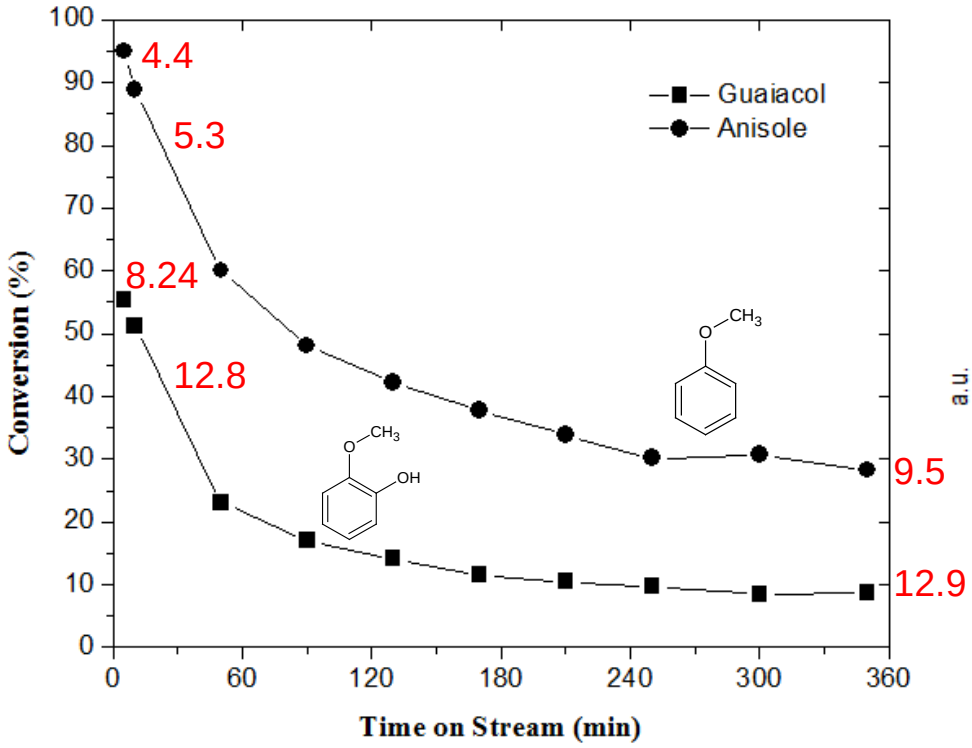


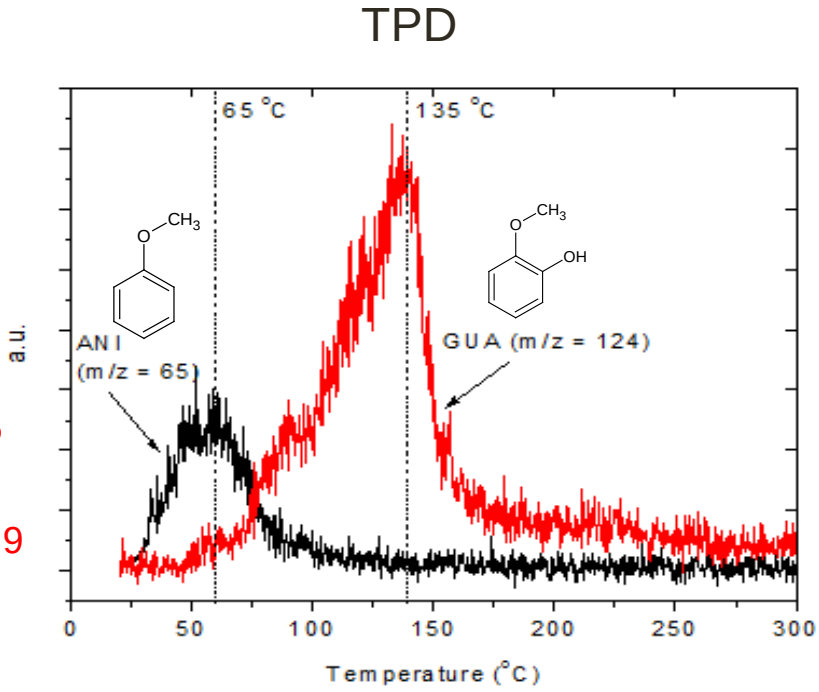
Reaction conditions: T= 300°C, P = 1 atm, mol H_2/mol feed = 60

Proposed Pathway



Guaiacol strong adsorption➔fast deactivation

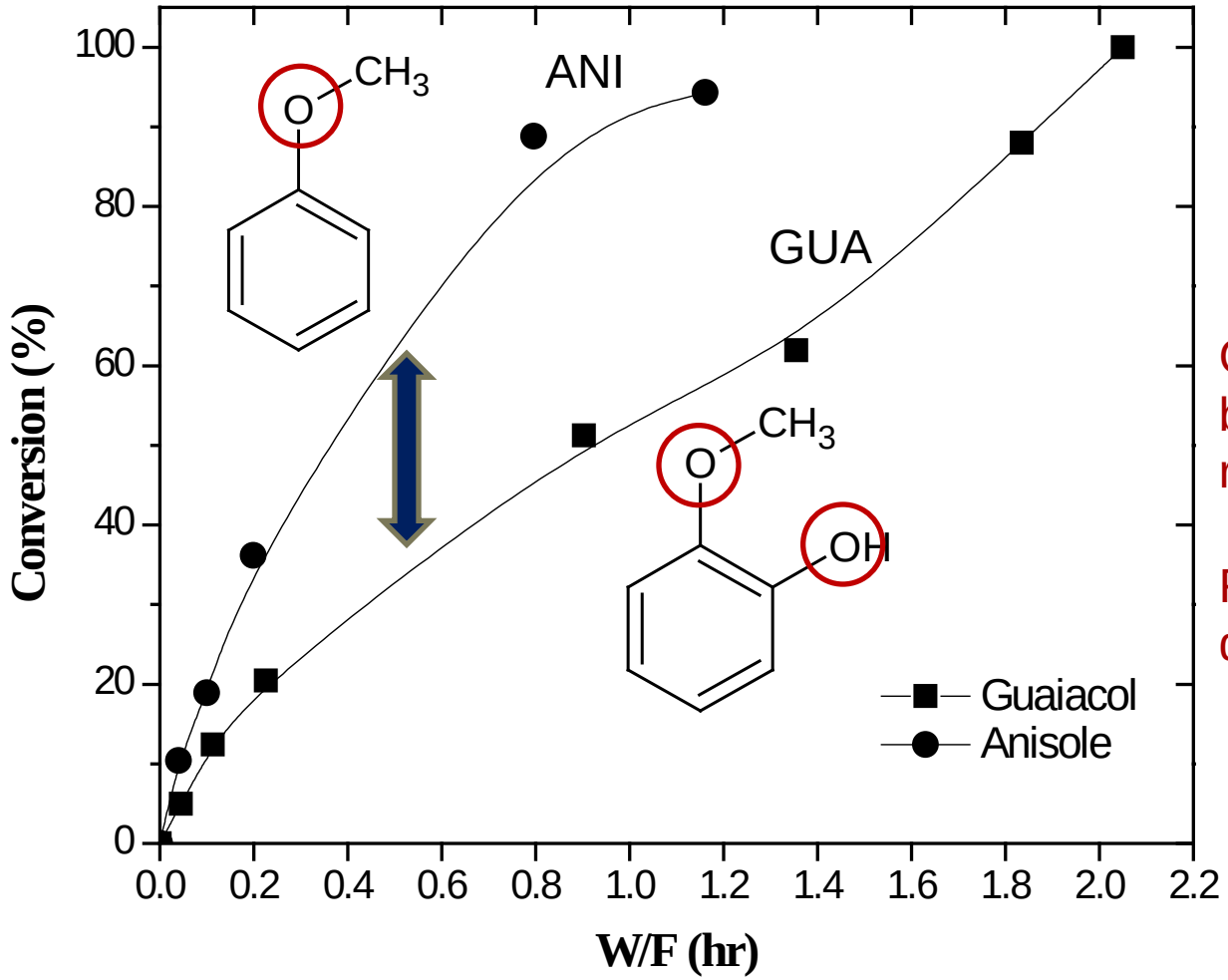




Catalyst= **Amorphous Silica-Alumina**

Reaction conditions: T= 300°C, P = 1 atm, mol H_2/mol feed = 60, W/F=1.2 hr

Anisole vs. Guaiacol



Guaiacol should be more reactive.

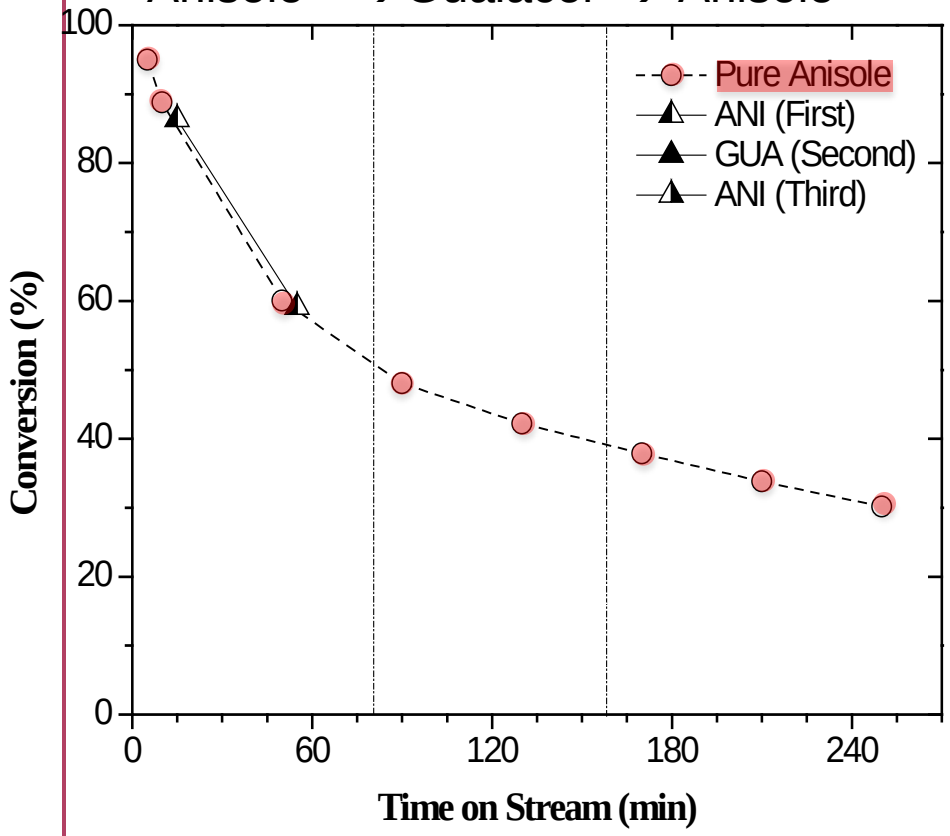
Faster deactivation ?

Catalyst= **Amorphous Silica-Alumina**
Reaction conditions: T= 300°C, P = 1 atm, mol H_2/mol feed = 60

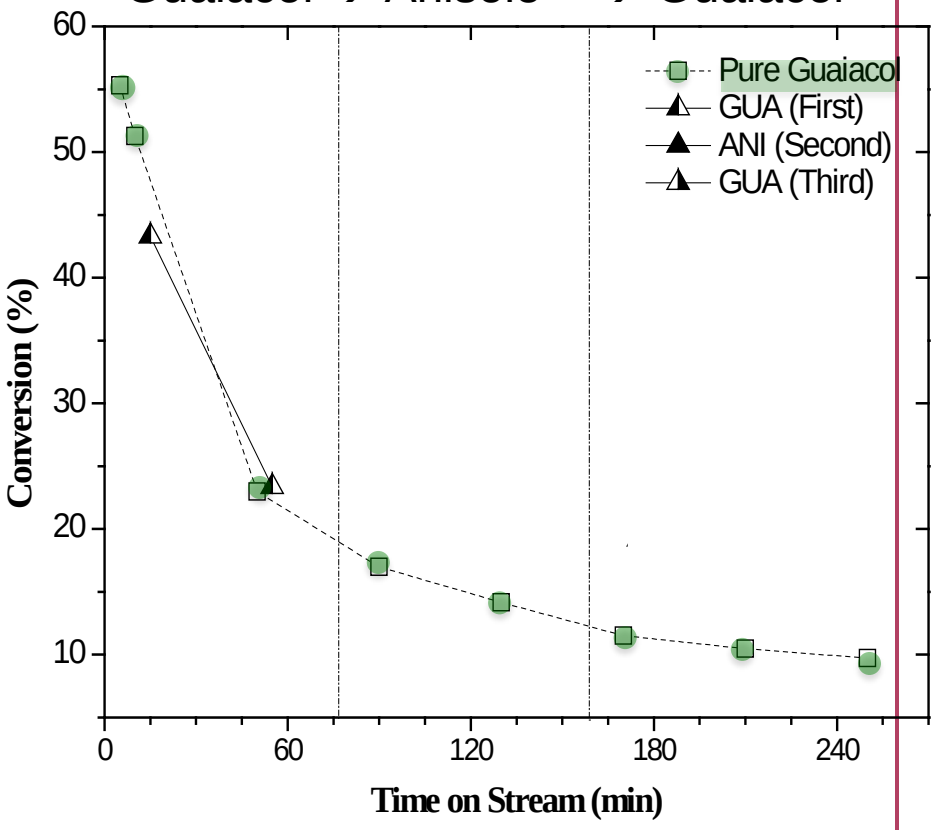
Anisole vs. Guaiacol

Issues over ASA: fast deactivation, no deoxygenation

Anisole →Guaiacol → Anisole



Guaiacol → Anisole → Guaiacol



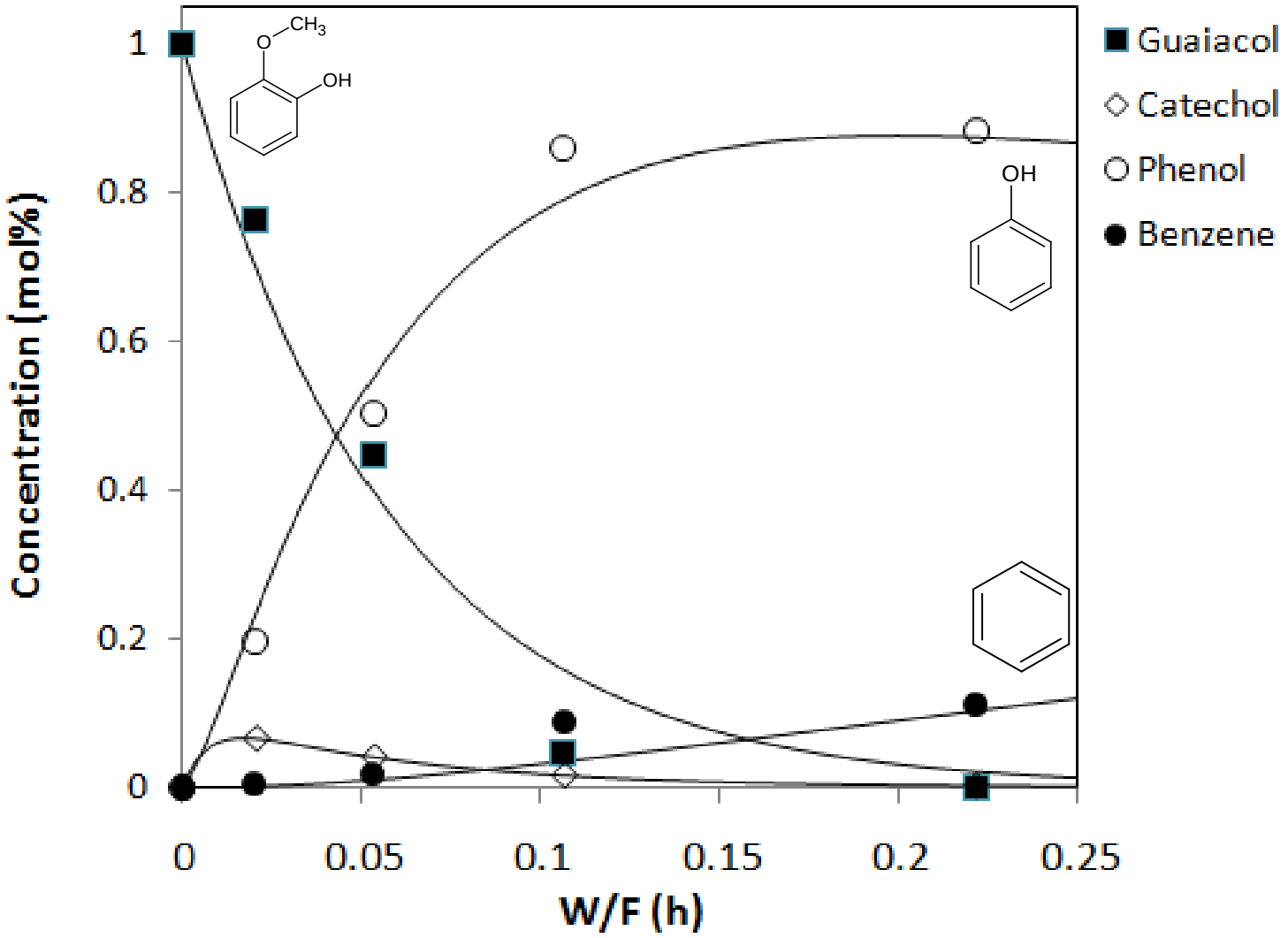
Effect of switching anisole and guaiacol feeds

Catalyst= **Amorphous Silica-Alumina**

Reaction conditions: T= 300°C, P = 1 atm, mol H_2/mol feed = 60, W/F=1.2 hr

Metal Catalyst

12 % of CH_3 is conserved on Ru/C

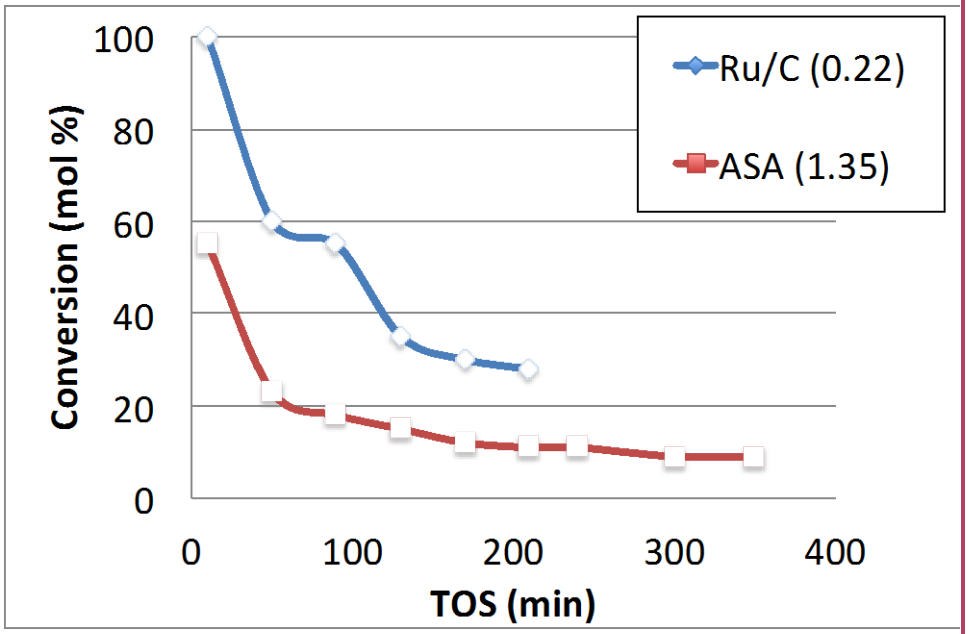


Catalyst= **5 wt% Ru/C**

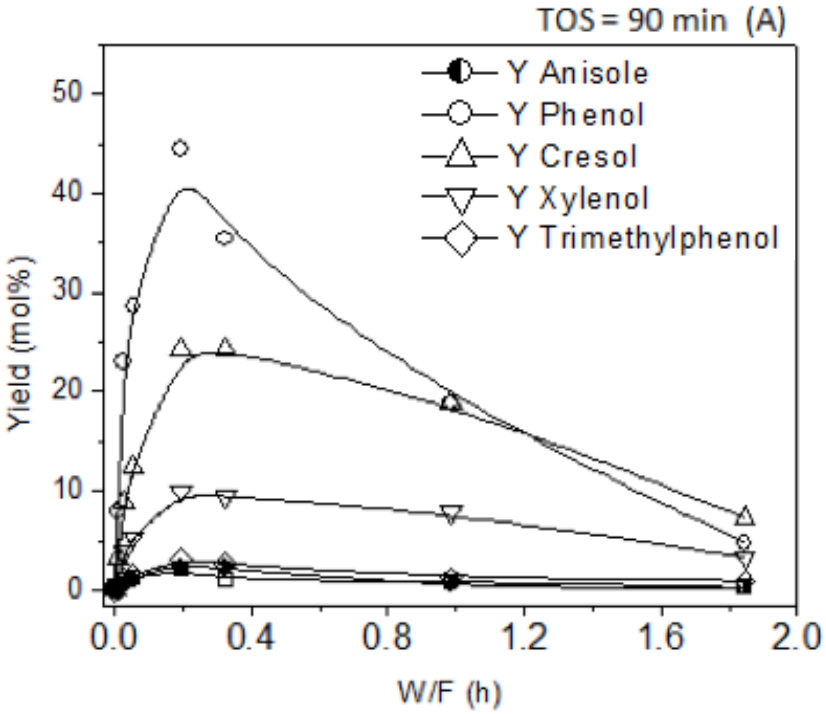
Reaction conditions: T= 400°C, P = 1 atm, mol H_2/mol feed = 60, W/F=1.2 hr

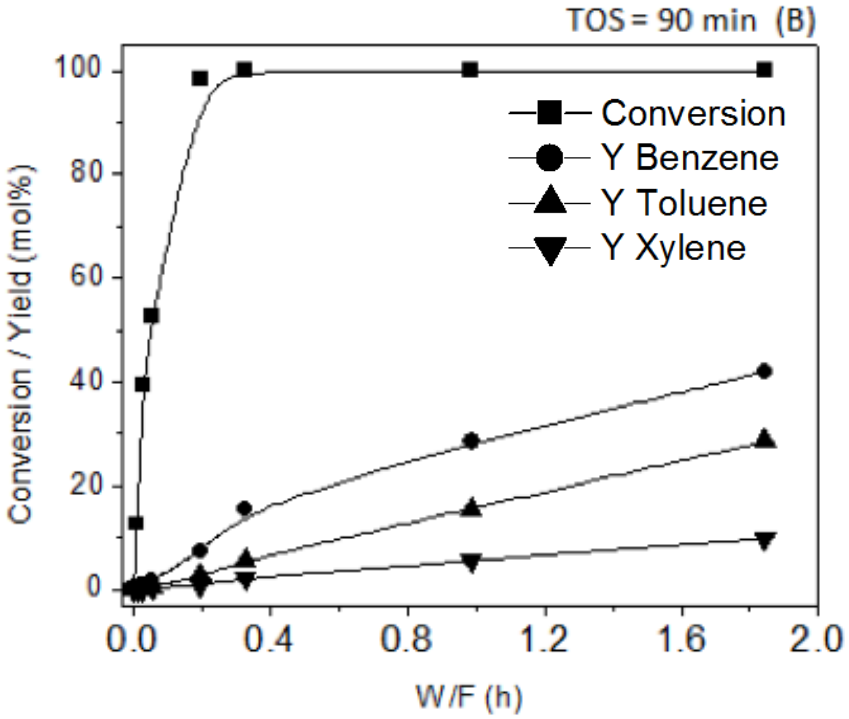
Issues with metal catalyst

- Loss of methyl groups
- Deactivation



Bifunctional Catalyst Ru/TiO_2

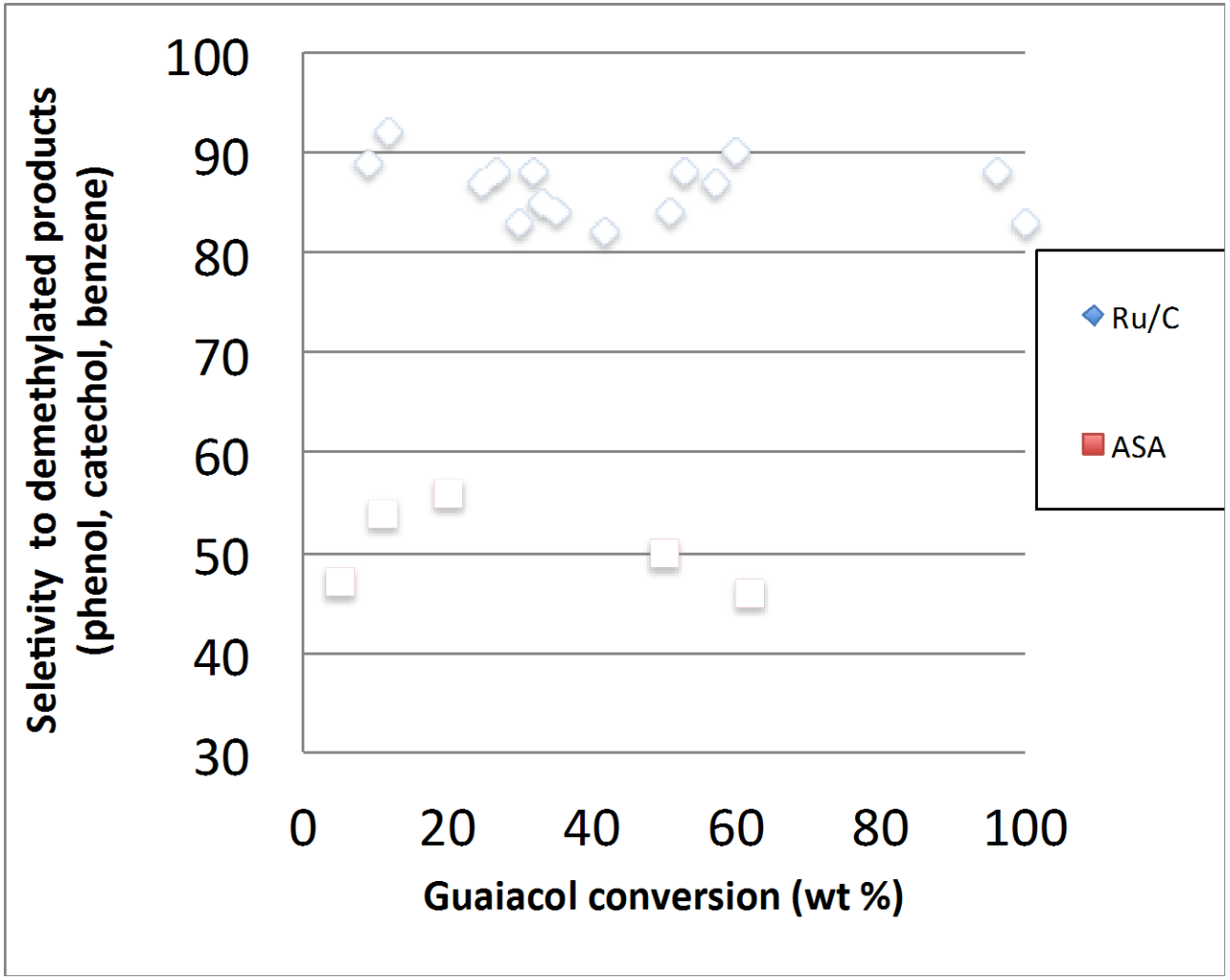




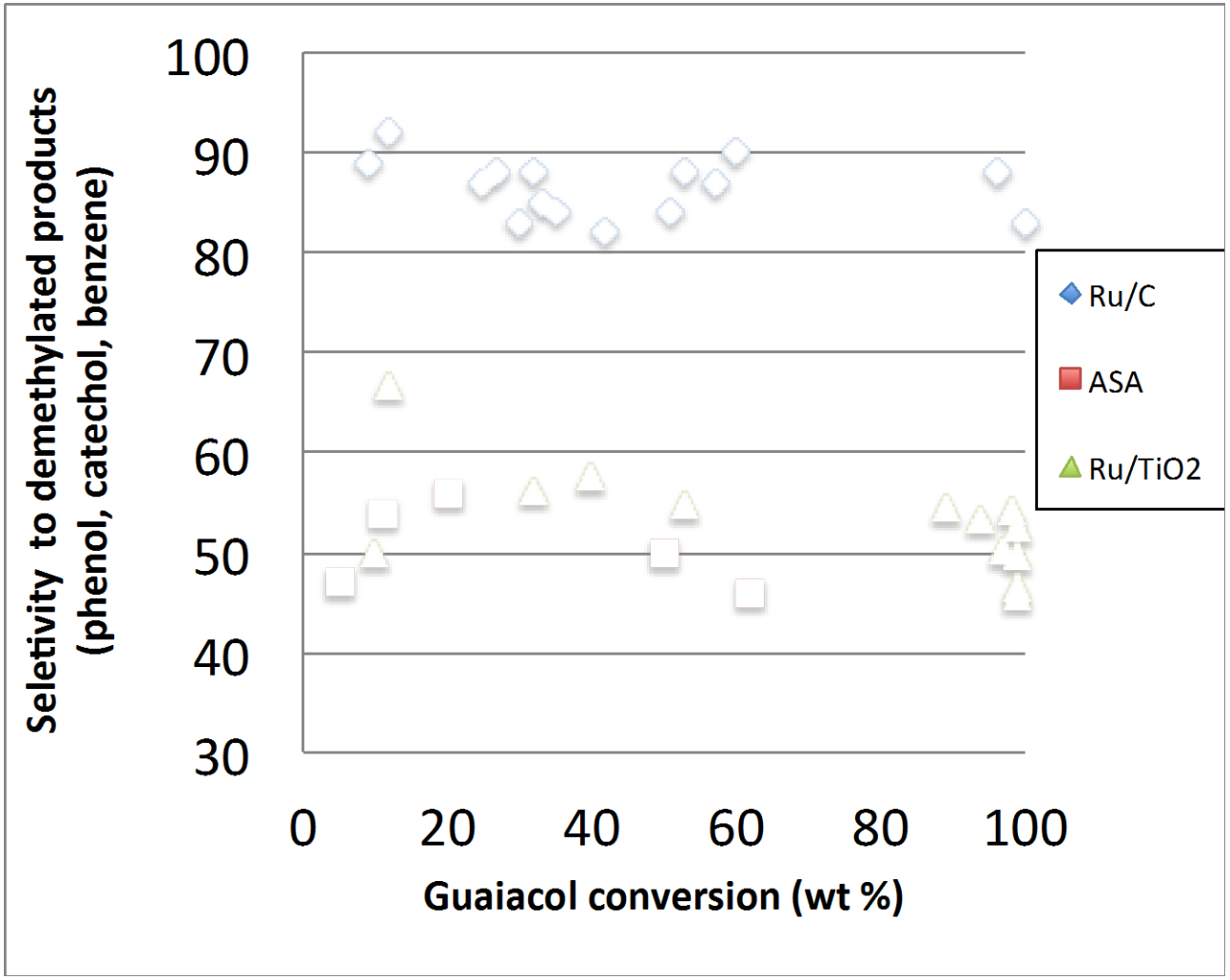
Preservation of methyl groups + production of aromatics

Catalyst= **5% Ru/TiO_2**
Reaction conditions: T= 400°C, P = 1 atm, mol H_2/mol feed = 60, W/F=1.2 hr

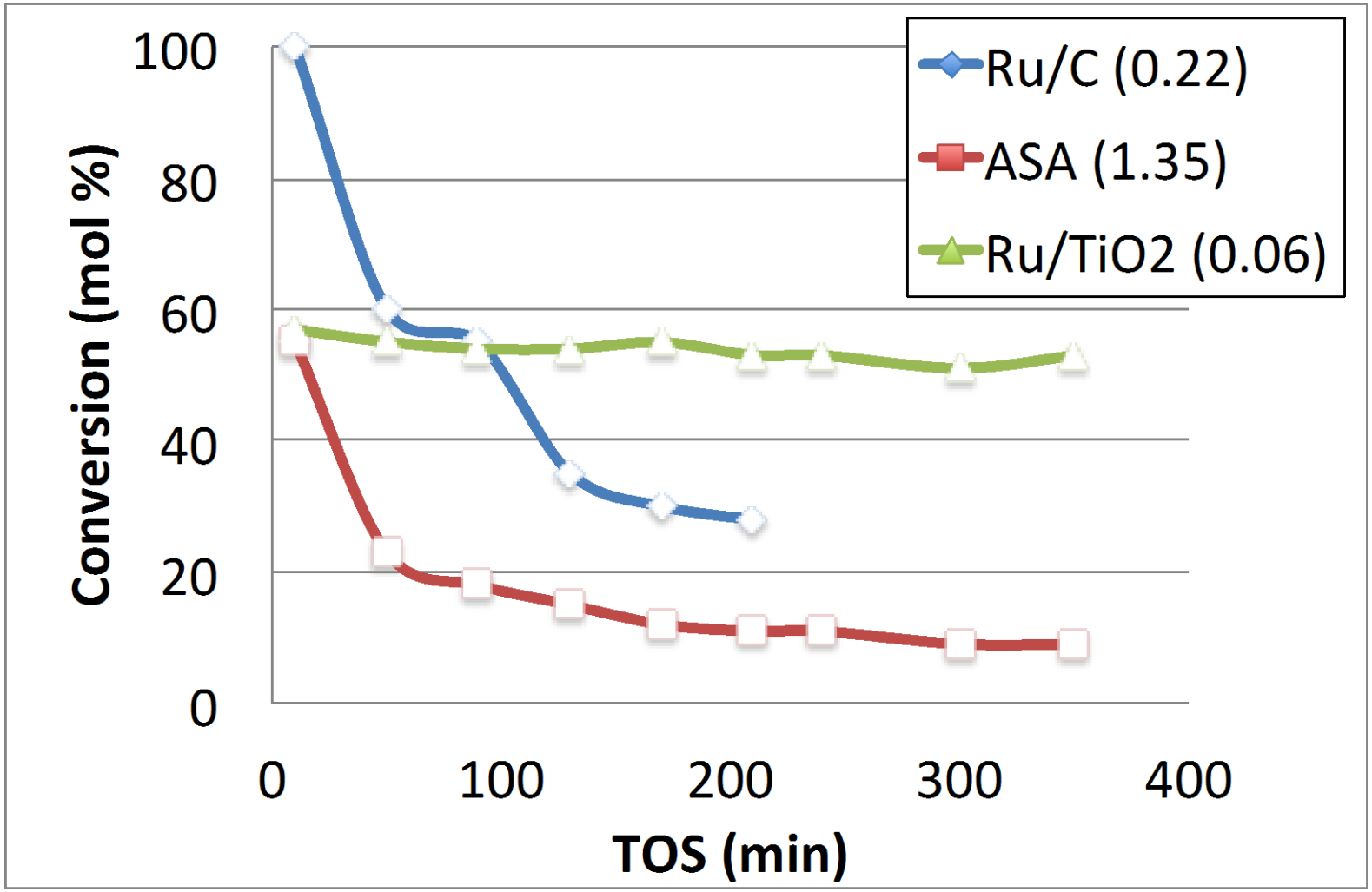
Conservation of methyl groups



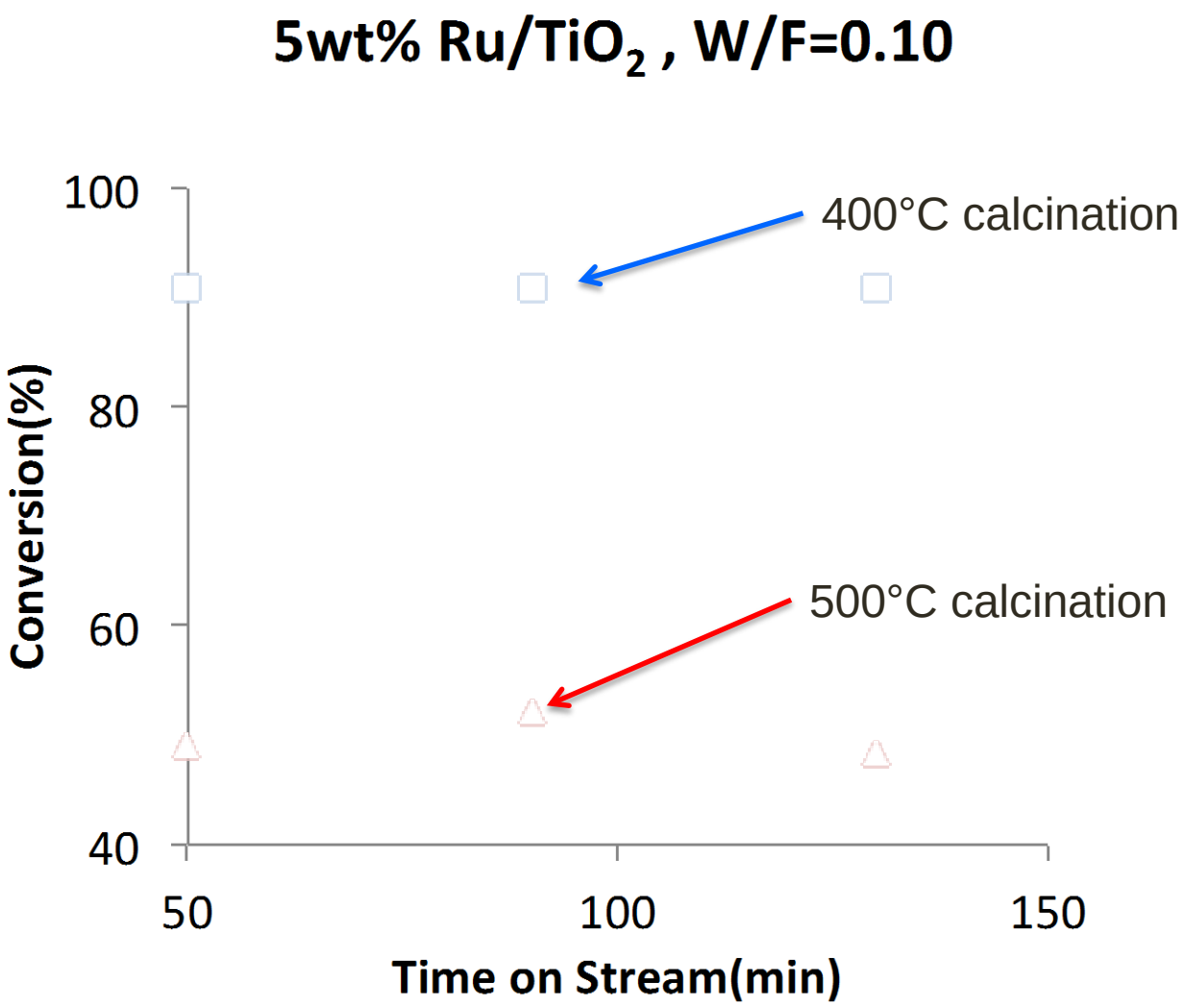
Conservation of methyl groups



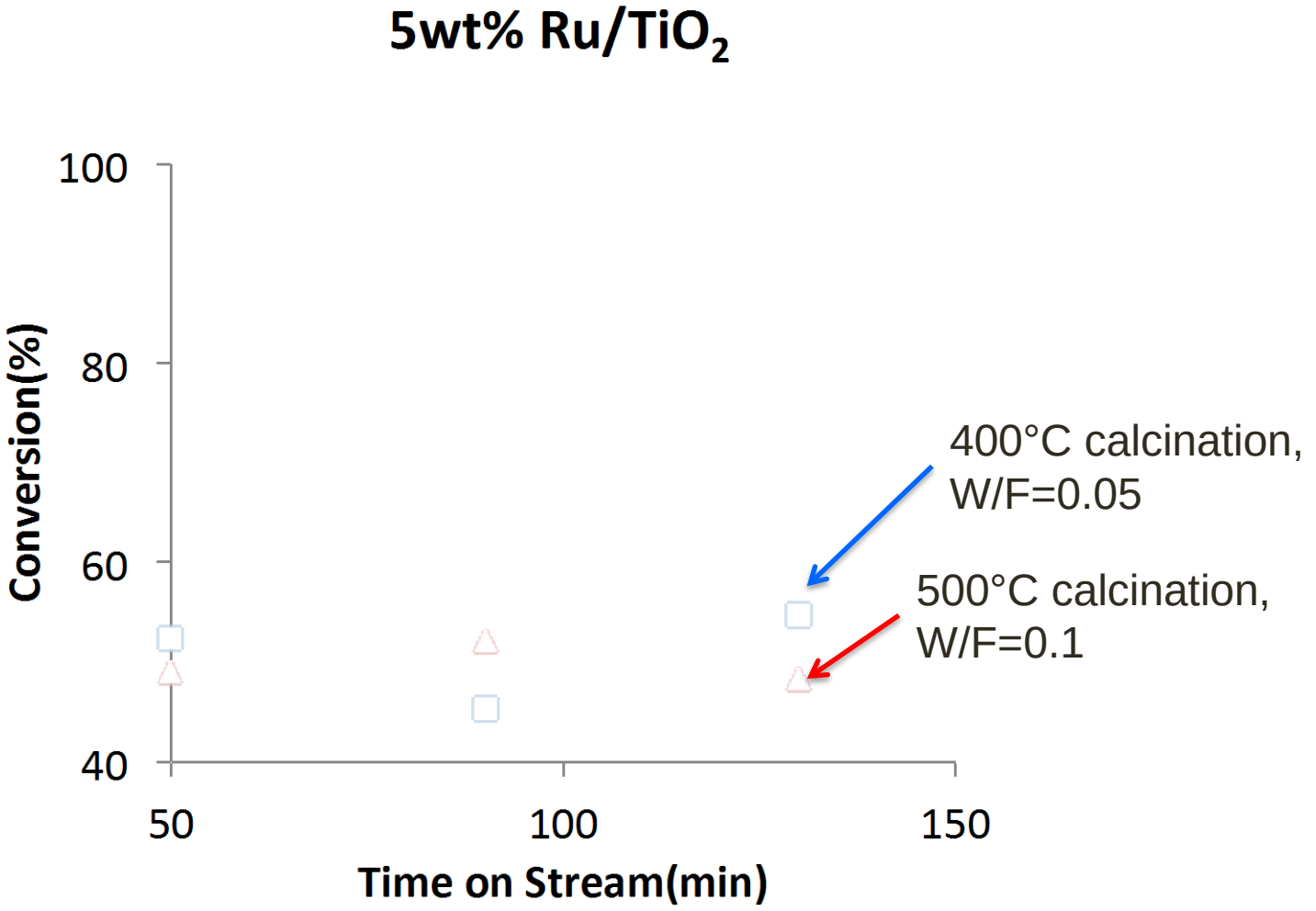
Stability


Ru/C (0.22)
ASA (1.35)
Ru/TiO2 (0.06)
Conversion (mol %)
100
80
60
40
20
0
0
100
200
300
400
TOS (min)

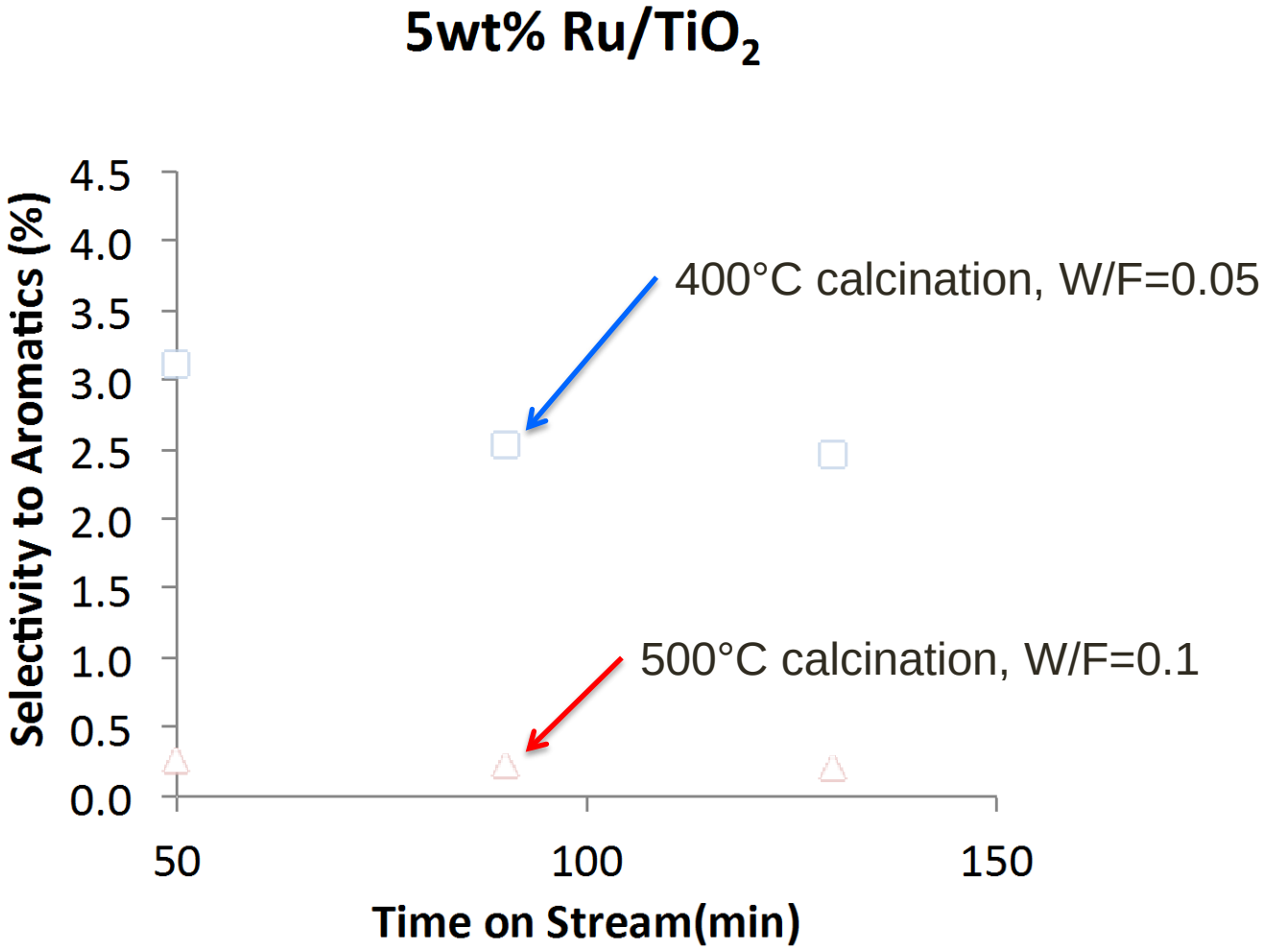
Influence of catalyst pretreatment



Influence of catalyst pretreatment



Selectivity to Aromatics



Summary

- Adsorption/Deactivation over ASA
  - Guaiacol>Anisole
- Importance of methyl transfer for C retention
- Ru/TiO_2 systems show promise in terms of activity, selectivity, and stability
- Pretreatment conditions strongly influence catalytic activity and selectivity

Thank You

- Sunya Boonyasuwat
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- Daniel Resasco
- Richard Mallinson
- Lance Lobban
- Friederike Jentoft
- Rolf Jentoft