Catalytic Reduction of Sulfur in Fluid Catalytic Cracking

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DAVISON CATALYSTS

GRACE Davison
Refining Technologies

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Outline

- Review of fluid catalytic cracking.
- Sulfur balance and sulfur cracking chemistry.
- Catalytic reduction of sulfur by Zn aluminate/alumina.

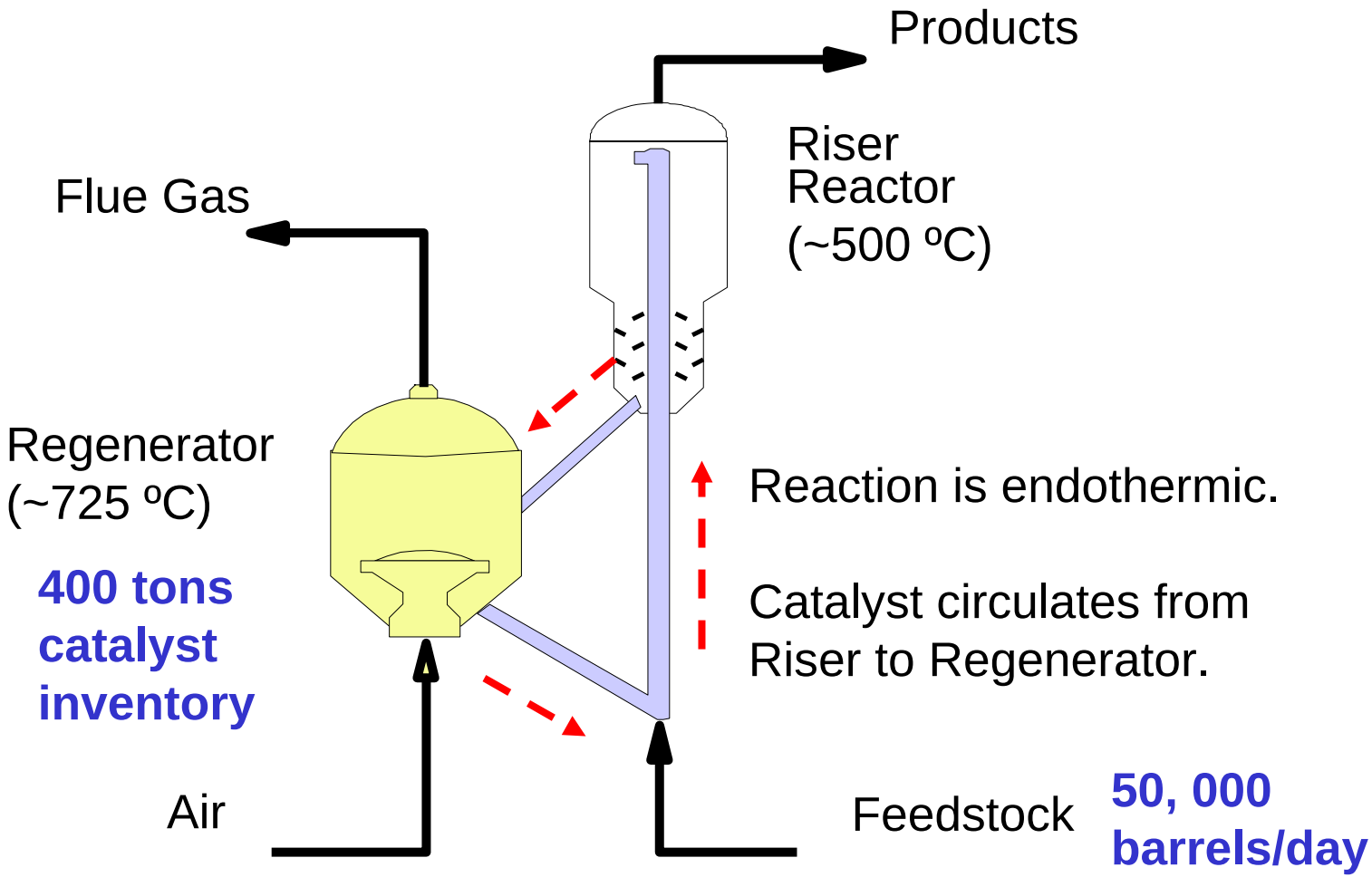
Fluid Catalytic Cracking

- Refinery process that “cracks” high molecular weight hydrocarbons to lower molecular weight.
- Refinery process that provides ~50 % of all transportation fuels indirectly.
- Provides ~35 % of total gasoline pool directly from FCC produced naphtha.
- ~80 % of the sulfur in gasolines comes from the FCC naphtha.

Sulfur in Gasoline

- Sulfur compounds reversibly poison the auto emission catalysts, increasing NOx and hydrocarbon emission. SOx emissions as well.
- World-wide regulations to limit the sulfur content of transportation fuels.
  - 10 - 30 ppm gasoline.
- Sulfur can be removed by hydrogenation chemistry.
  - Expensive.
  - Lowers fuel quality.

Fluid Catalytic Cracking Unit



Carbon Distribution

Feed

MW ~330 g/mole

H2	~0.05 %	Flare
C1	~1.0 %	Flare
C2-C4	~14-18 %	Petrochem
C5-C11	~50 %	Naphtha
C12-C22	~15-25 %	LCO
C22+	~5-15 %	HCO
Coke	~3-10 %	Regen

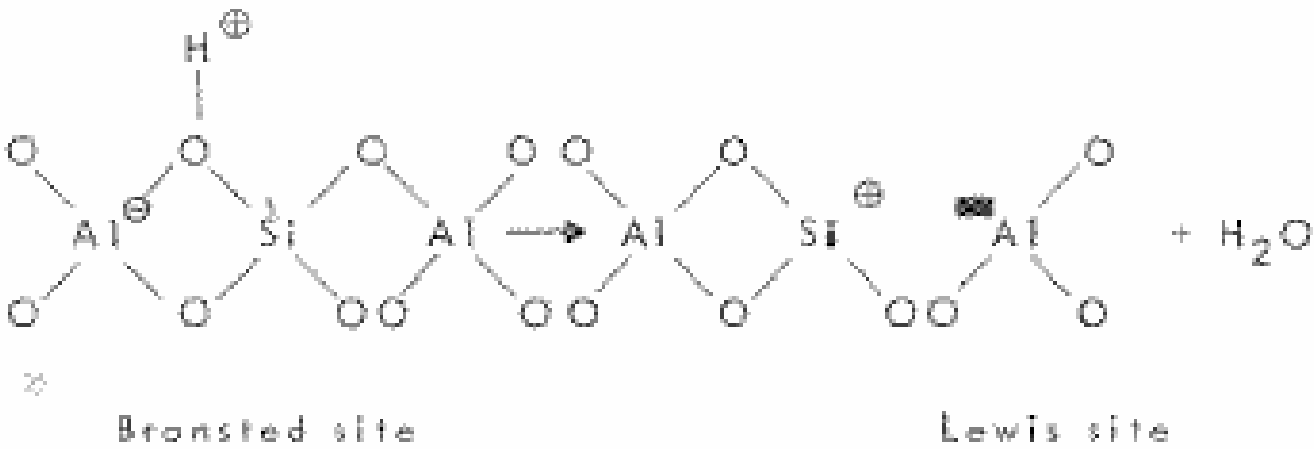
Catalyst Consumption

- 0.25 – 0.75 #’s/barrel
- About 300,000 tons catalyst/year world wide, for about 300 refiners.
- Consumption depends on feedstock quality, mainly irreversible poisoning by vanadium

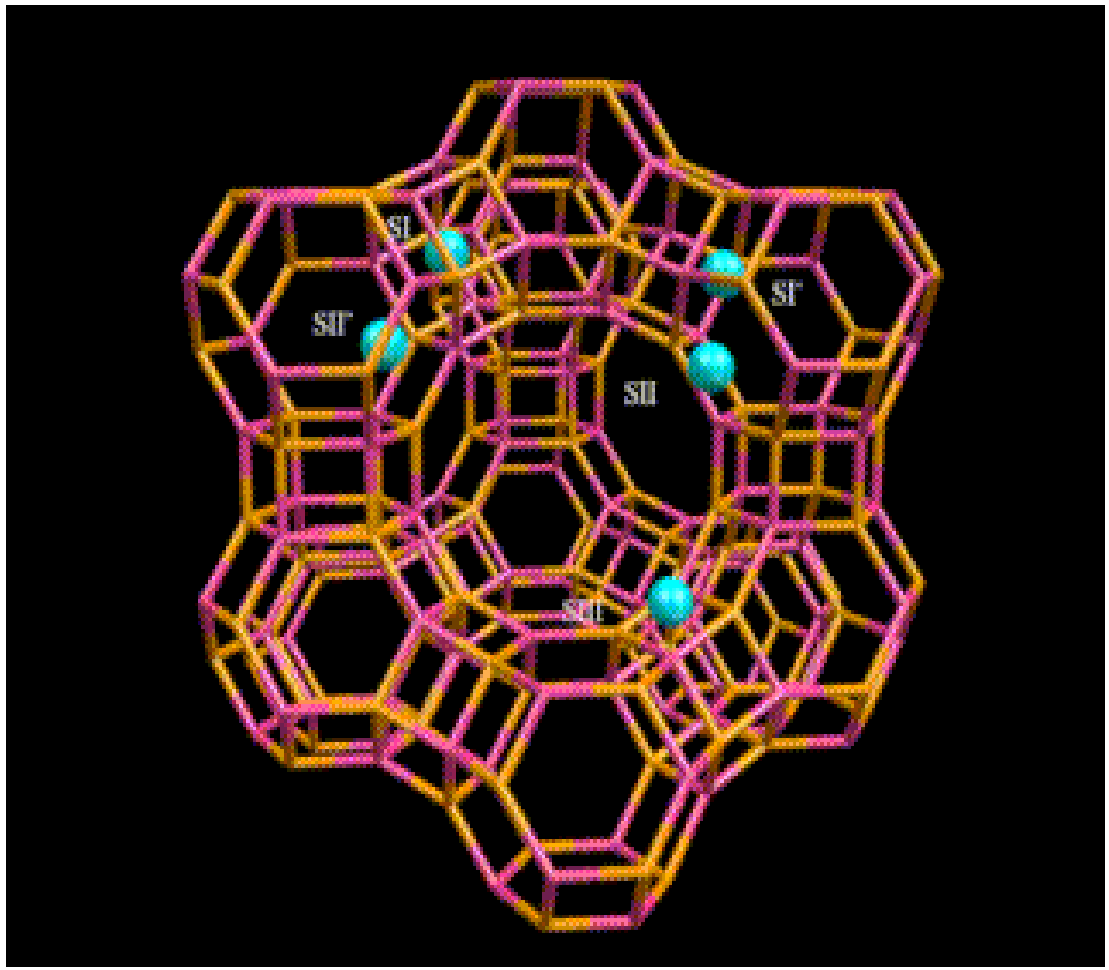
FCC Catalysts

- 10 - 50 % Y type zeolite, usually USY
- 0 - 13 % Rare earth on zeolite
- 0 - 80 % active silica/alumina matrix
- 0 - 50 % binder and kaolin
- Single component or blends
- Additives for olefins, SOx, NOx, CO
- SULFUR REDUCTION TECHNOLOGY

Solid acid catalysis



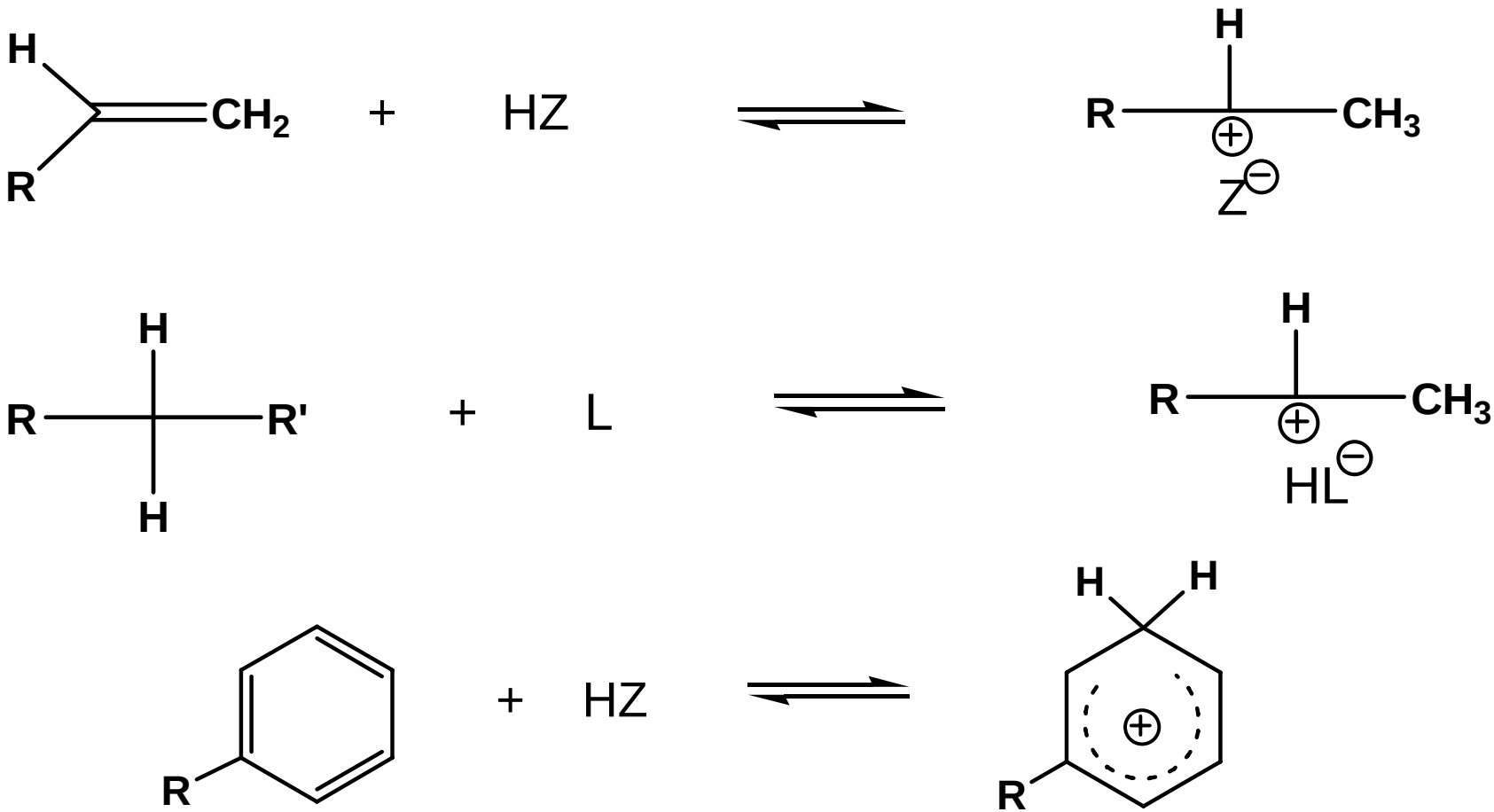
Zeolite Y structure



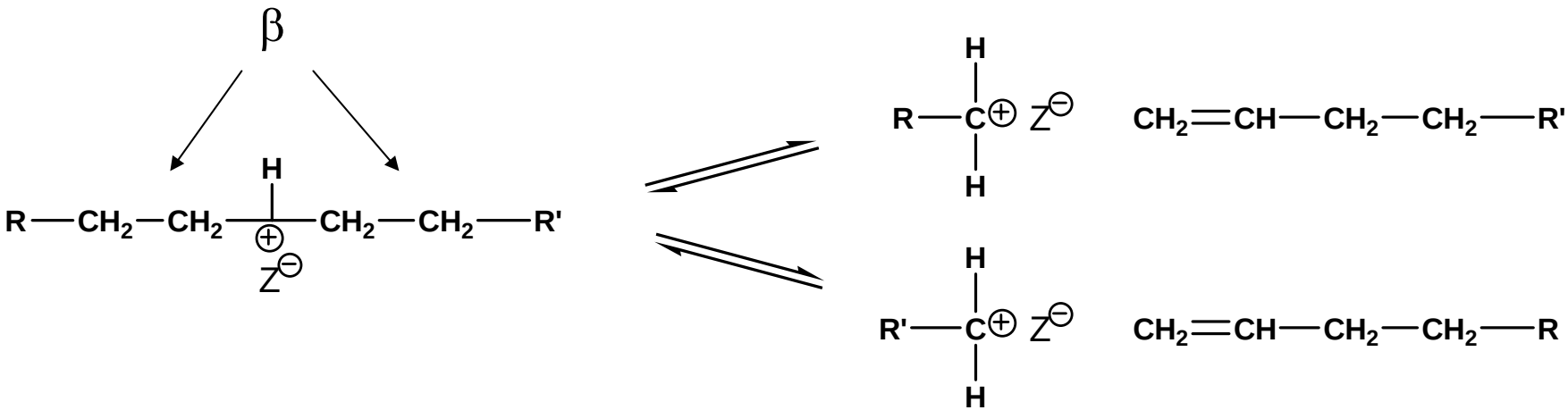
Cracking is Catalyzed by Solid Acid/Hydrocarbon Interactions

- Initiation: Hydride abstraction by a Lewis site or carbocation ion formation by a Brønsted site.
- Propagation: Through primarily β-scission.
- Product selectivities governed by stability of product and the precursor carbocation.
- Isomerization, alkylation occur readily

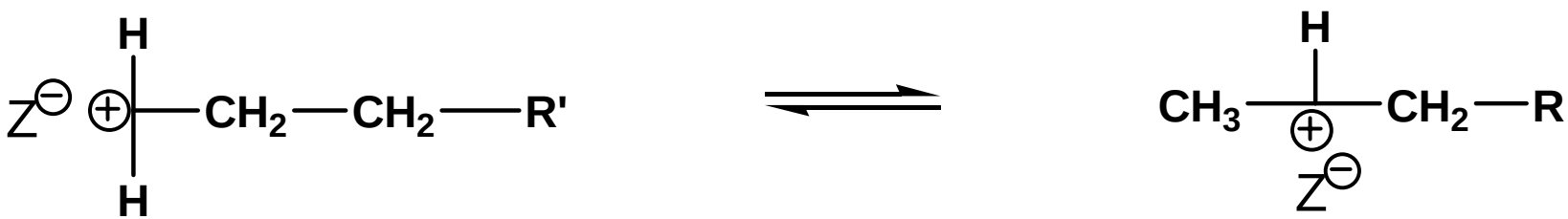
Formation of carbocation transition states



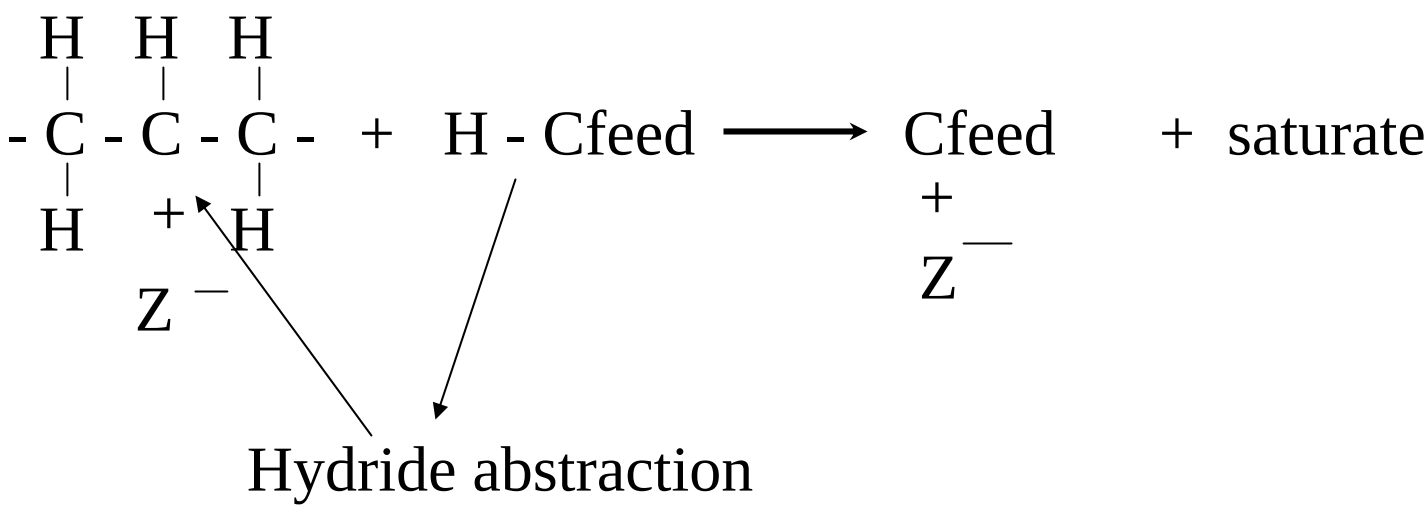
Beta scission



Charge isomerization



Hydride Transfer (simplified)

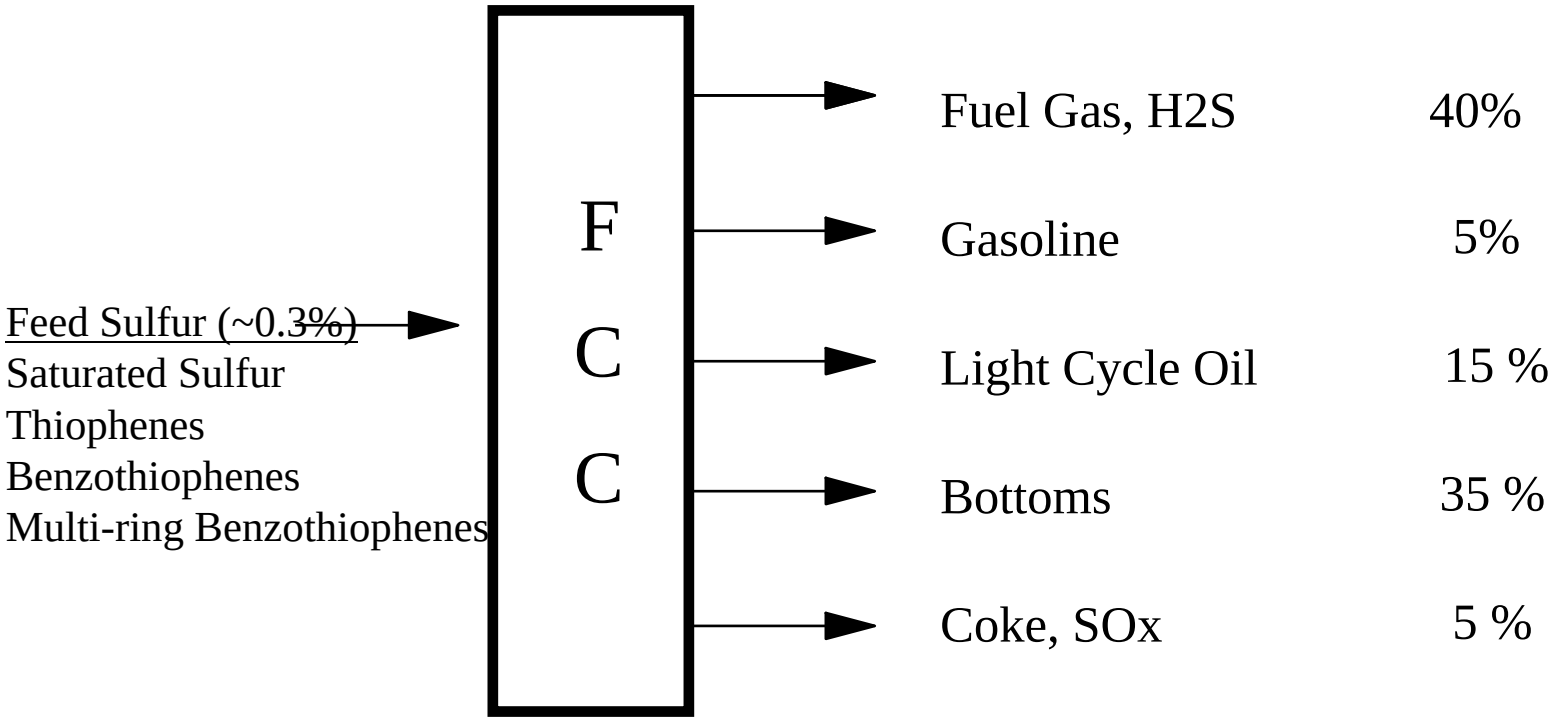


High Brønsted site density favors hydride transfer.
Catalysts can be tailored with high or low site density.

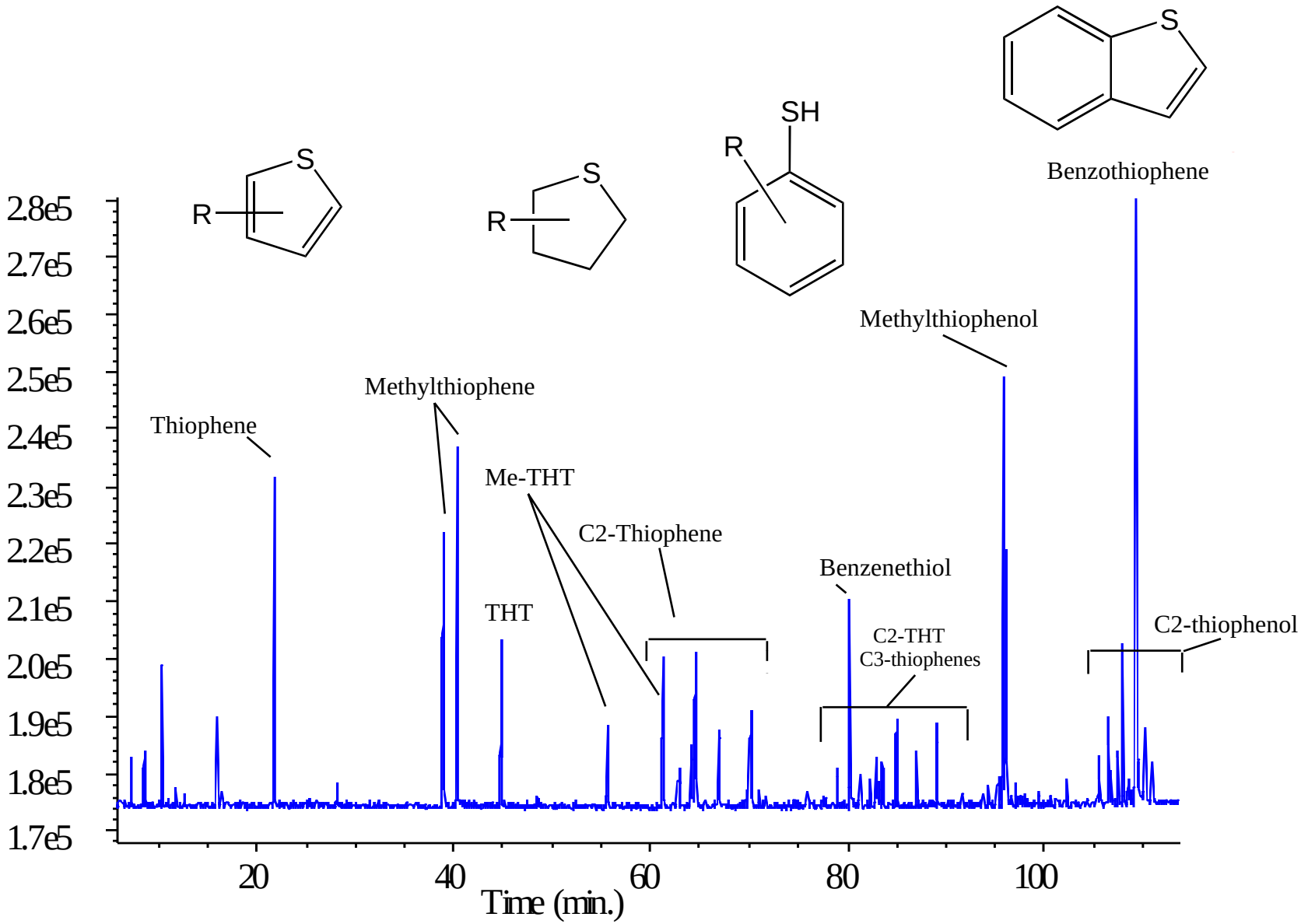
Feedstocks

- “Average” feed ~ 1.0 wt. % Sulfur
- “Average” feed MW ~ 300 gr/mole
- ~ one in ten feed molecules contain S
- S content ranges from 0 - 4.5 %

Sulfur Balance in a FCC Unit



Sulfur Species in FCC Gasoline (by GCAED)



Reaction Pathways of Sulfur Species in FCC

Sulfur Species in Feedstock		Sulfur Species in FCC Gasoline
Multi-Ring Aromatic Thiophenes	→	
Alkylbenzothiophenes	→	
Alkylthiophenes	→	?
Alkyl Sulfides, Mercaptans (Including cyclic sulfides)	→	
H2S + DiOlefin or Olefin	→	

Reaction Chemistry of S Compounds

(Which Feedstock Sulfur Species End Up in Gasoline?)

- Spike a low sulfur (0.3wt% S) base feedstock with model S compounds (0.7% wt% S).
- Look for yield changes in Microactivity Testing
- Compounds tested:

Thiols (octanethiol)

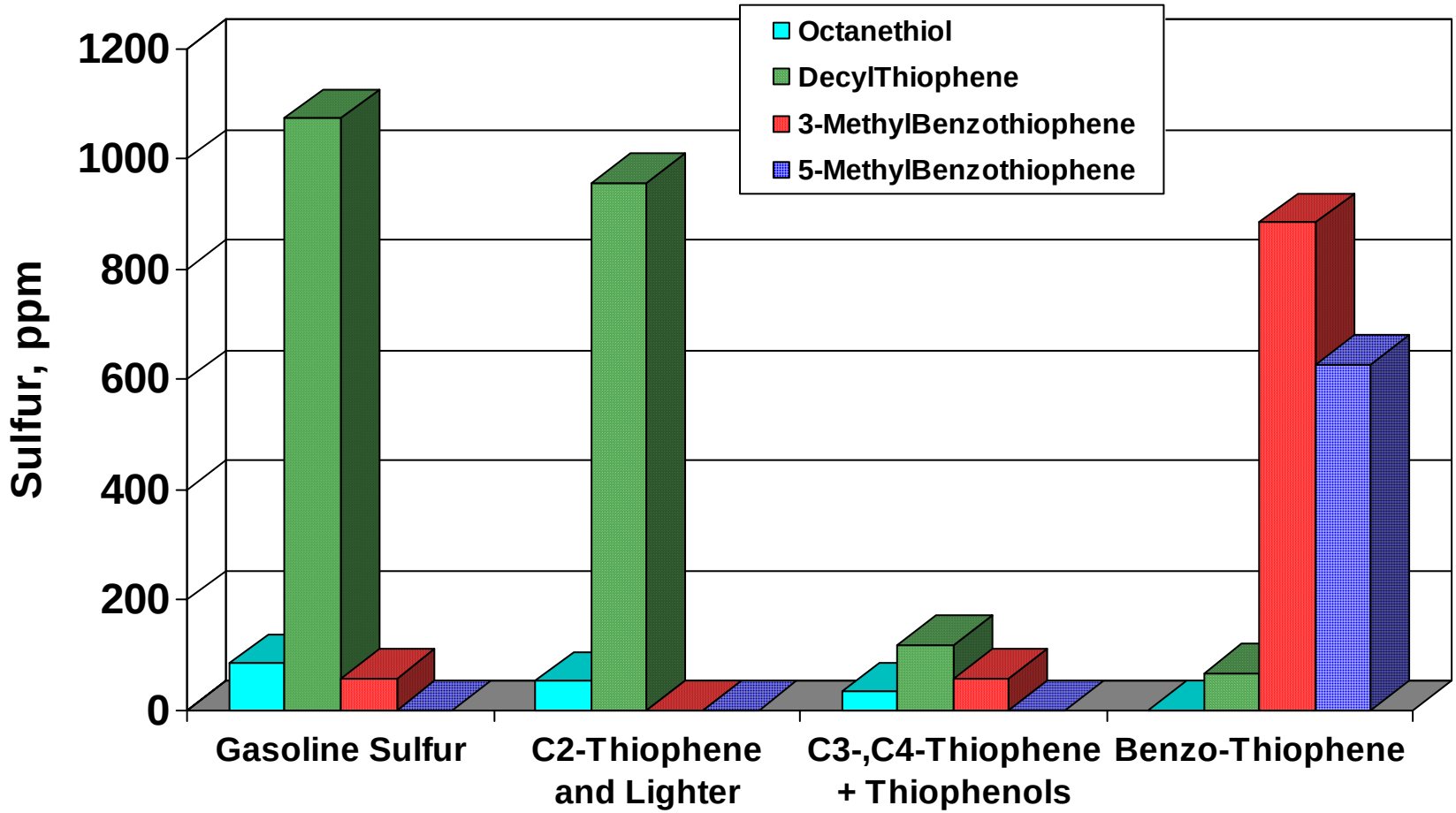
Sulfides (di-n-butylsulfide)

Alkylthiophenes (n-hexylthiophene, n-decylthiophene)

Alkylbenzothiophenes (3- and 5-methylbenzothiophene)

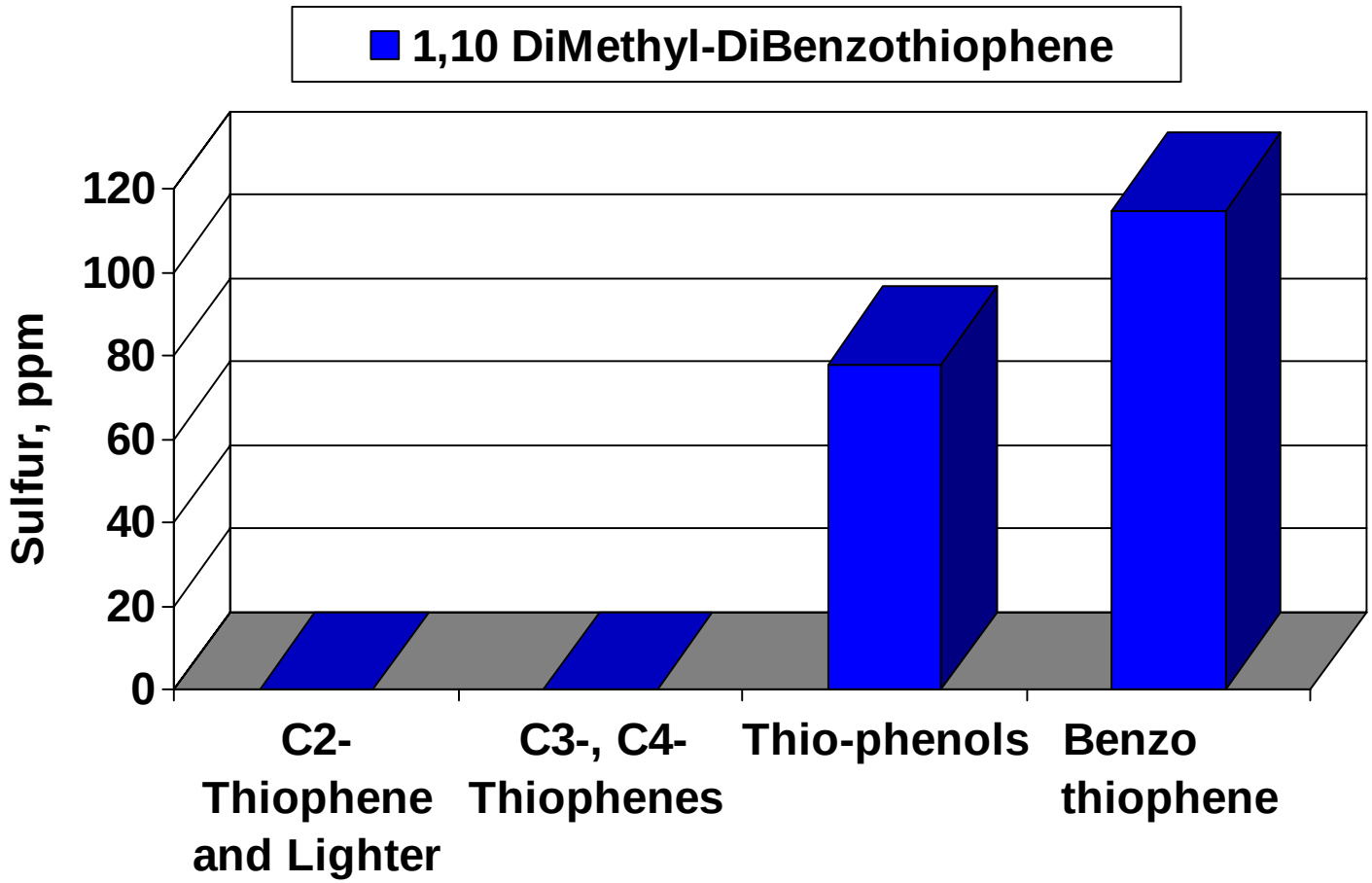
Alkyldibenzothiophene (1,10-dimethyldibenzothiophene)

Delta Yields of Gasoline Range Sulfur
Base Feedstock Spiked with Model S Compounds (0.7% S)



Delta Yields of Gasoline Range Sulfur

Base Feedstock (2.8% S) Spiked with Dimethyldibenzothiophene (0.45% S)



Recombination of H_2S and diolefin

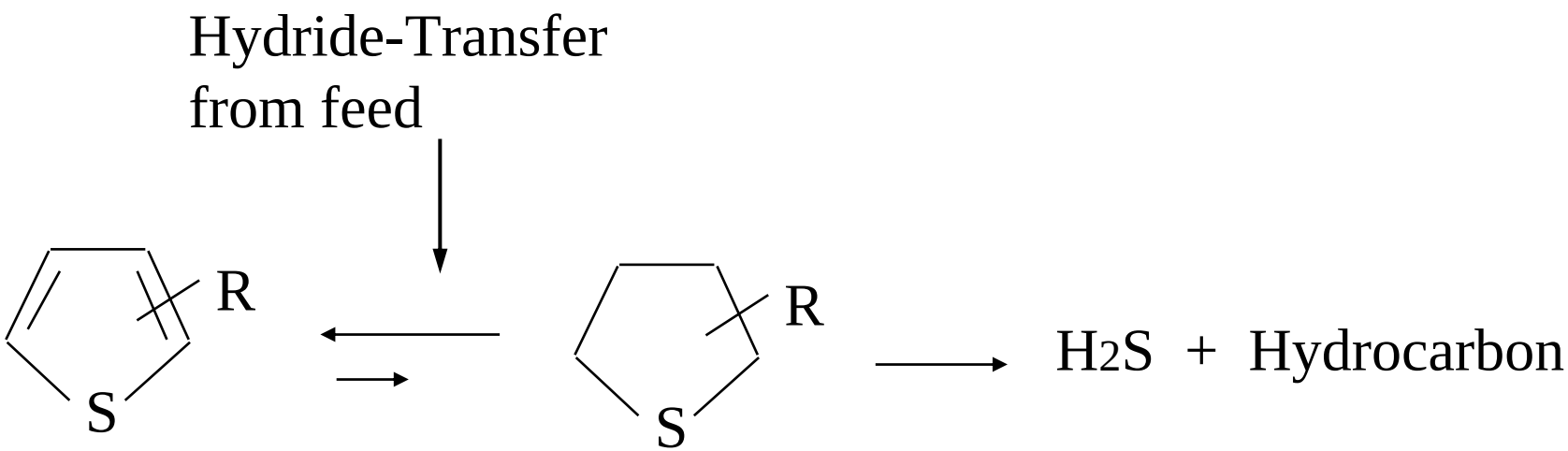
DCR Testing: Polysulfide and diolefin addition to a low sulfur feedstock

			(1% S)	Di-Olefin +
	Base	**2% Di-Olefin**	**Polysulfide**	**Polysulfide**
Mercaptans, ppm	5.1	7.3	47.4	30.7
C_0-C_4 Thiophenes, ppm	44.4	50.7	68.0	145.9
BenzoThiophene, ppm	13.3	11.2	11.5	9.9

Reaction Pathways of Sulfur Species in FCC

Sulfur Species in Feedstock		Sulfur Species in FCC Gasoline
Multi-Ring Aromatic Thiophenes	→	Small amount to benzothiophene
Alkylbenzothiophenes	→	Benzothiophene by dealkylation Small amount to thiophenols
Alkylthiophenes	→	Thiophenes by dealkylation Small amount to benzothiophene
Alkyl Sulfides, Mercaptans (Including cyclic sulfides)	→	Thiophenes by cyclization, aromatization
H2S + DiOlefin	→	Thiophenes

Hydride Transfer Controls Rate of Thiophenic Cracking



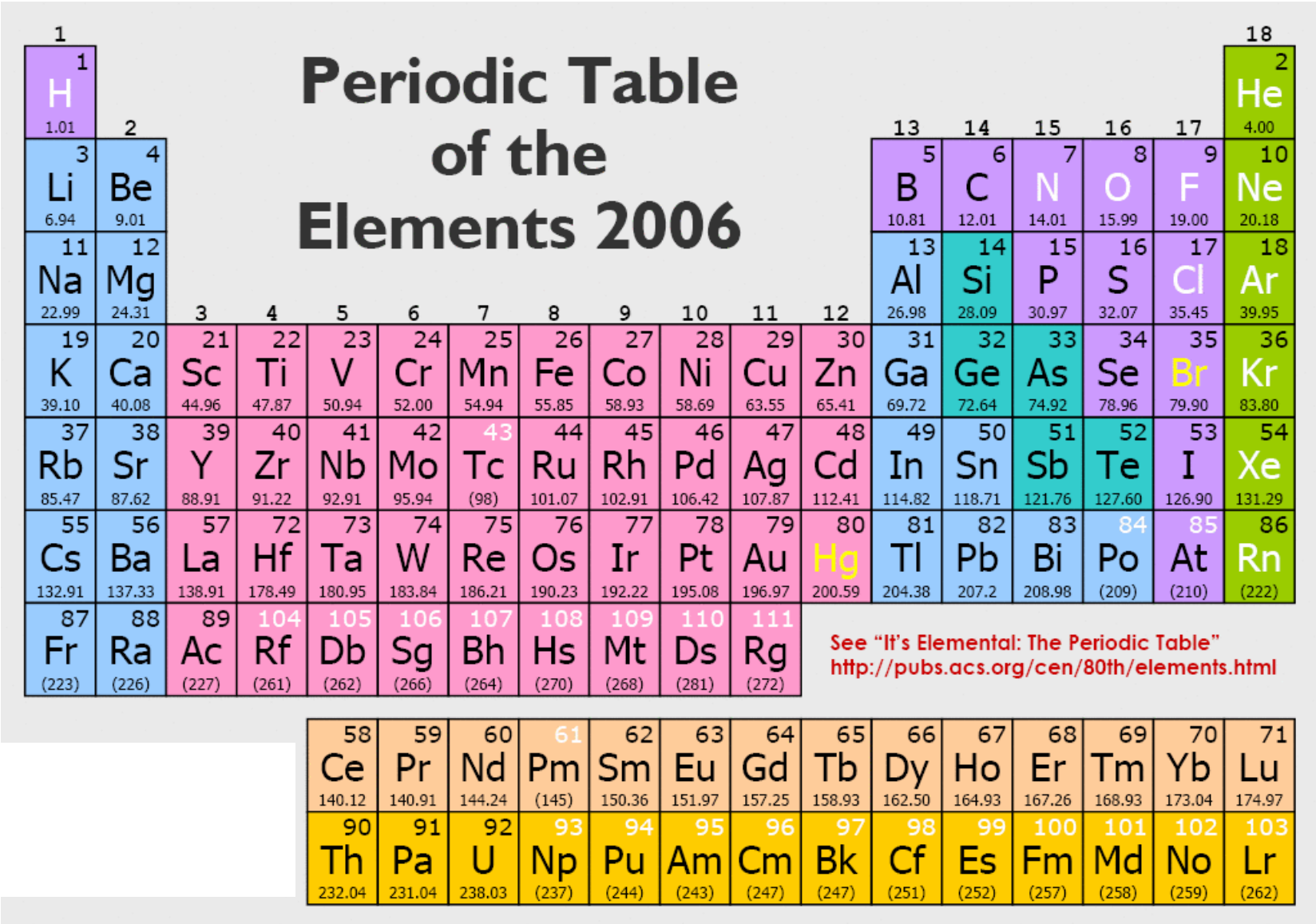
Very stable and
Not-so Lewis basic sulfur

Less stable and
More Lewis basic sulfur

A Catalytic Approach

- Zn Aluminate on γ-alumina.
- Solid Lewis Acid.
- Used as an additive (~10 - 75%) with FCC catalyst.
- Reduces sulfur in gasoline by 20-45% without affecting other yields.
- Most of reduction occurs in light (C3-) thiophenes.

Why Zn?


Periodic Table of the Elements 2006
1 H 1.01
2 He 4.00
3 Li 6.94
4 Be 9.01
5 B 10.81
6 C 12.01
7 N 14.01
8 O 15.99
9 F 19.00
10 Ne 20.18
11 Na 22.99
12 Mg 24.31
13 Al 26.98
14 Si 28.09
15 P 30.97
16 S 32.07
17 Cl 35.45
18 Ar 39.95
19 K 39.10
20 Ca 40.08
21 Sc 44.96
22 Ti 47.87
23 V 50.94
24 Cr 52.00
25 Mn 54.94
26 Fe 55.85
27 Co 58.93
28 Ni 58.69
29 Cu 63.55
30 Zn 65.41
31 Ga 69.72
32 Ge 72.64
33 As 74.92
34 Se 78.96
35 Br 79.90
36 Kr 83.80
37 Rb 85.47
38 Sr 87.62
39 Y 88.91
40 Zr 91.22
41 Nb 92.91
42 Mo 95.94
43 Tc (98)
44 Ru 101.07
45 Rh 102.91
46 Pd 106.42
47 Ag 107.87
48 Cd 112.41
49 In 114.82
50 Sn 118.71
51 Sb 121.76
52 Te 127.60
53 I 126.90
54 Xe 131.29
55 Cs 132.91
56 Ba 137.33
57 La 138.91
72 Hf 178.49
73 Ta 180.95
74 W 183.84
75 Re 186.21
76 Os 190.23
77 Ir 192.22
78 Pt 195.08
79 Au 196.97
80 Hg 200.59
81 Tl 204.38
82 Pb 207.2
83 Bi 208.98
84 Po (209)
85 At (210)
86 Rn (222)
87 Fr (223)
88 Ra (226)
89 Ac (227)
104 Rf (261)
105 Db (262)
106 Sg (266)
107 Bh (264)
108 Hs (270)
109 Mt (268)
110 Ds (281)
111 Rg (272)
See "It's Elemental: The Periodic Table"
http://pubs.acs.org/cen/80th/elements.html
58 Ce 140.12
59 Pr 140.91
60 Nd 144.24
61 Pm (145)
62 Sm 150.36
63 Eu 151.97
64 Gd 157.25
65 Tb 158.93
66 Dy 162.50
67 Ho 164.93
68 Er 167.26
69 Tm 168.93
70 Yb 173.04
71 Lu 174.97
90 Th 232.04
91 Pa 231.04
92 U 238.03
93 Np (237)
94 Pu (244)
95 Am (243)
96 Cm (247)
97 Bk (247)
98 Cf (251)
99 Es (252)
100 Fm (257)
101 Md (258)
102 No (259)
103 Lr (262)

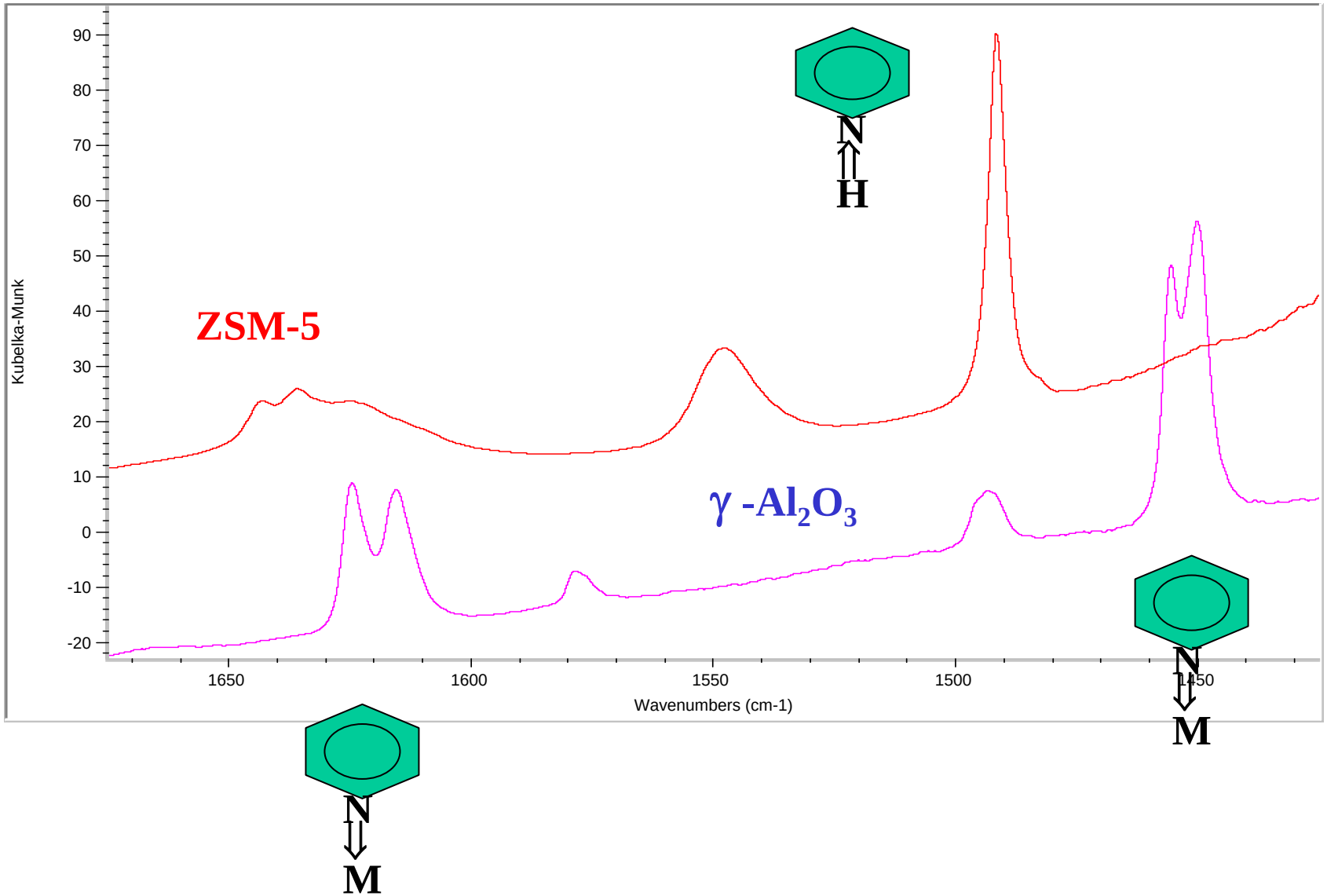
$Zn(AlO_2)_2$ on γ-Al_2O_3

- Nominal 17 % $Zn(AlO_2)_2$ 83 % γ-Al_2O_3
- ~150 m^2/gr surface area
- Nominal monolayer of zinc (10 % Zn) on pseudo-boehmite
- Converted to aluminate at 500 °C
- Both $Zn(AlO_2)_2$ and γ-Al_2O_3 spinel structures

Lewis Acidity

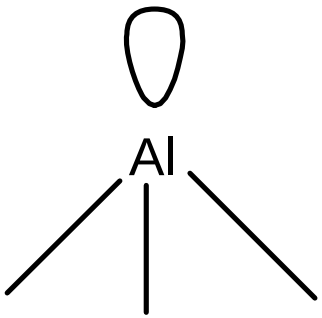
- $Zn(AlO_2)_2$ and γ-Al_2O_3 have only Lewis acidity.
- $Zn(AlO_2)_2$ increases the Lewis acidity of the γ-Al_2O_3.
- Use pyridine DRIFTS for acid type determination.

Probe Lewis and Bronsted Acid Sites by Pyridine-IR analysis

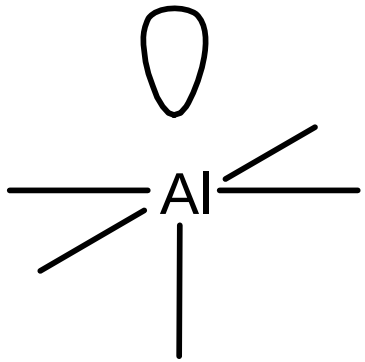


Alumina Lewis acid sites

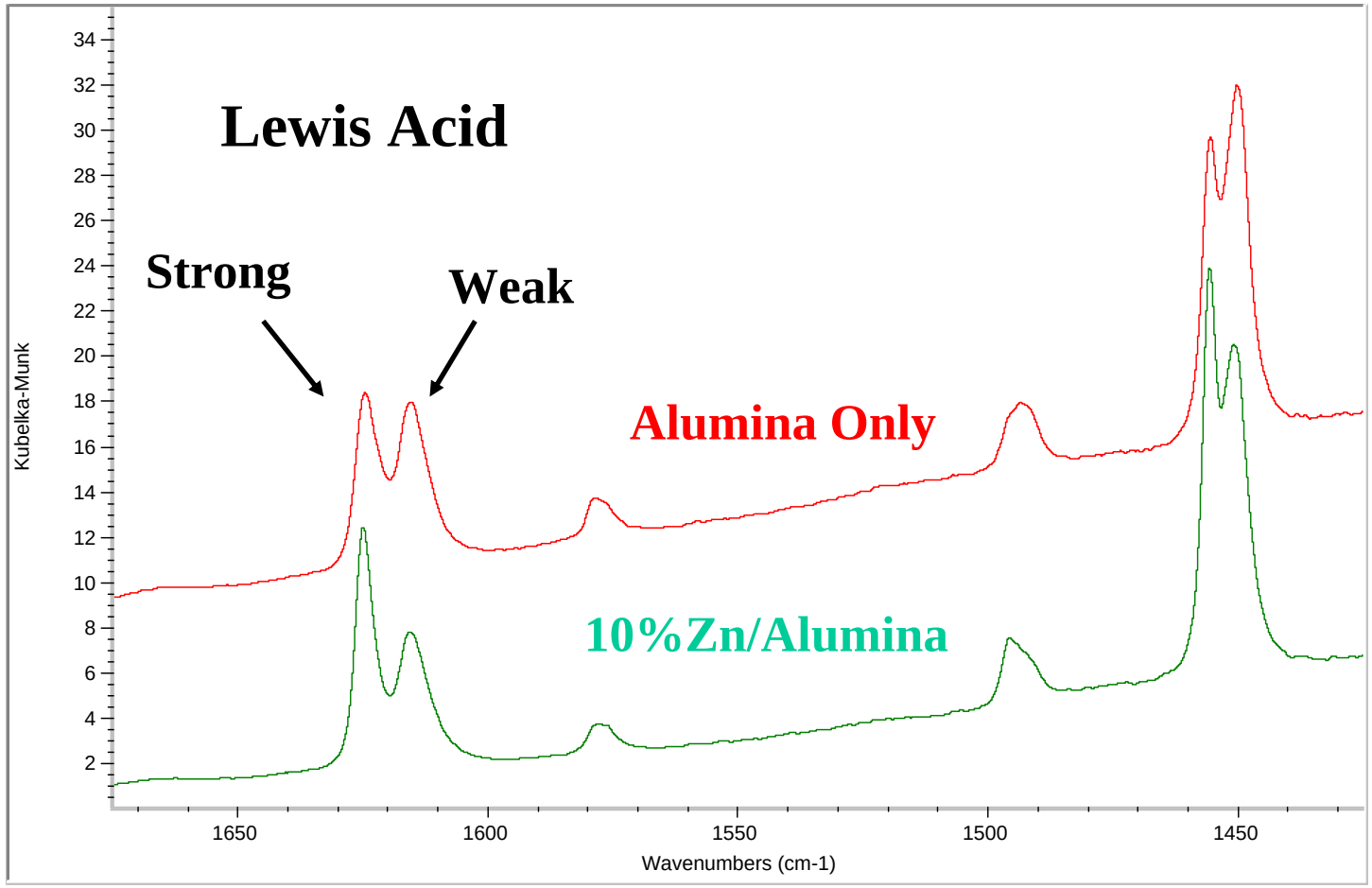
Strong



Weak

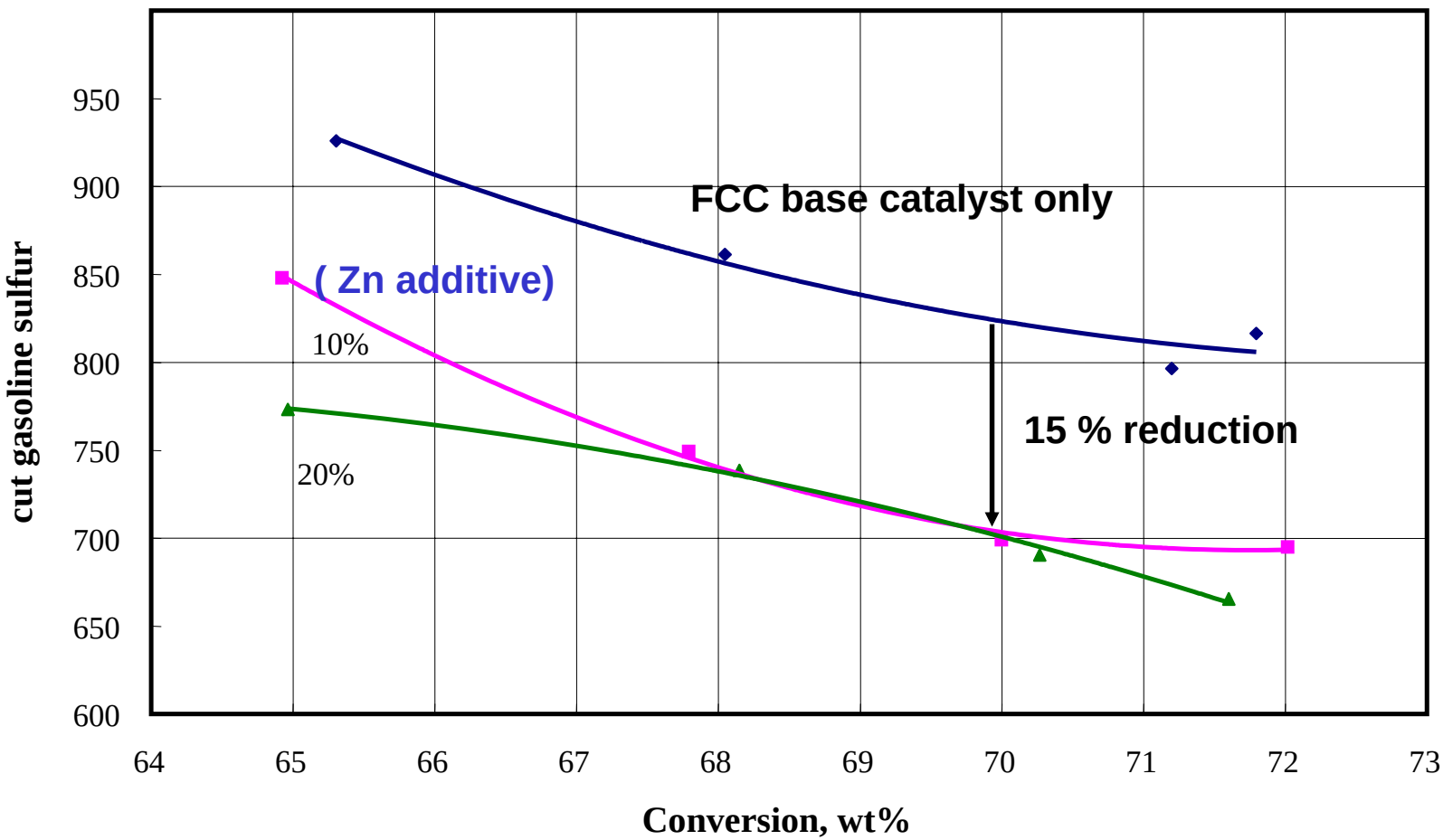


Zn aluminate/alumina vs. alumina



Simple Additive Approach

(No Optimization of Hydride Transfer & sulfur activity)

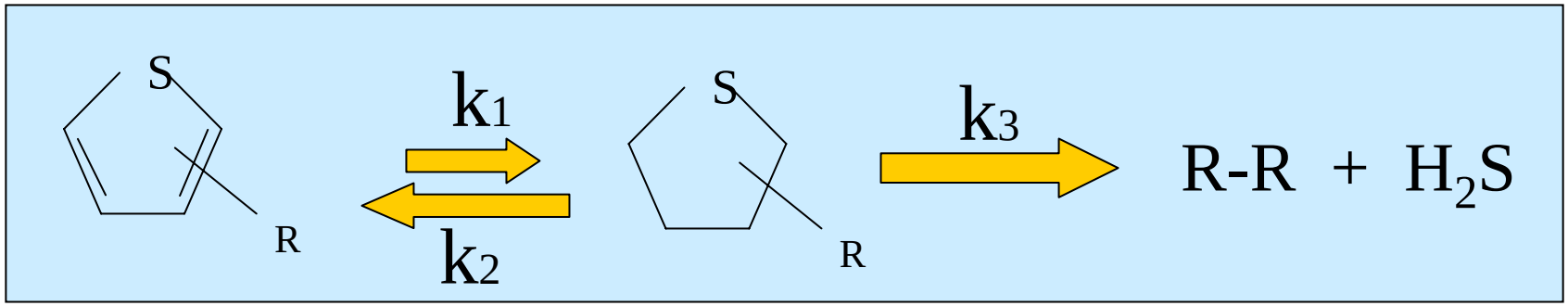


REUSY and Zn aluminate/alumina

MAT at 525 °C. Feedstock contains 1% S.

	REUSY	REUSY + 5 % Zn aluminate
Std.Conv. Wt%	70	70
C/O	3.78	3.80
H2	0.05	0.05
C1+C2	1.74	1.73
LPG	16.49	16.21
C5+Gaso	48.67	48.73
LCO	20.27	20.39
640+Btms	9.75	9.60
Coke W% Feed	2.90	3.09
mercaptans	0.57	0.15
thiophene	55.62	40.35
C1-thiophene	140.22	91.52
tetrahydrothiophene	31.85	10.91
C2-thiophene	151.97	102.06
C3-thiophene + thiophenol	72.91	67.06
C4-thiophene + C1, C2 thiophenol	55.10	57.09
benzothiophene	387.61	365.13
tot w/benzo	895.86	734.28
ex benzo	508.25	369.15
%total S conv		18.0
% ex benzo		27.4

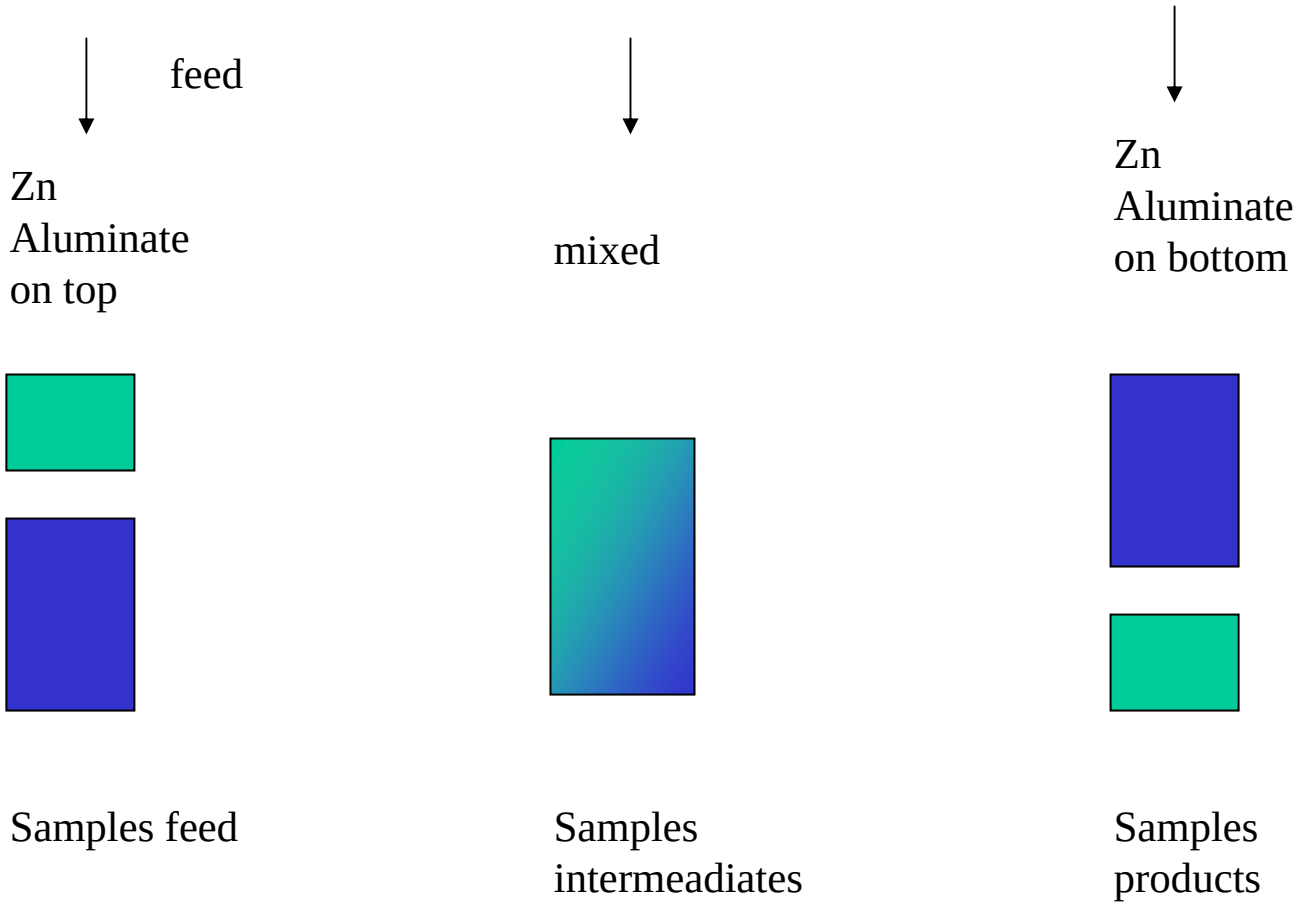
Working hypothesis



$\mathbf{k_1}$ → Hydride Transfer → Catalyst site density

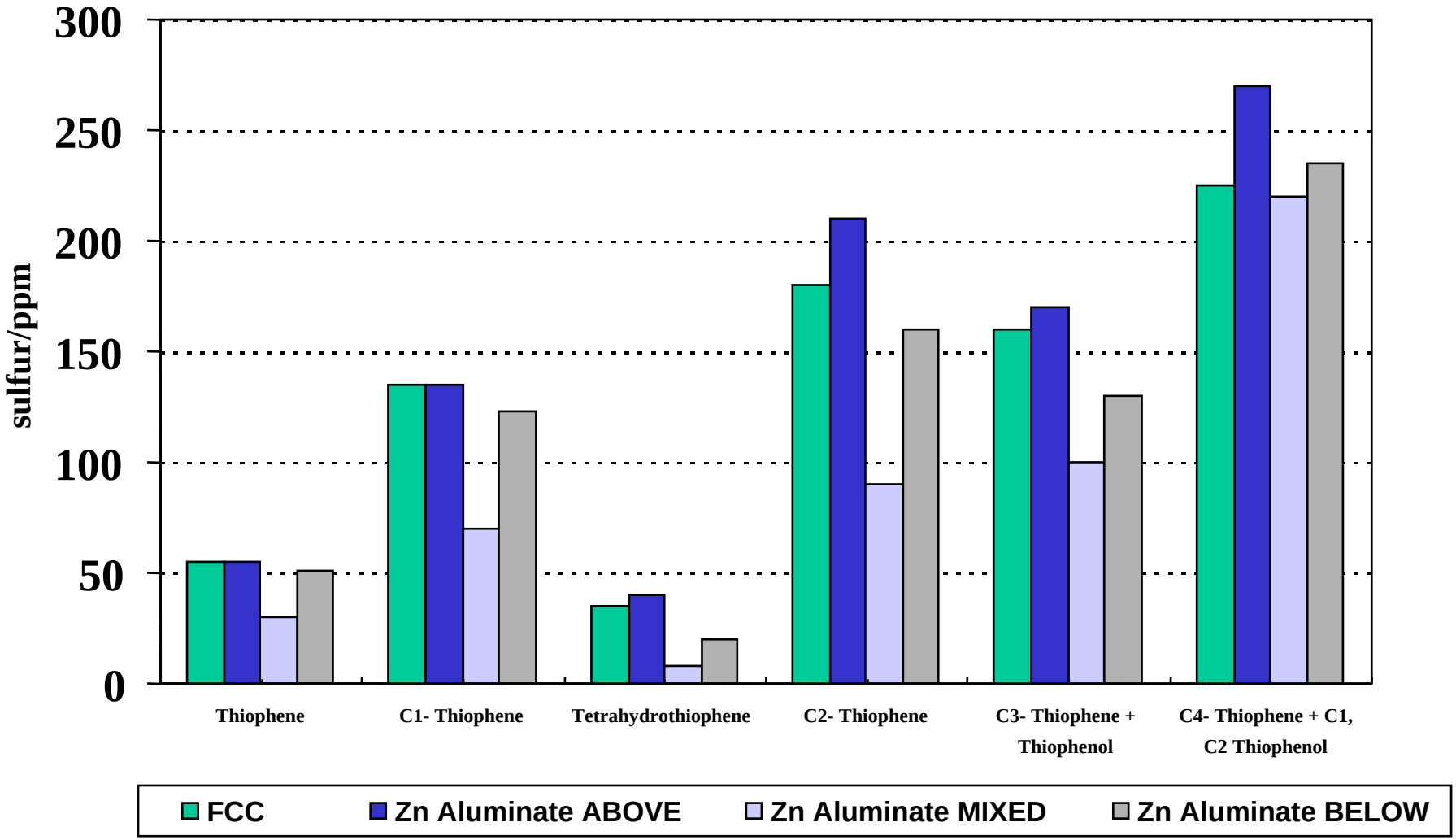
$\mathbf{k_3}$ → Zn/Alumina

Fixed Bed Layered Studies



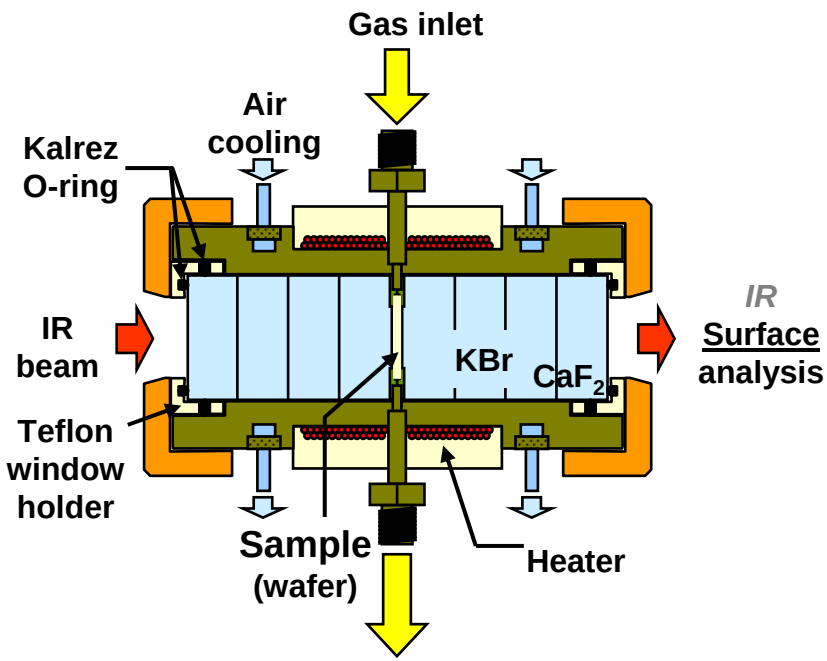
Sulfur Yields vs Zn Aluminate Location

FCC cat w/10% Zn Aluminate Feedstock Contains 1.7% S



Experimental : *operando study* at U. of Caen

- Reactors :
  - Classical catalytic reactor
  - **IR reactor cell :**



Gas outlet : *IR, GC* and MS Gas analysis

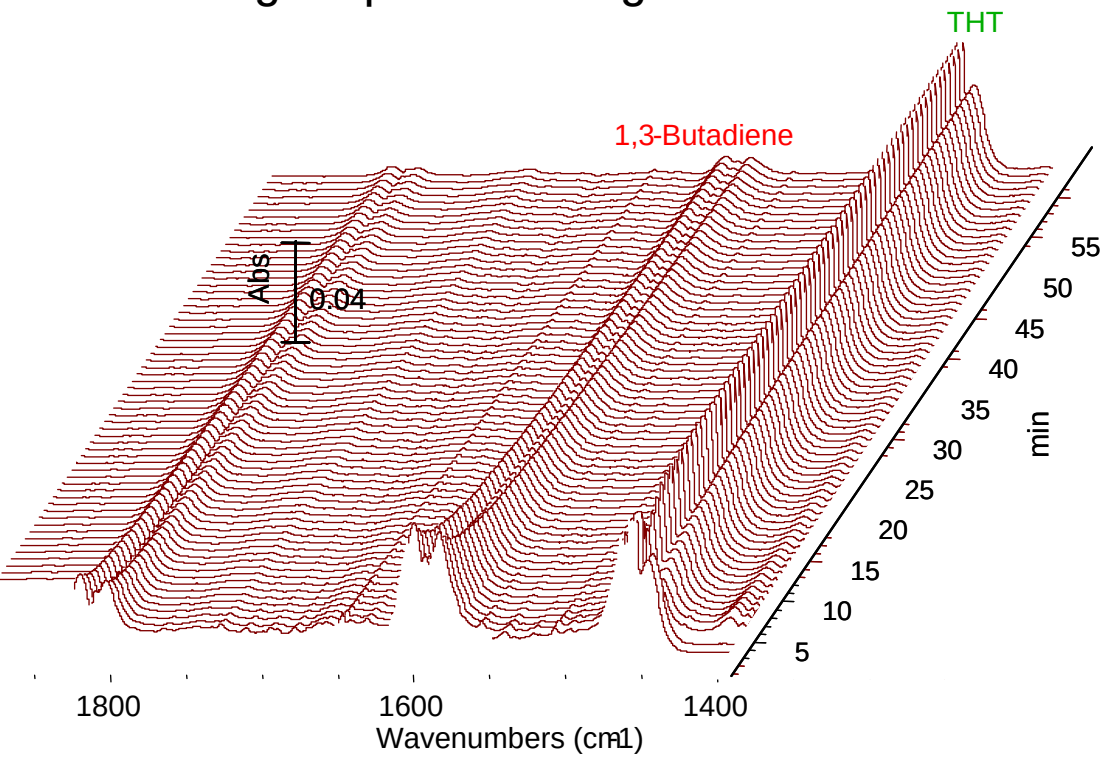
simultaneously : adsorbed species
products of a reaction

Summary of pure compound *operando* studies on Zn/alumina and neat alumina

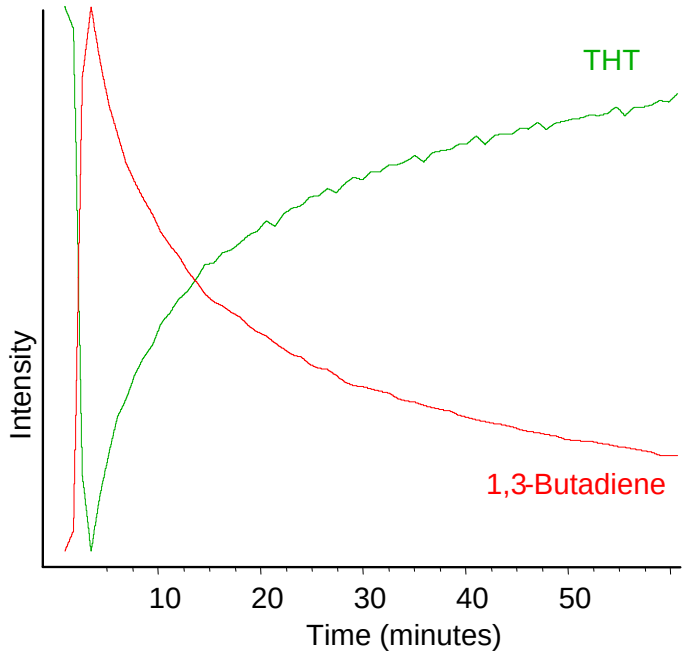
- No reaction with thiophene.
- Tetrahydrothiophene readily decomposes.
- Evidence that paired Lewis/Brønsted sites are the active sites. More work.

Reaction of tetrahydrothiophene over Zn/alumina at 723 ºK

IR gas spectra during the reaction



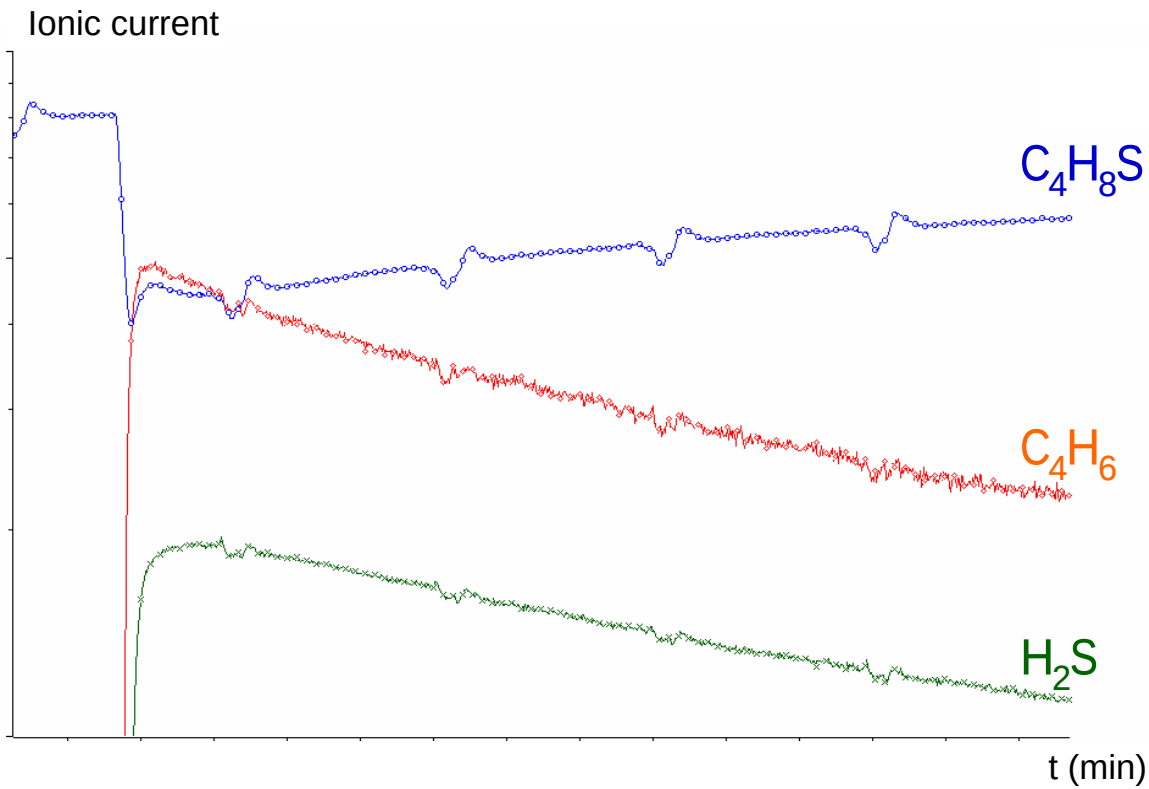
IR Chemigram



- Consumption of THT ;
- Formation of 1,3-butadiene.

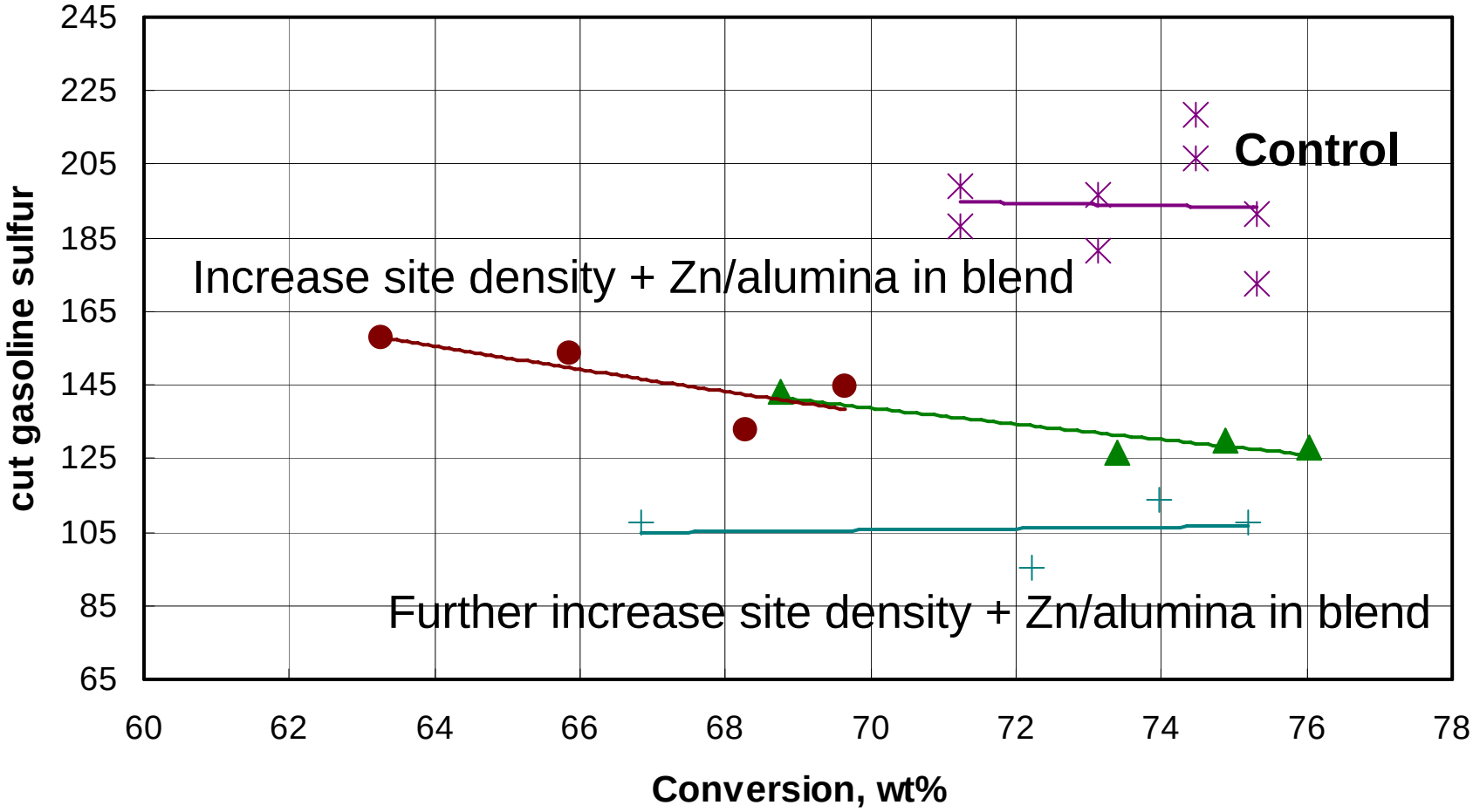
Work done at U. of Caen

Mass spec analysis during reaction with tetrahydrothiophene

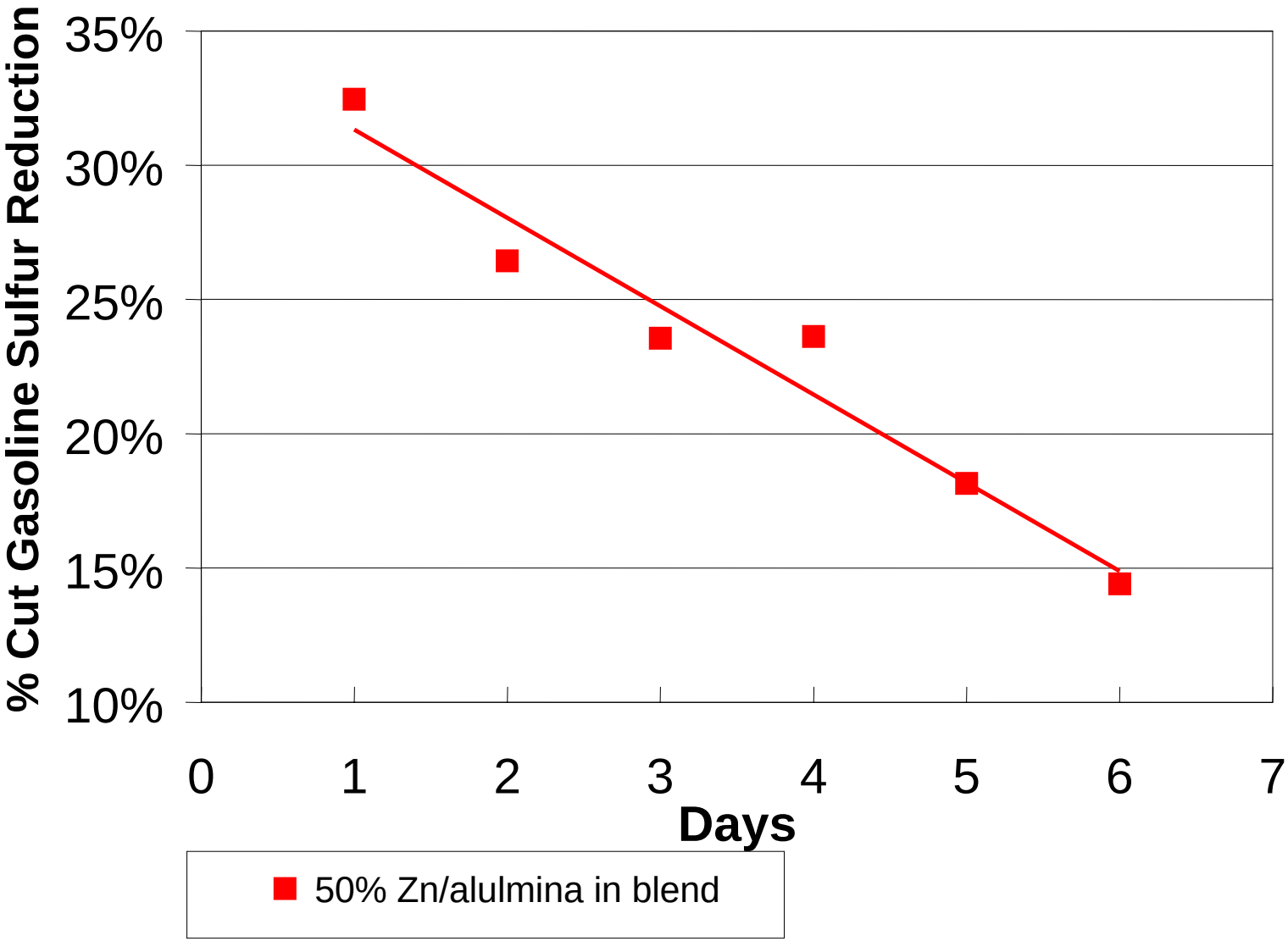


Maximize Sulfur Reduction Approach

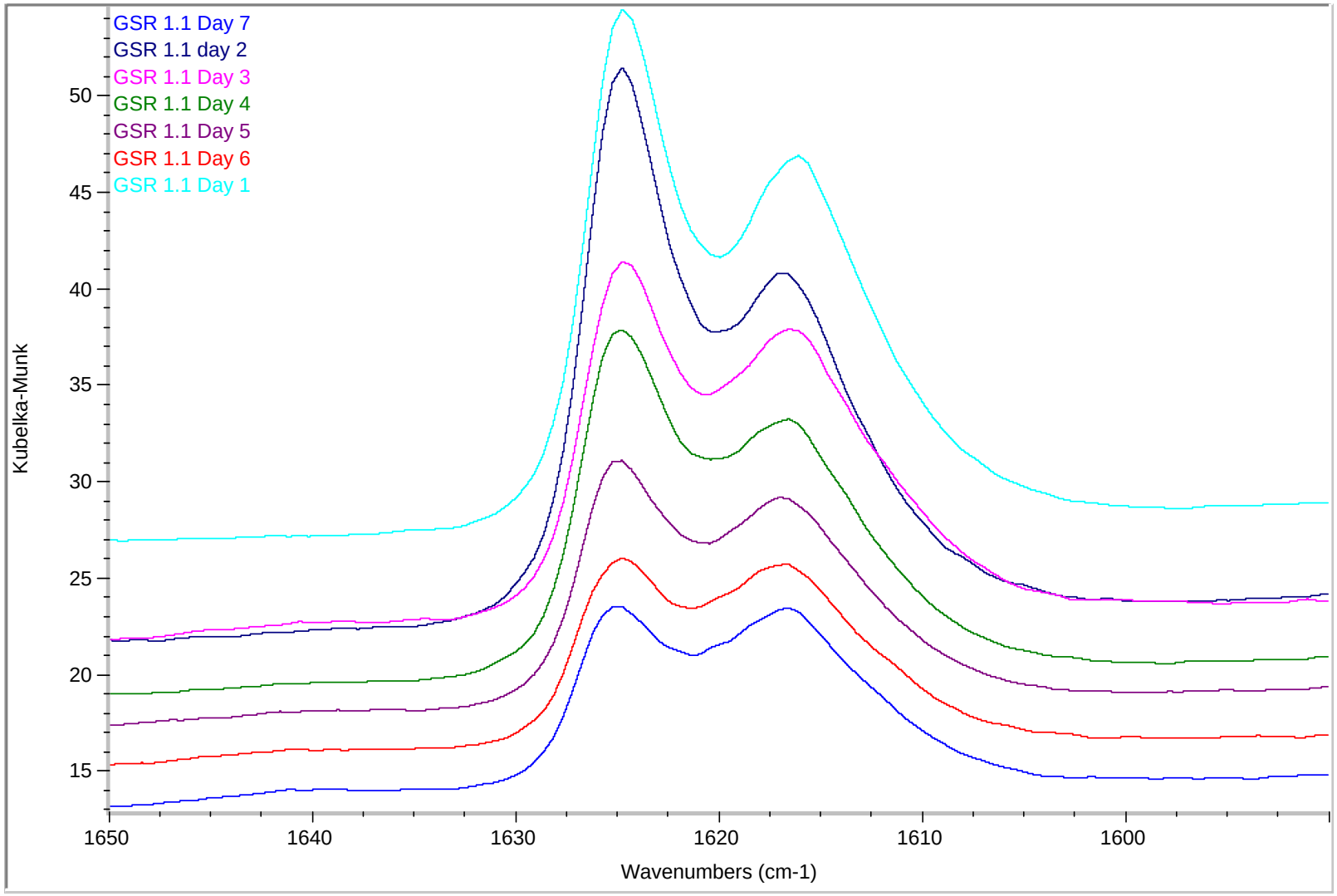
(Optimize Hydride Transfer & sulfur activity)



Deactivation of sulfur reduction activity

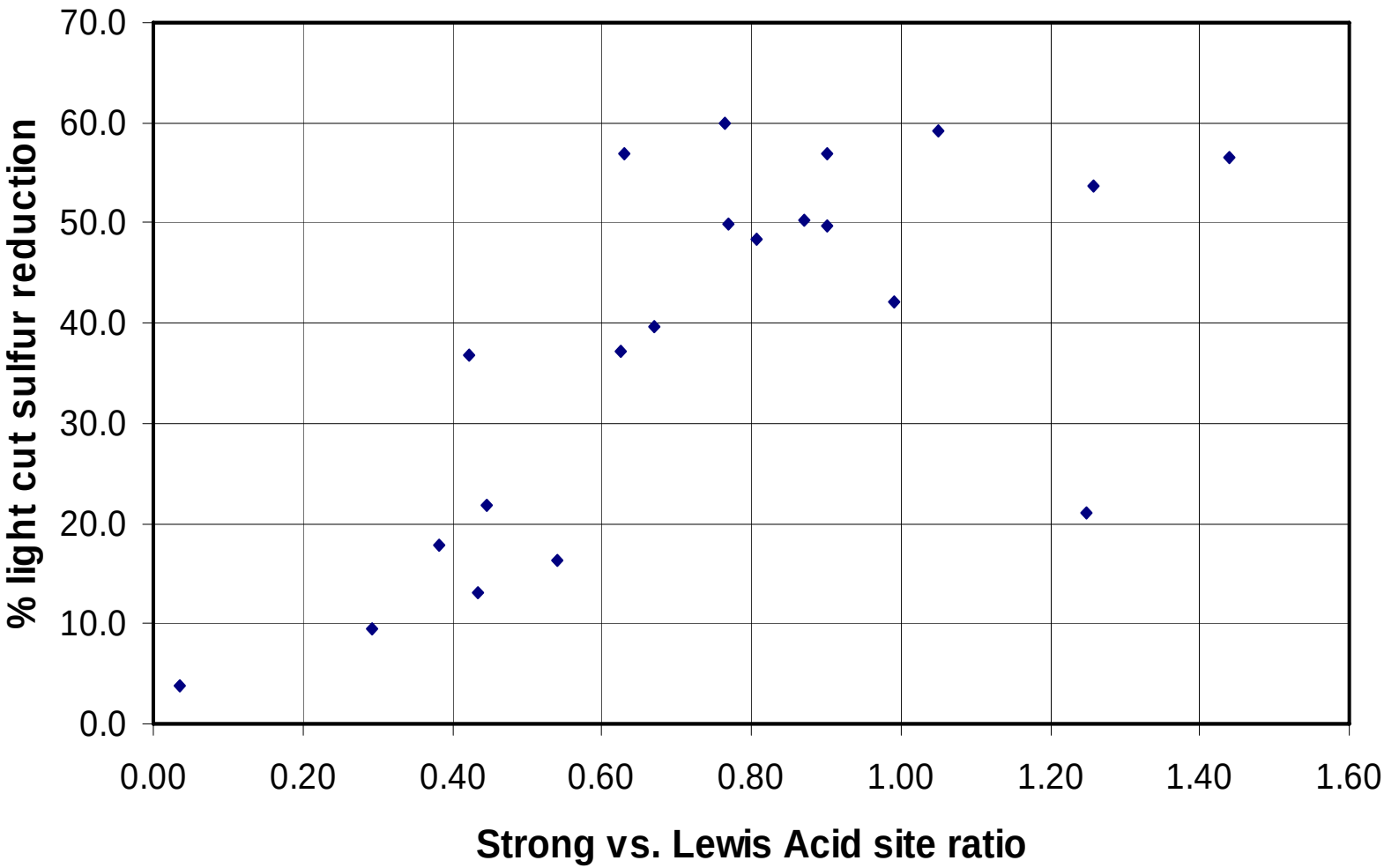


Deactivation Mechanism

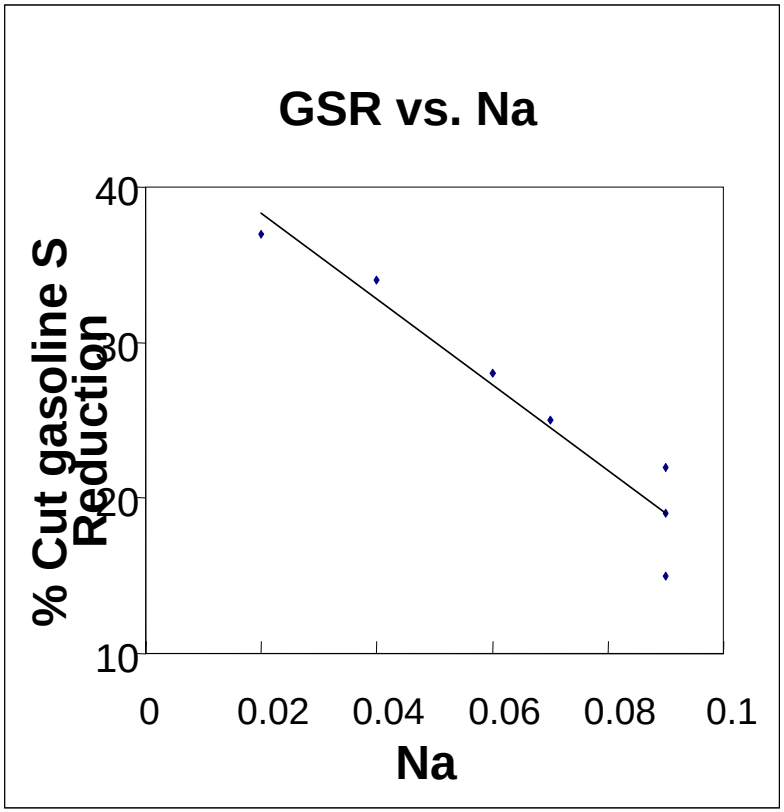


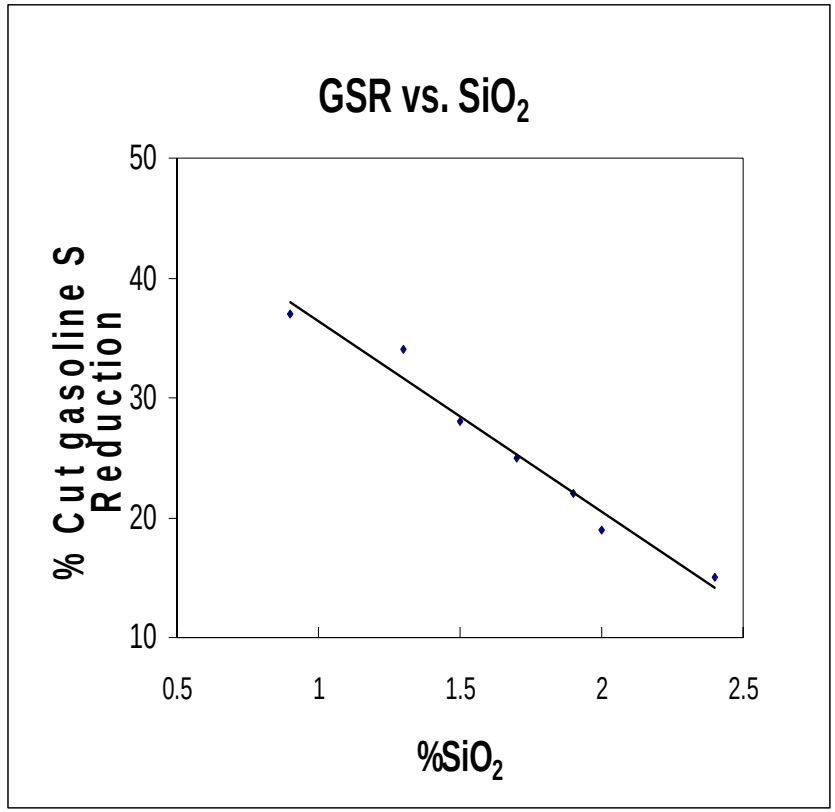
1. Strong Lewis Acid 1625cm^{-1}
2. Weak Lewis Acid 1616cm^{-1}

% light sulfur reduction vs. Strong/ weak Lewis sites ratio



Na and SiO_2 Poisoning of Zn/Al_2O_3





Summary

- Zn aluminate catalyzes the decompositon of saturated sulfur species.
- Maximum sulfur reduction activity is achieved by the optimization of hydride transfer activity of the base FCC catalyst and use of Zn aluminate up to 50 % reduction.
- Currently this technology is in over 40 units world wide and is expected to double in 2006.
- New technology, that does not deactivate, is in commercial trial with excellent performance.