Enhanced Acidic and Catalytic Properties of Modified Sulfonic Acid Resins

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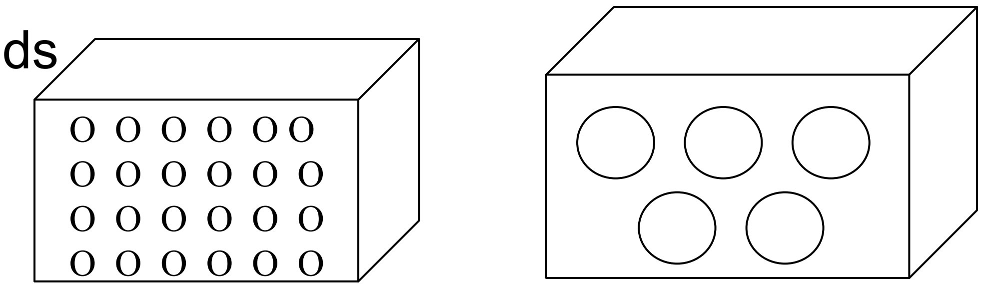
HUDDERSFIELD

1 Homogeneous Acid Catalysts: $AlCl_3$, H_2SO_4, HF - DISPOSAL!!

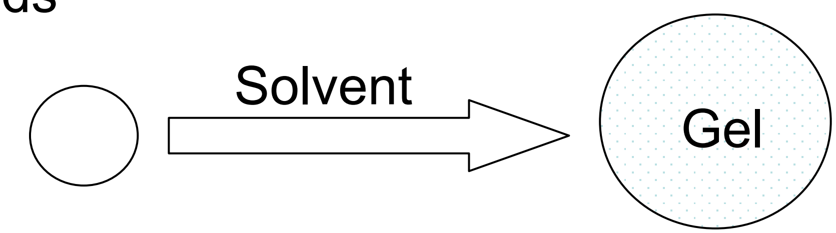
2 Heterogeneous Acid Catalysts

A) Rigid Solid Acids

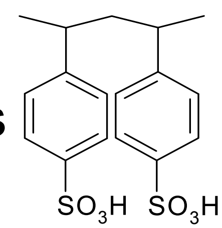


1 nm pores X   10 nm pores OK

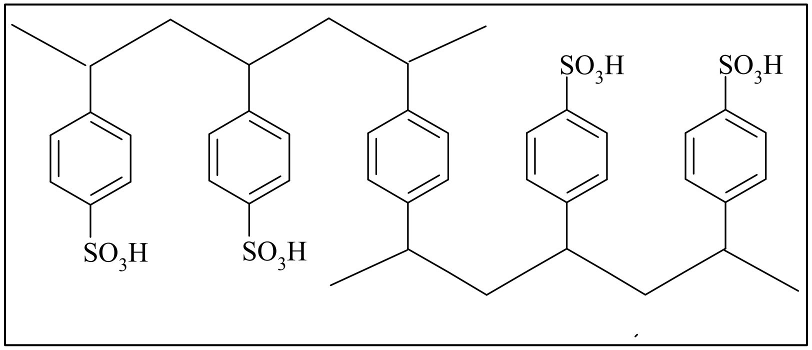
B) Non-Rigid Solid Acids



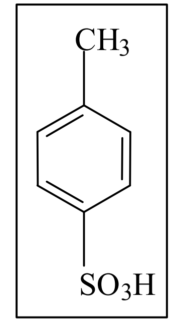
e.g. Sulfonated Polystyrene Resins



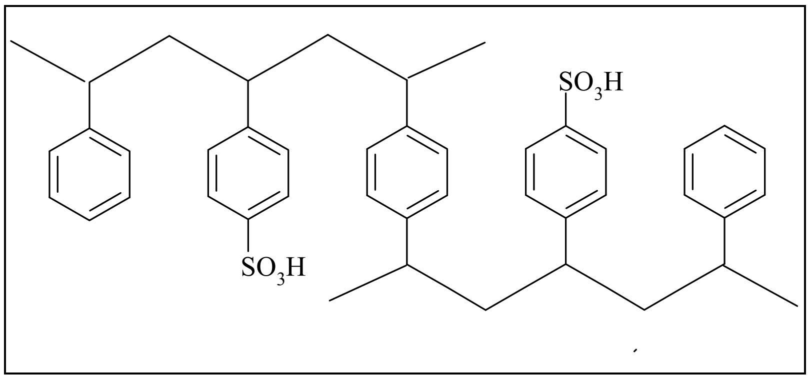
Sulfonated polystyrene



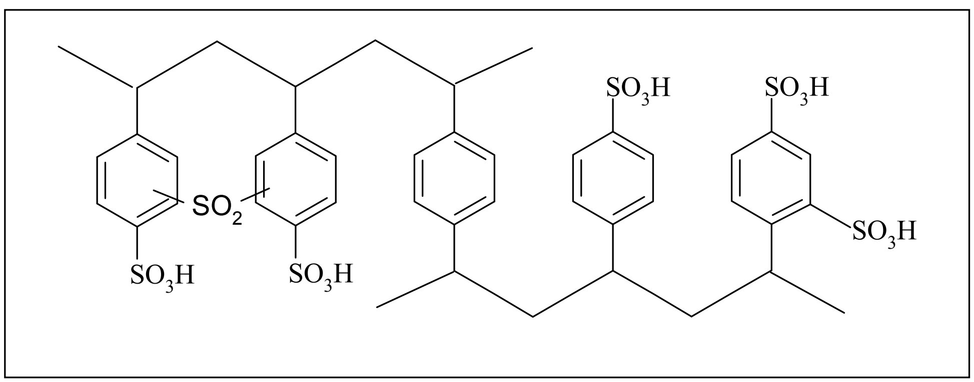
$[H^+]$
4.9 mmol g^{-1}



p-toluenesulfonic acid



$[H^+]$
2.9 mmol g^{-1}



$[H^+]$
5.4 mmol g^{-1}

Surface Acidity Characterisation

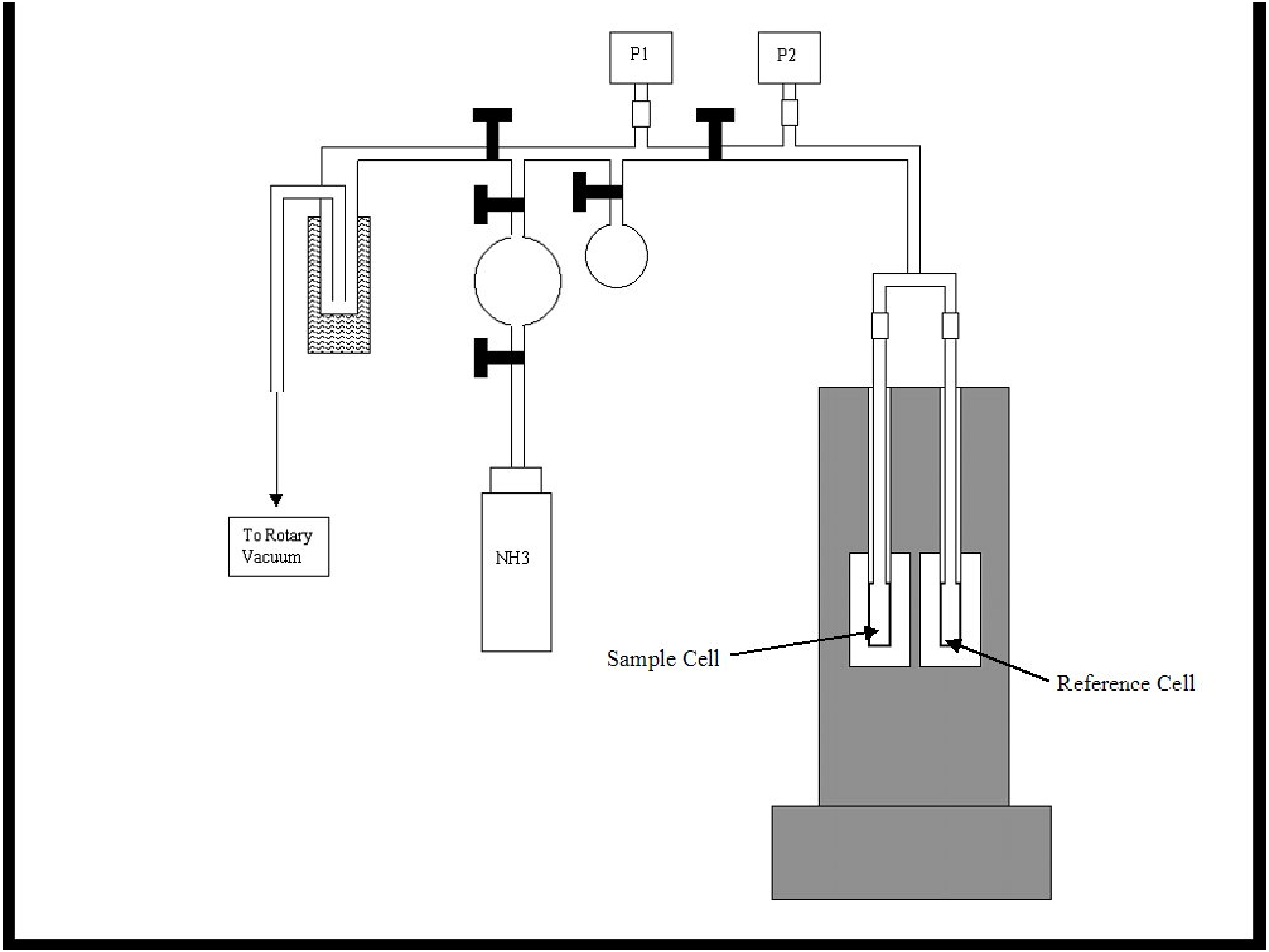
Base Temperature Programmed Desorption

Base Adsorption Calorimetry

NMR – direct or with probe (eg triethylphosphine)

IR – direct or with probe

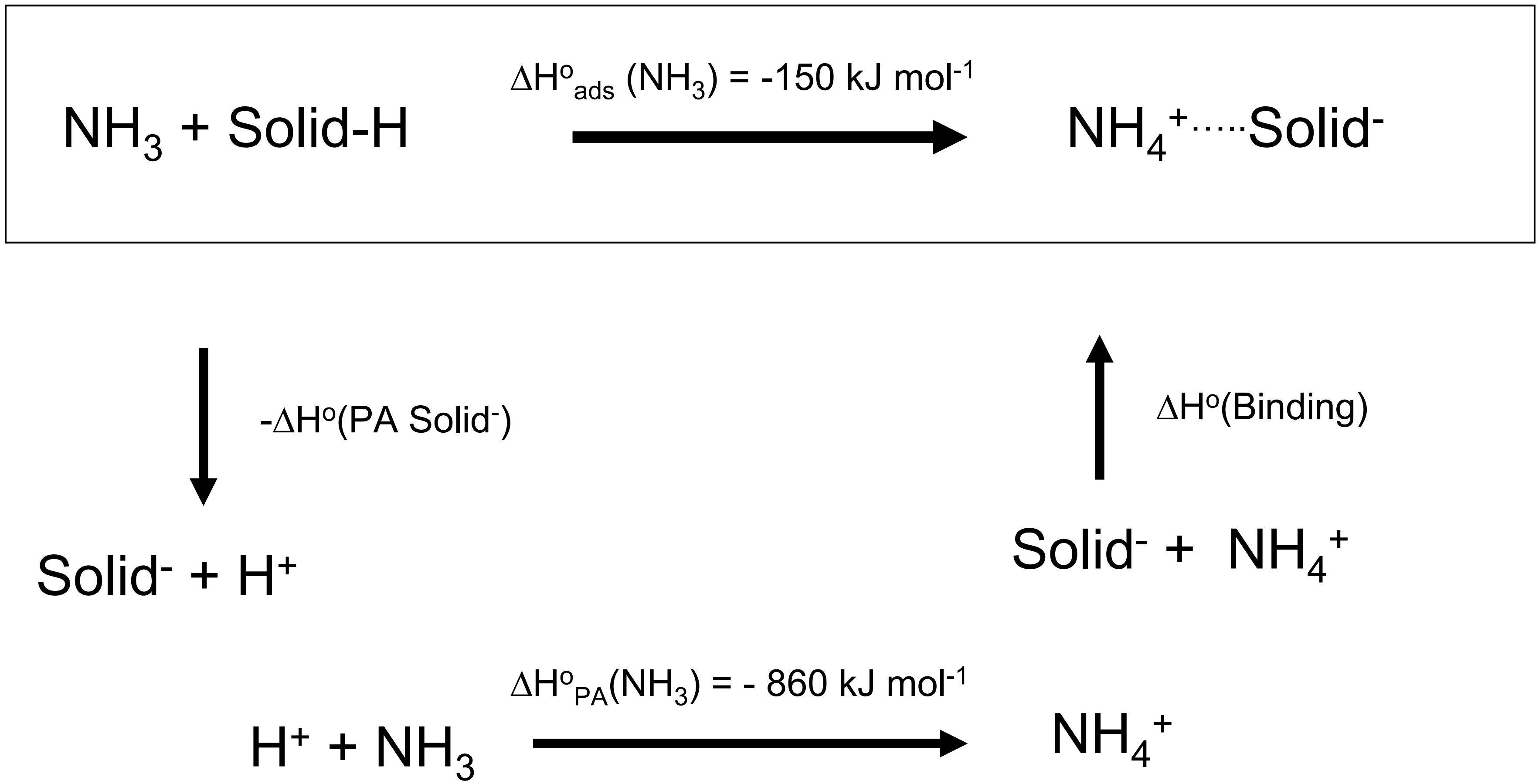
Hammett Indicators (eg dicinnamalacetone pKa -3.0
benzalacetophenone pKa -5.6)

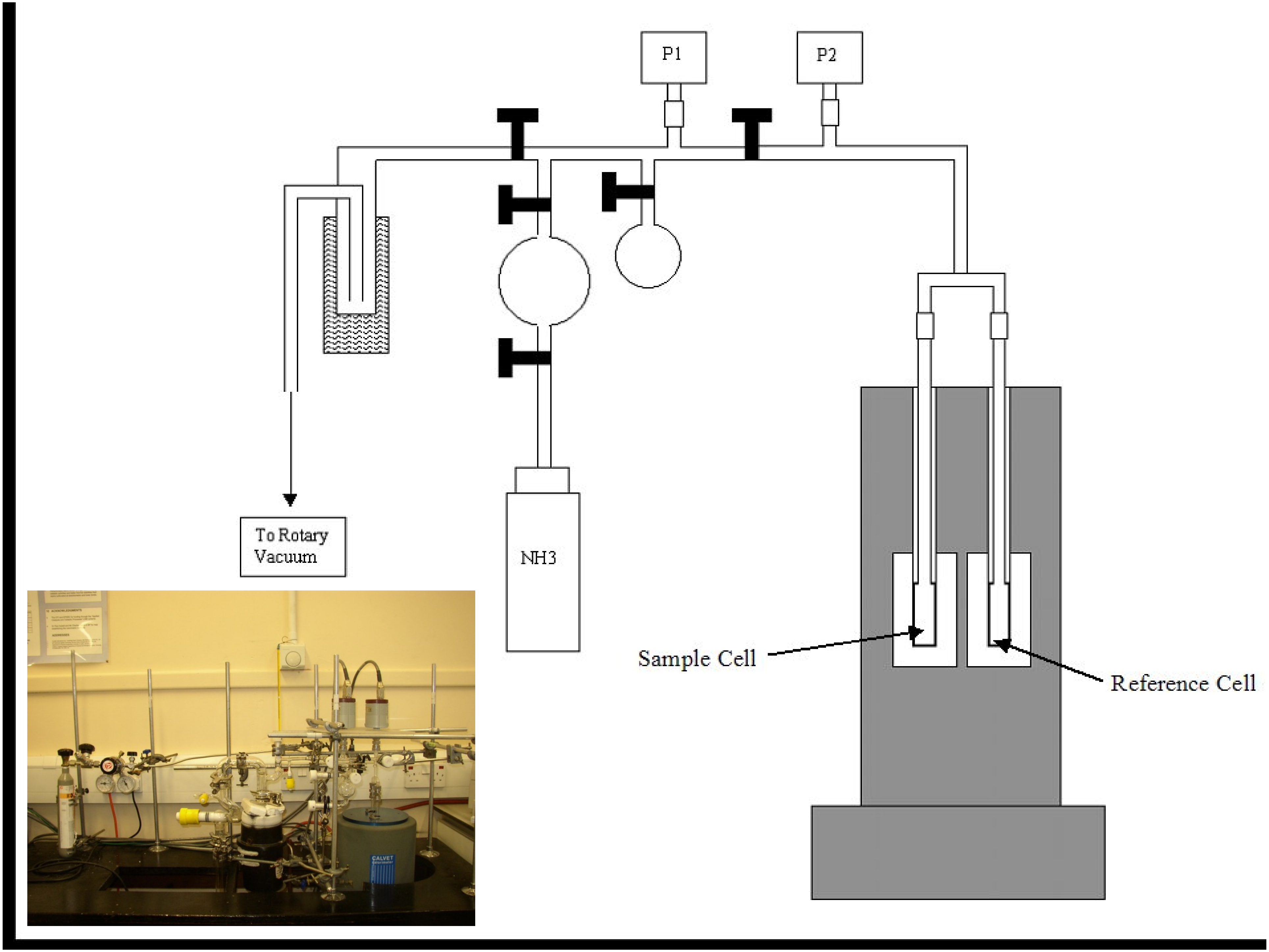

P1
P2
To Rotary Vacuum
NH3
Sample Cell
Reference Cell

Enthalpy of NH_3 Adsorption (as a measure of acid site strength)

$$NH_3 + \text{Solid-H} \xrightarrow{\Delta H^o_{ads}(NH_3) = -150 \text{ kJ mol}^{-1}} NH_4^+ \cdots\cdots \text{Solid}^-$$

Enthalpy of NH_3 Adsorption (as a measure of acid site strength)




P1
P2
To Rotary Vacuum
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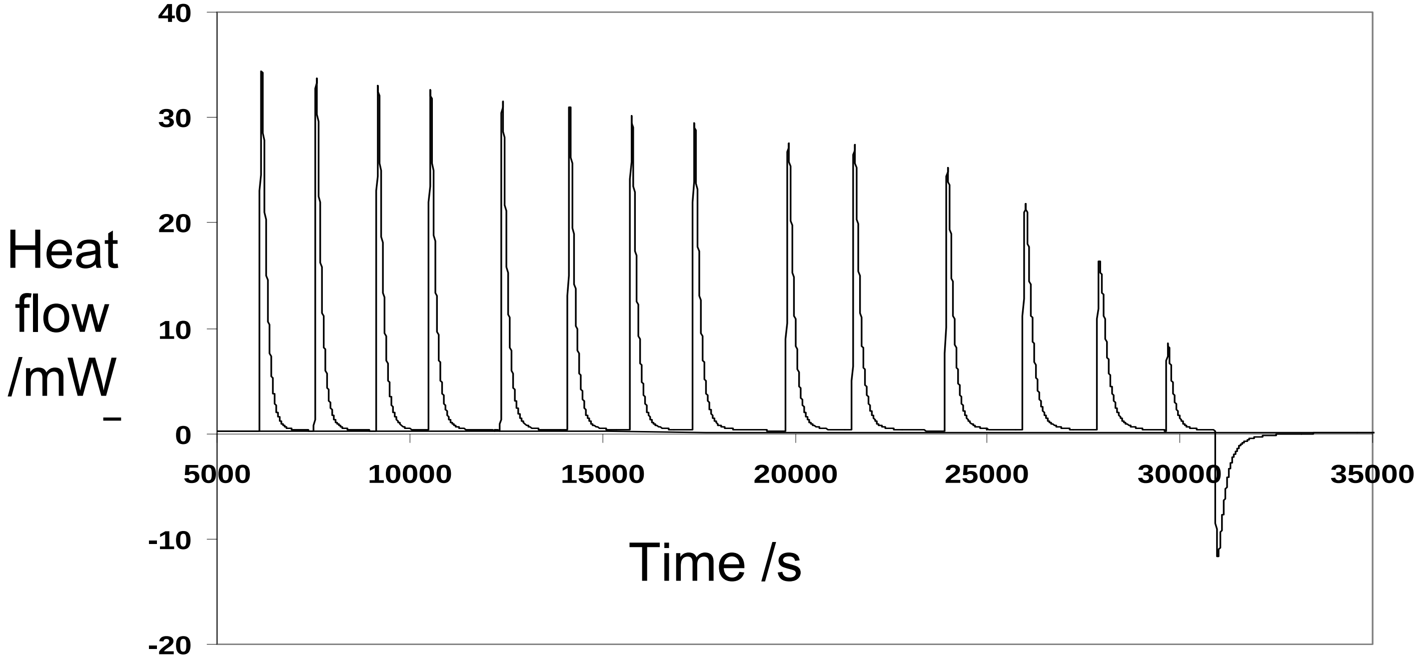
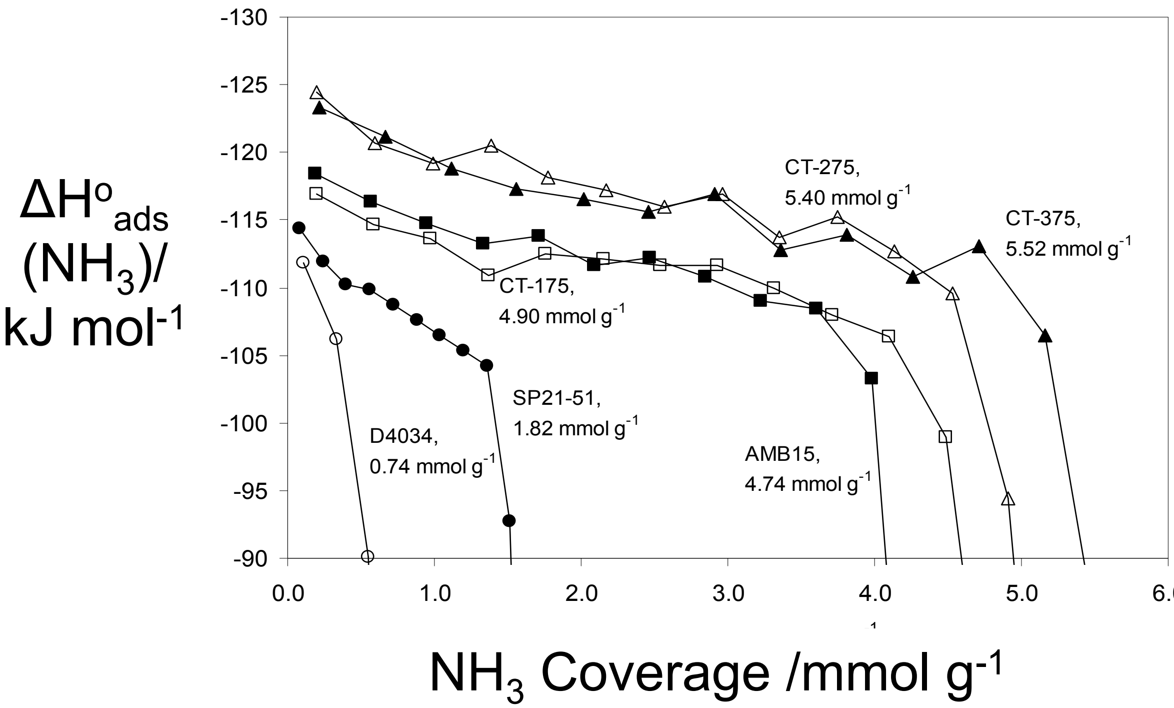
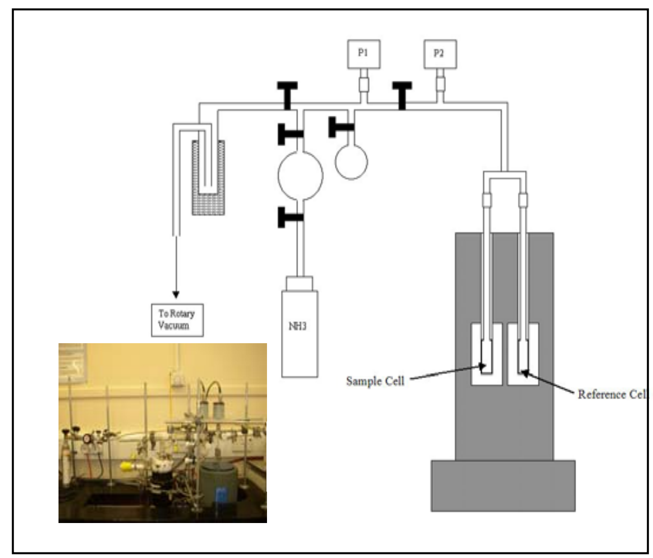
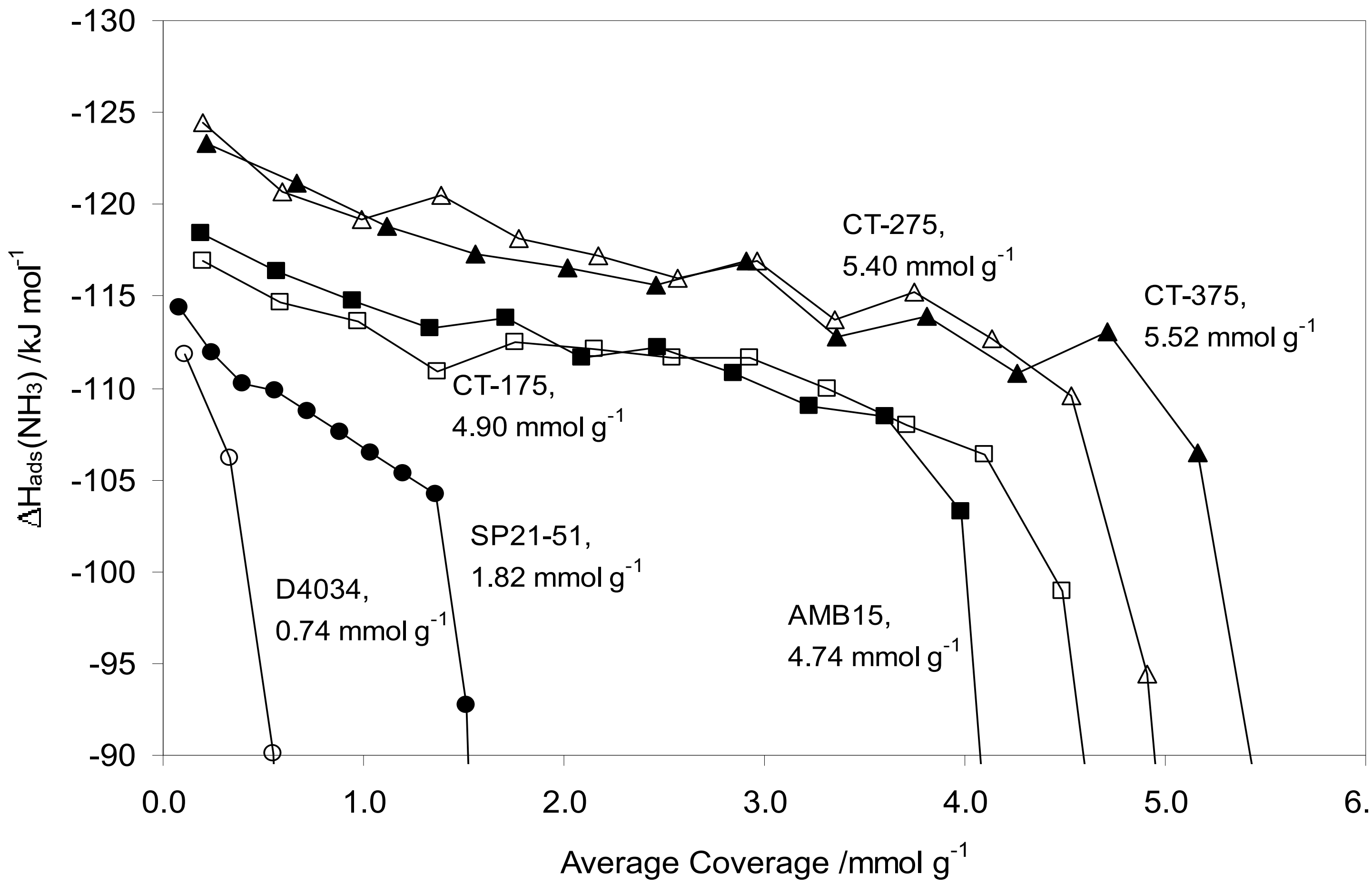
Reference Cell

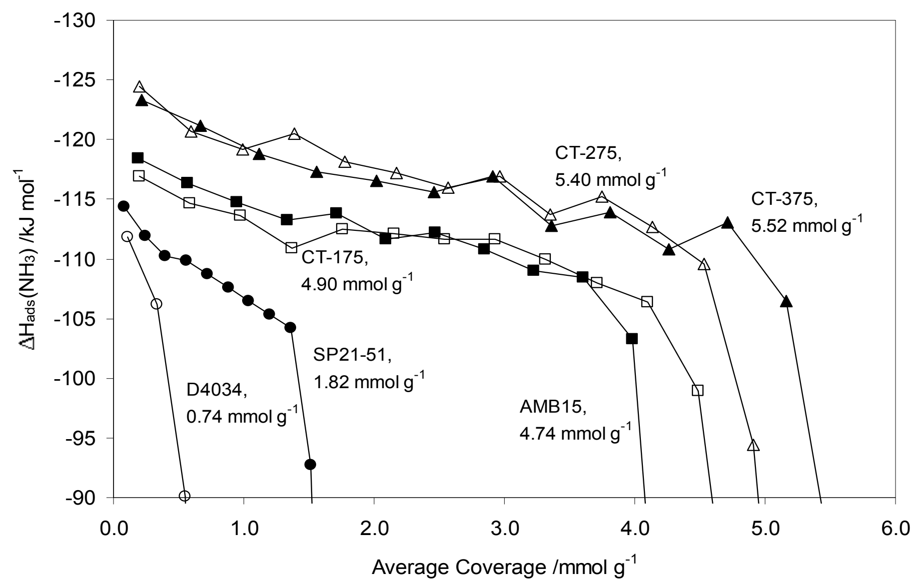

Heat flow /mW
Time /s
40
30
20
10
0
-10
-20
5000
10000
15000
20000
25000
30000
35000

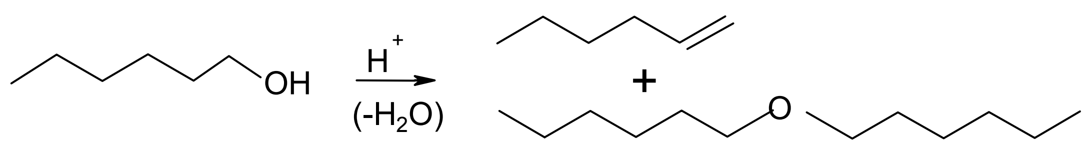

ΔH$^o_{ads}$ (NH_3)/ kJ mol^{-1}
NH_3 Coverage /mmol g^{-1}
CT-275, 5.40 mmol g^{-1}
CT-375, 5.52 mmol g^{-1}
CT-175, 4.90 mmol g^{-1}
SP21-51, 1.82 mmol g^{-1}
D4034, 0.74 mmol g^{-1}
AMB15, 4.74 mmol g^{-1}
-130
-125
-120
-115
-110
-105
-100
-95
-90
0.0
1.0
2.0
3.0
4.0
5.0
6.0


P1
P2
To Rotary Vacuum
NH3
Sample Cell
Reference Cell

Molar enthalpy of adsorption of NH_3 vs. amount of NH_3 adsorbed on macroporous sulfonated polystyrene beads at 100 °C







Catalyst	Reaction Rate /10^{-2} μmol converted g^{-1} h^{-1}	Specific Activity /10^{-3} μmol converted $mmol^{-1}$($-SO_3H$) h^{-1}	Selectivity/ [Hexene]/[Ether]
Amb15 ([H^+] = 4.7 mmol g^{-1})	2.5	5.3	1.4
CT-175 ([H^+] = 4.9 mmol g^{-1})	2.3	4.7	1.0
CT-275 ([H^+] = 5.4 mmol g^{-1})	7.6	14.1	1.4

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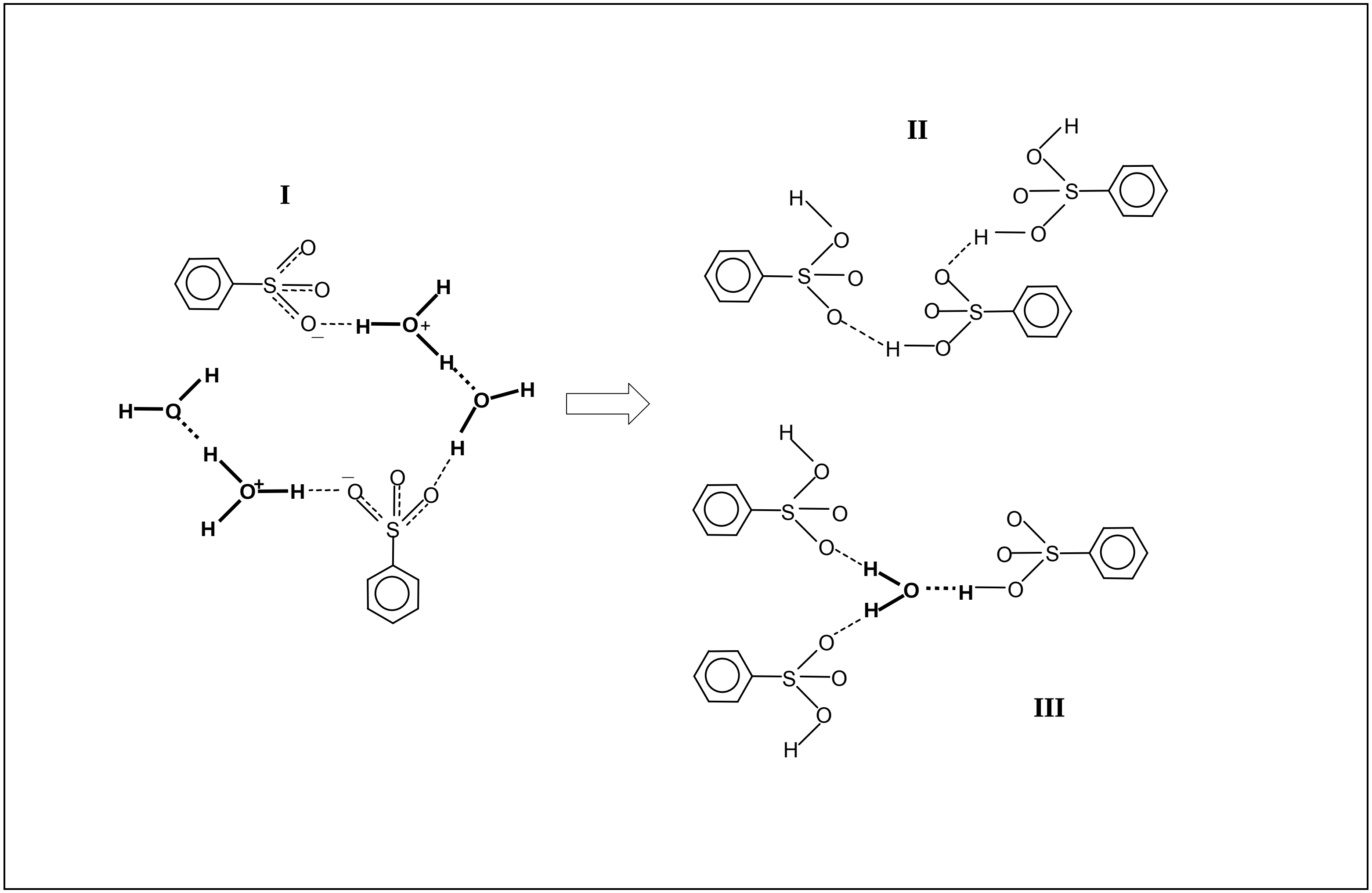
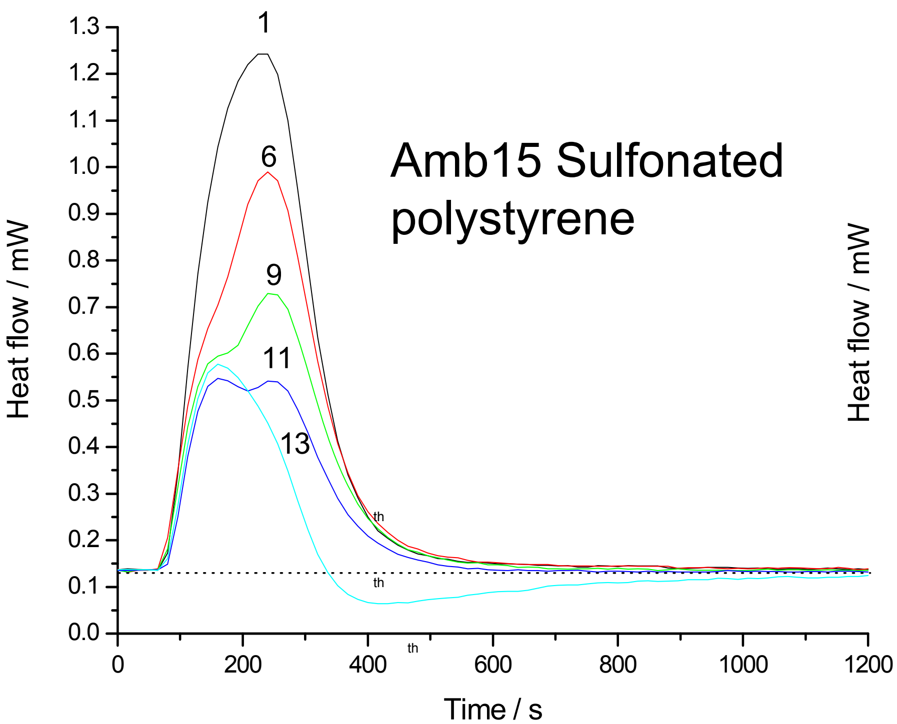
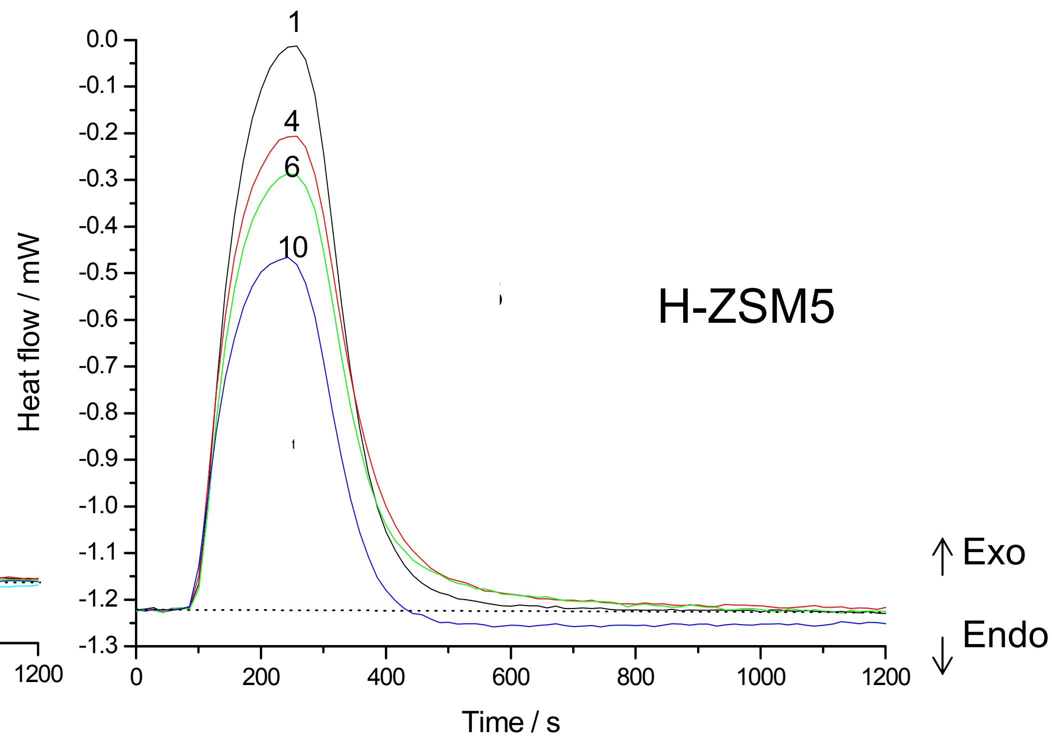
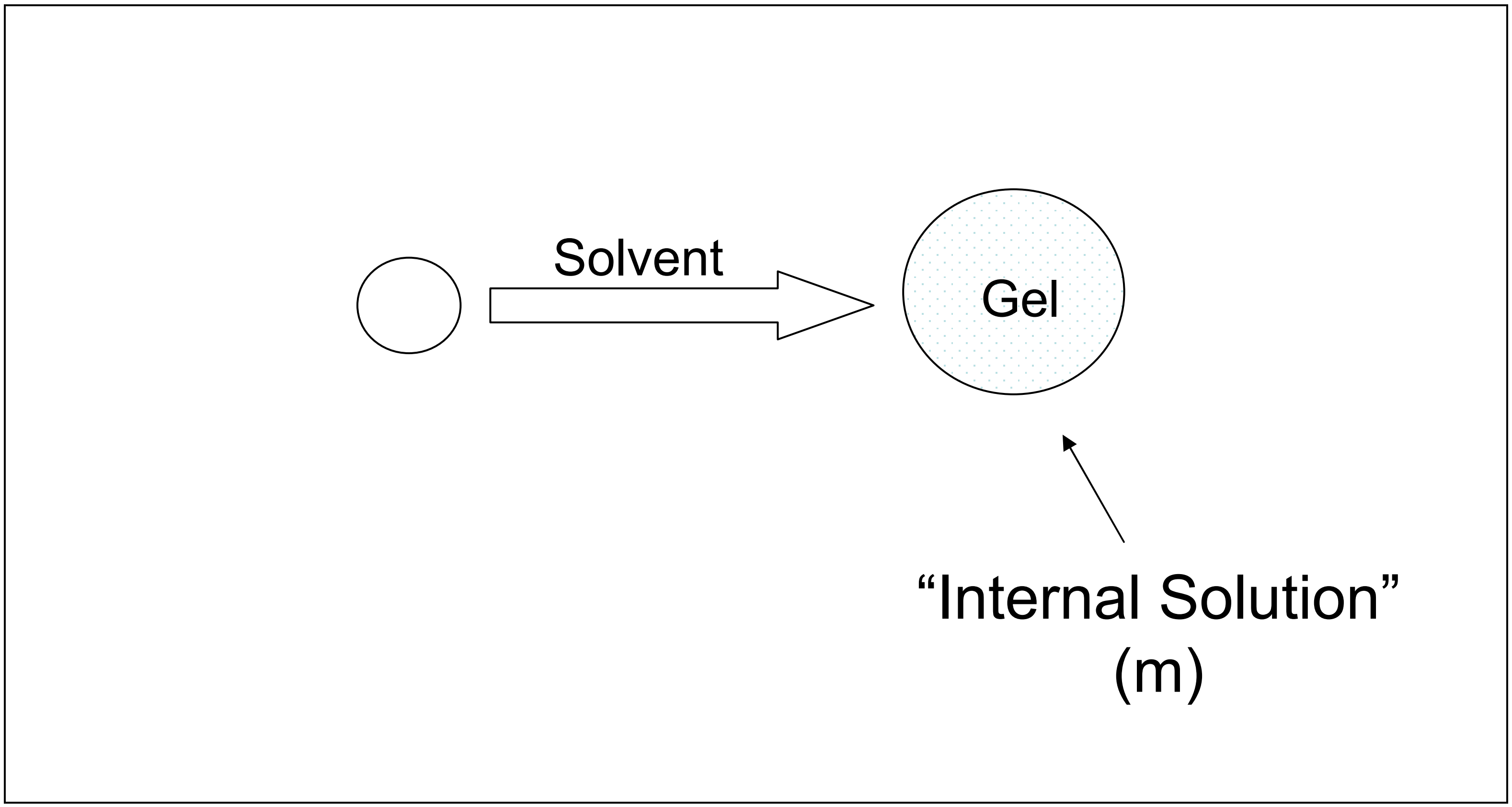

I
II
III

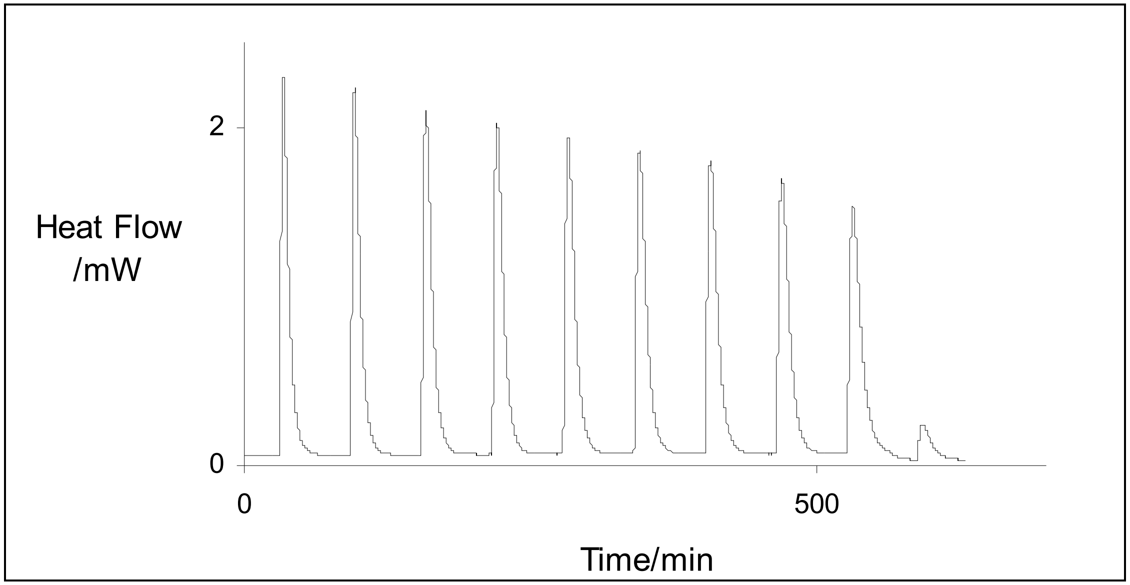
NH_3 Adsorption from He



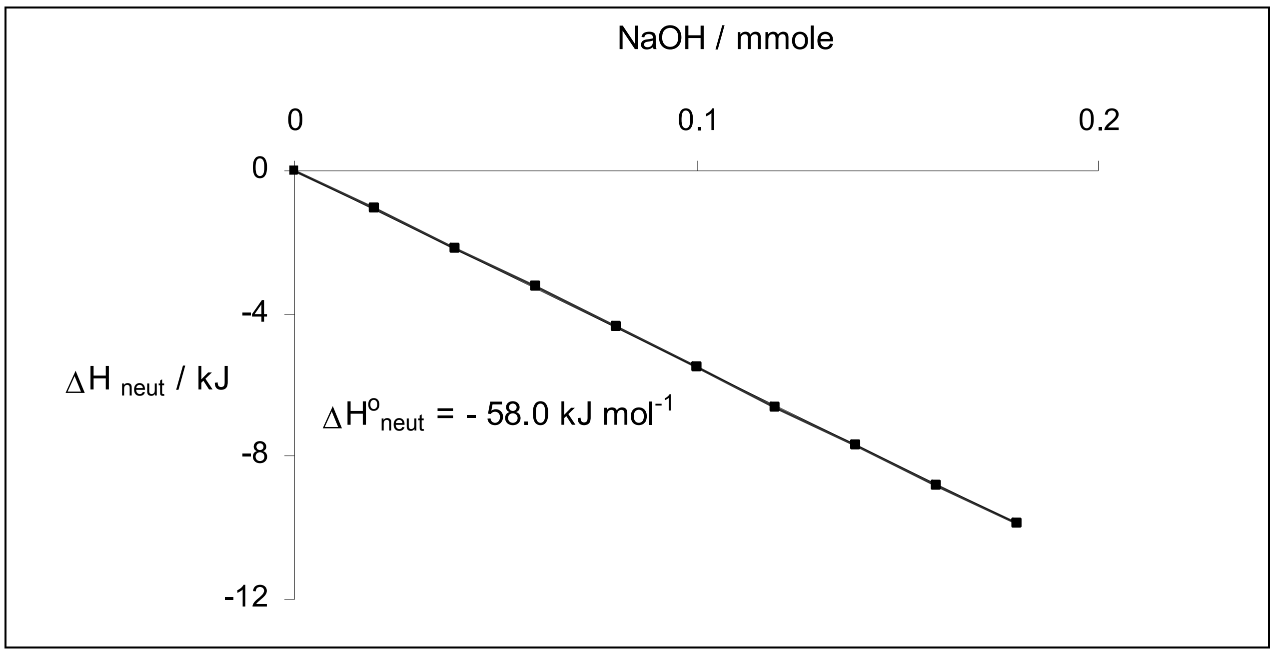


The shape of the calorimeter signal changes as the solid acid becomes progressively saturated - Signals for pulses 1, 6, 9, 11 and 13.

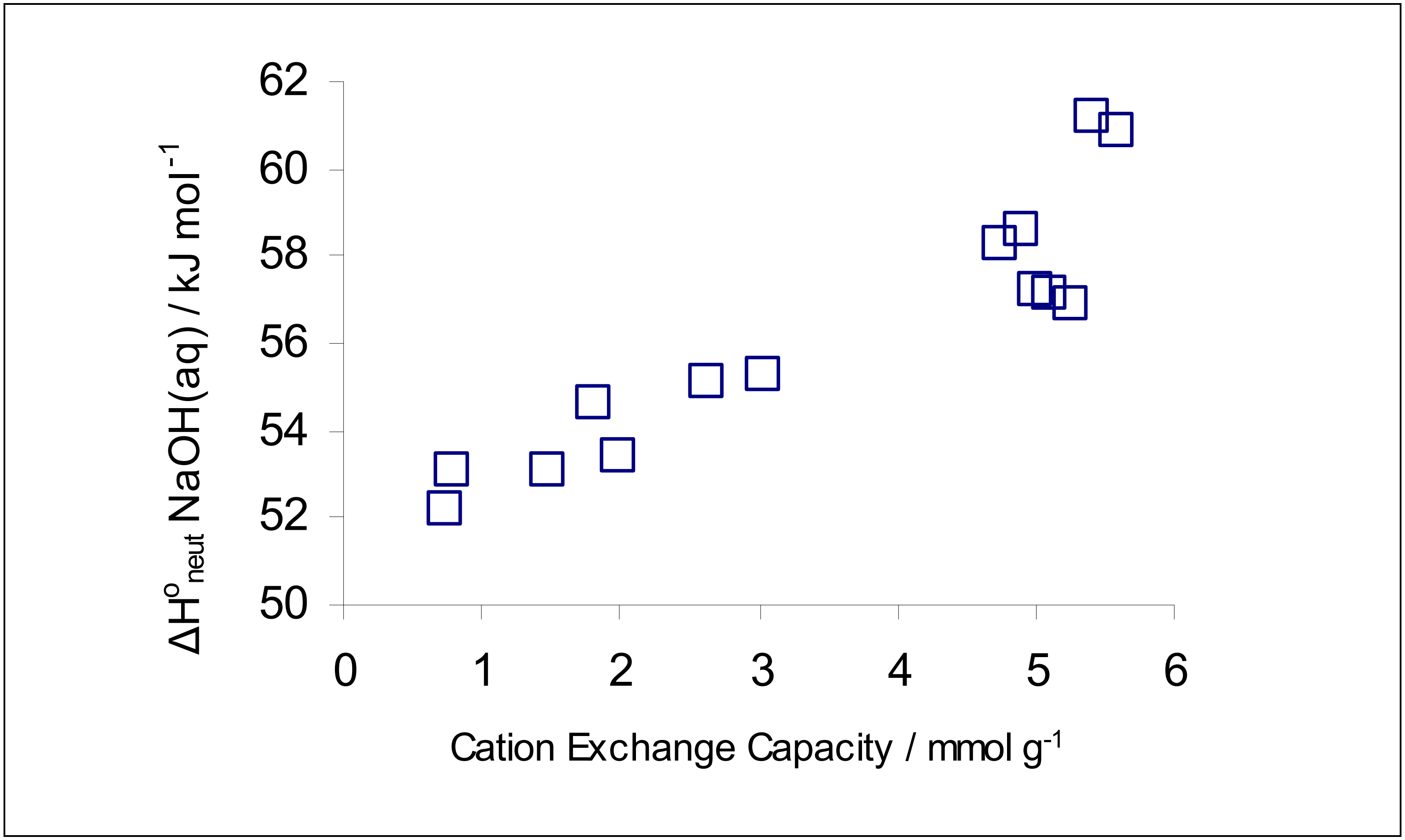

Solvent
Gel
"Internal Solution"
(m)



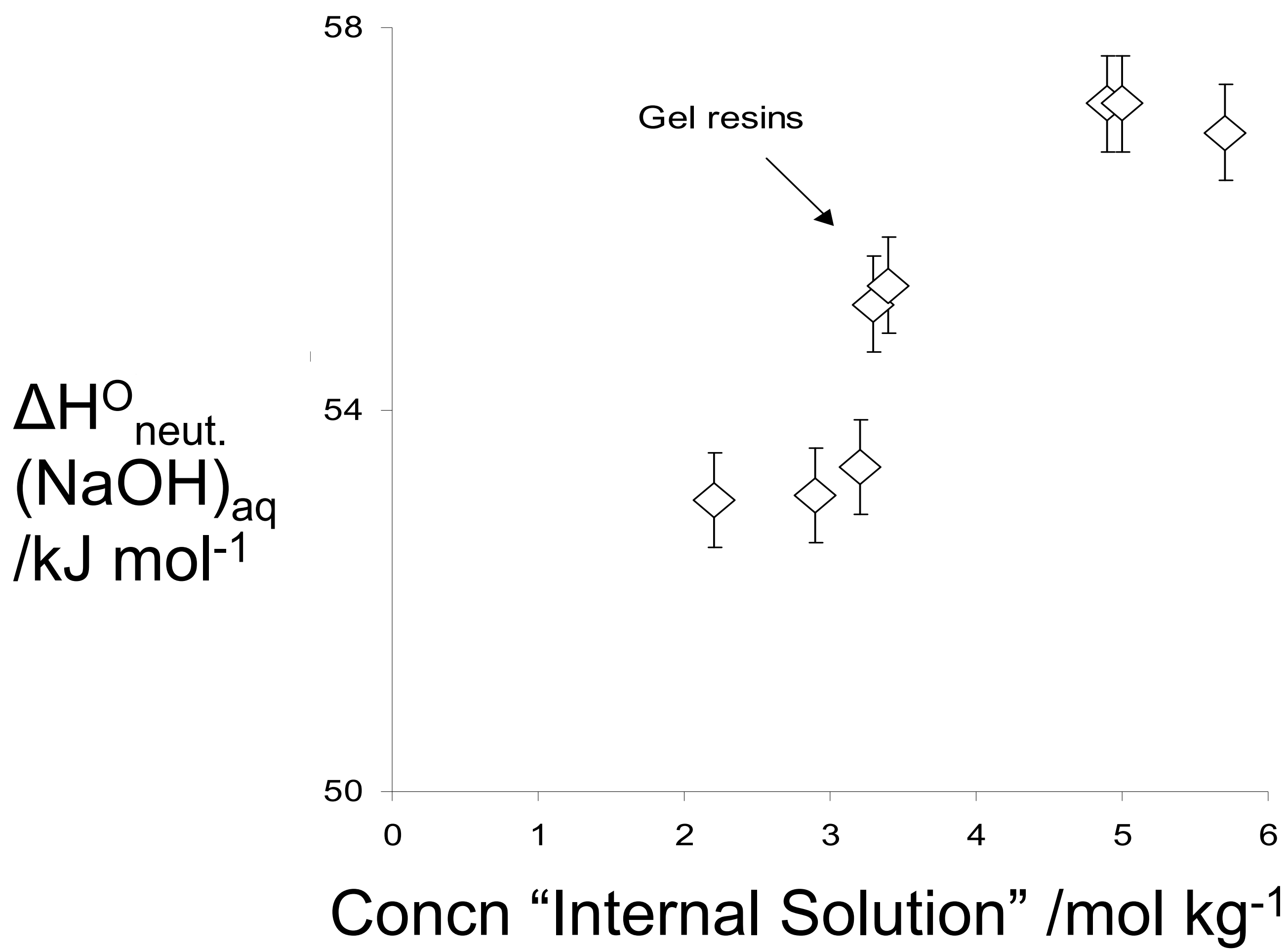
Aqueous Titration Microcalorimetry - Hydrated Sulfonated Resins with 0.1 M NaOH solution



Liquid Titration Calorimetry
$\Delta H^{O}_{neut.}$ $(NaOH)_{aq}$- Sulfonated Polystyrene Resins - Dependence on Level of Sulfonation



Liquid Titration Calorimetry Sulfonated Resins
$\Delta H^{O}_{neut.}$ $(NaOH)_{aq}$- vs Concn “Internal Solution”



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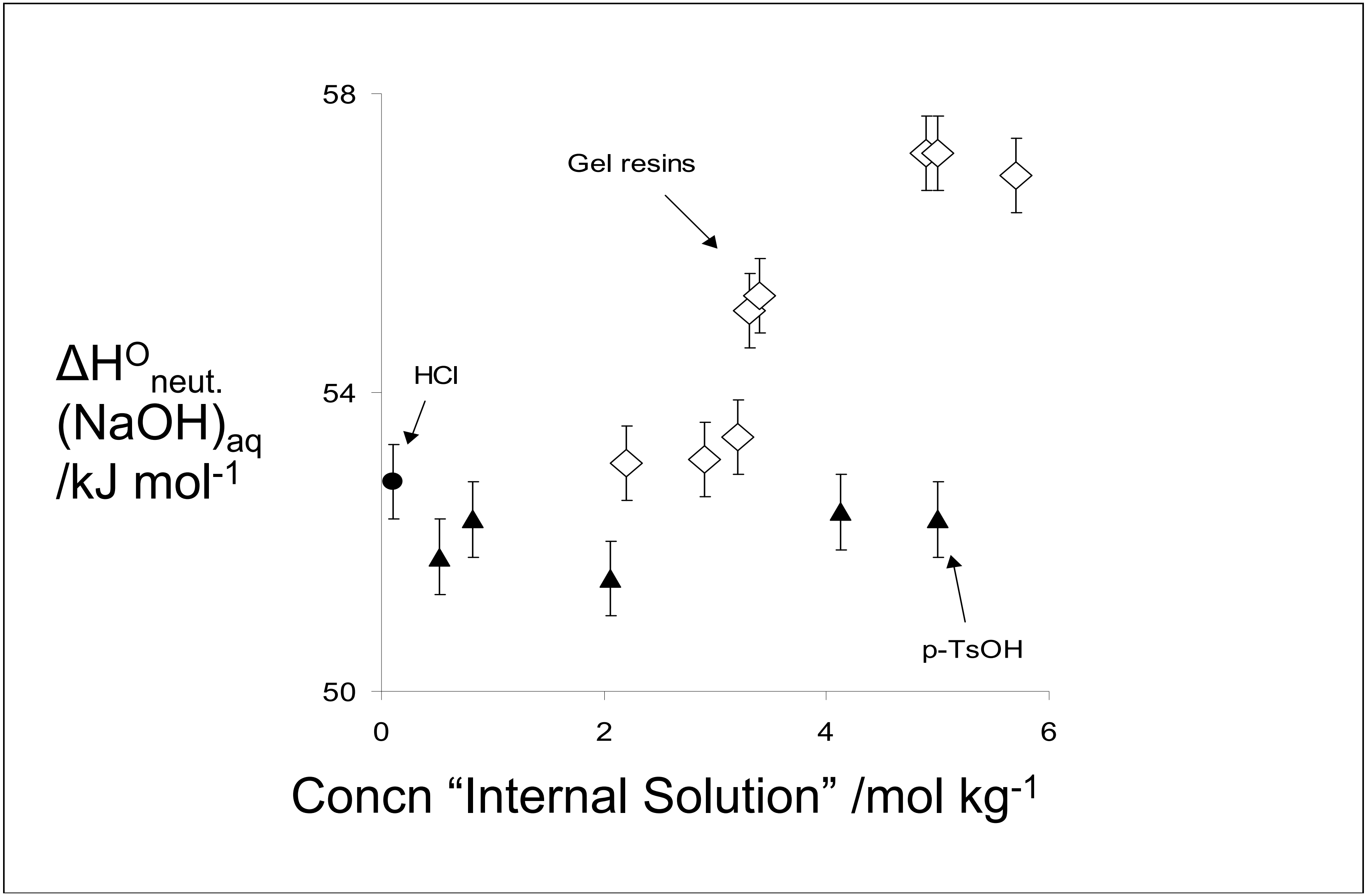
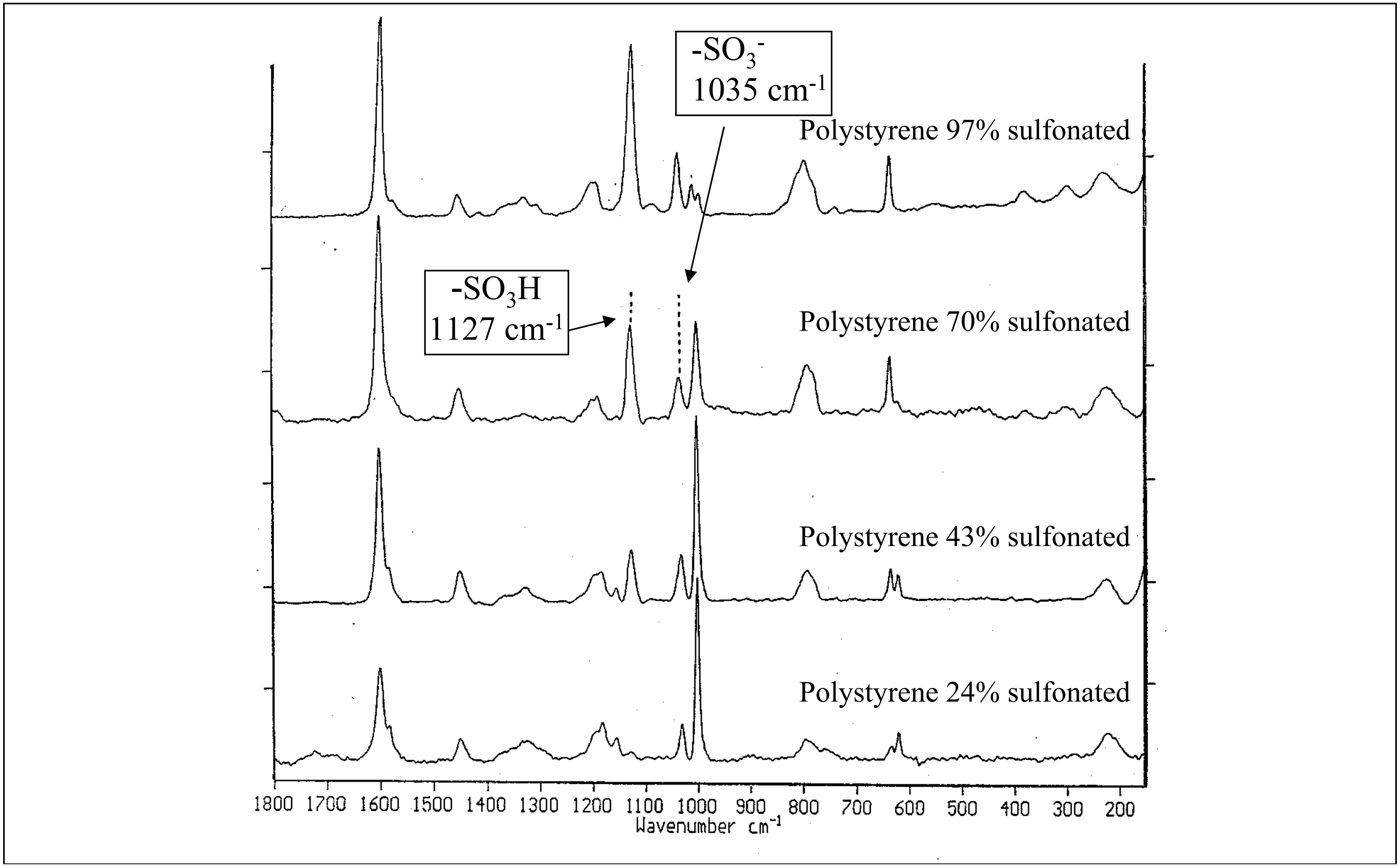
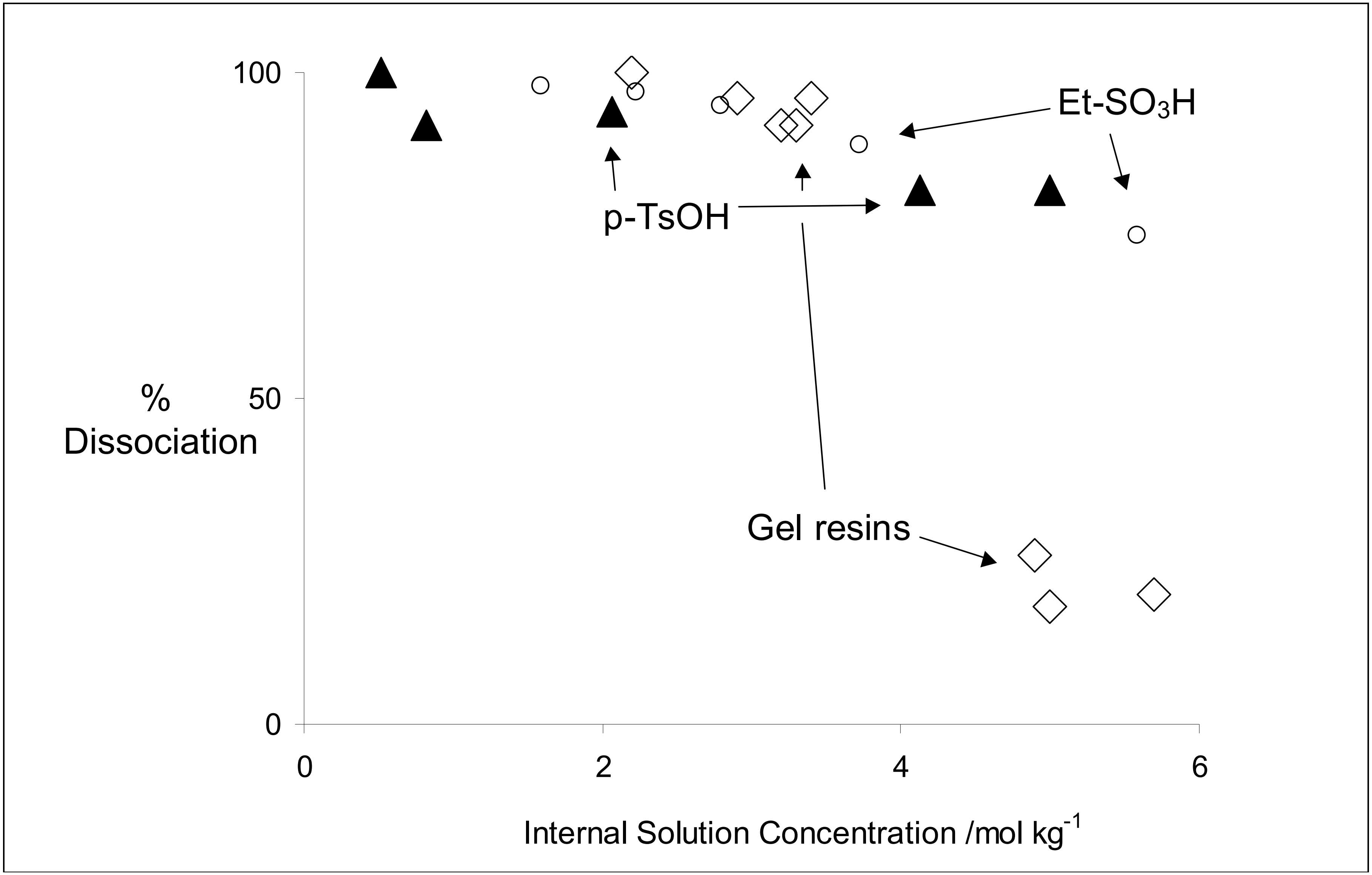


FT-Raman Spectroscopy
- Hydrated Sulfonated Resins (H^+ Form)



Degree of Acid Dissociation vs Concn of Internal Solution - FT-Raman Data



Conclusions

Sulfonated Polystyrene (Hydrated)

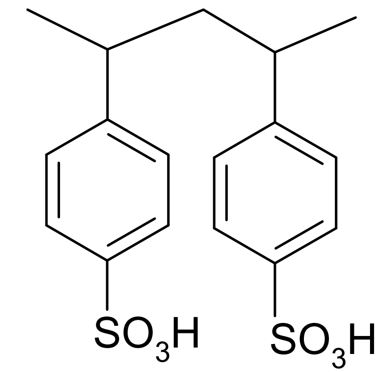
High sulfonation

= reduced acid dissocation
= increased acid strength
= higher catalytic activity

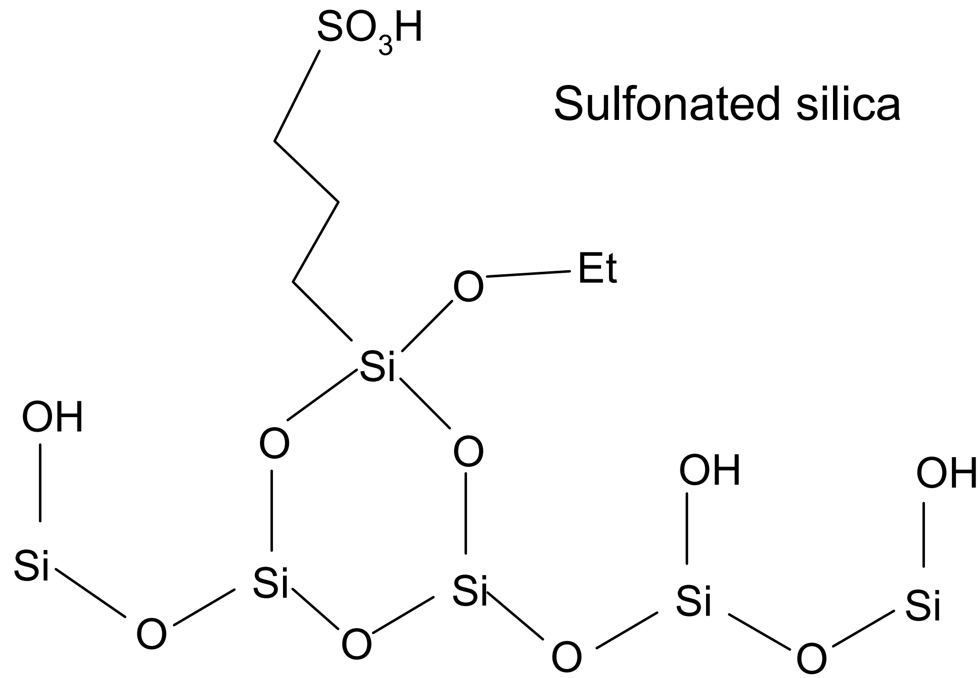
Effective acid catalysts in water

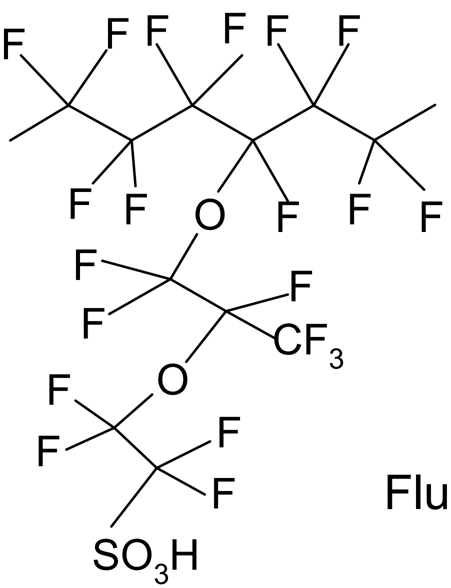
Enhanced acid strength/activity not seen in other supported sulfonic acids

Sulfonated polystyrene

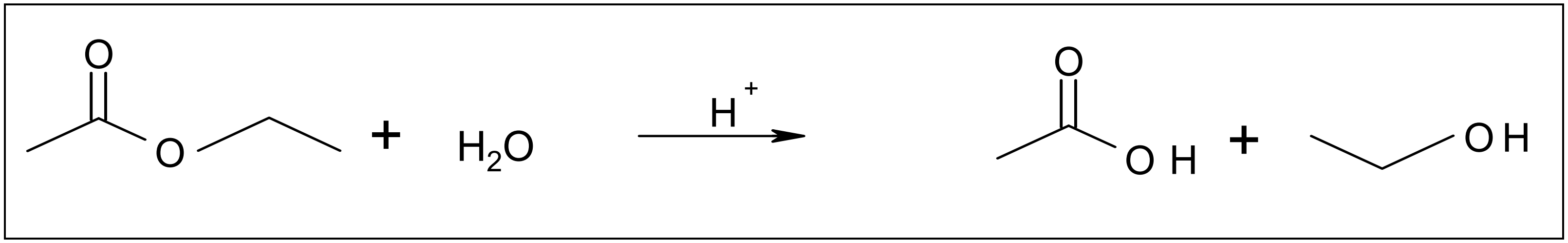


Sulfonated silica





Fluorinated polyethylene – “Nafion”



Catalyst	Acid Site Concentration /mmol g^{-1}	$\Delta H^{o}_{neut.}$ (aq. NaOH) /kJ mol^{-1}	Initial Rate (TON) /mol (acid-mol)$^{-1}$ min^{-1}
Polystyrene-SO_3H			
AMB-15	4.74	-58.3	2.5
AMB-35	5.4	-61.2	4.6
Silica-SO_3H			
MCM41-1	1.2	-54.6	2.7
MCM41-2	1.31	-54.9	2.7
MCM41-3	2.8	-54.5	2.7
SBA-15	1.15	-54.9	2.6
Aqueous Strong Acids			
0.1 mol dm^{-3} HCl	-	-52.8	
0.5 mol dm^{-3} *p*-TsOH	-	-52.4	

Physical characteristics of Amberlyst resin powders

Sulfonated polystyrene resin (≤ 125 μm)	Cation exchange capacity[a] /mmol g^{-1}	Surface area[b] /$m^2 g^{-1}$	Pore volume[c] /$cm^3 g^{-1}$	Average pore size /nm
Amberlyst 70	2.55	1.0	0.002	29.3
Amberlyst 15	4.7	37.3	0.203	24.0
Amberlyst 35	5.2	40.7	0.218	24.2

a Rohm and Haas data.[5]
b BET adsorption isotherm using N_2.
c Total volume of pores with diameters 1.7-300 nm (BJH).

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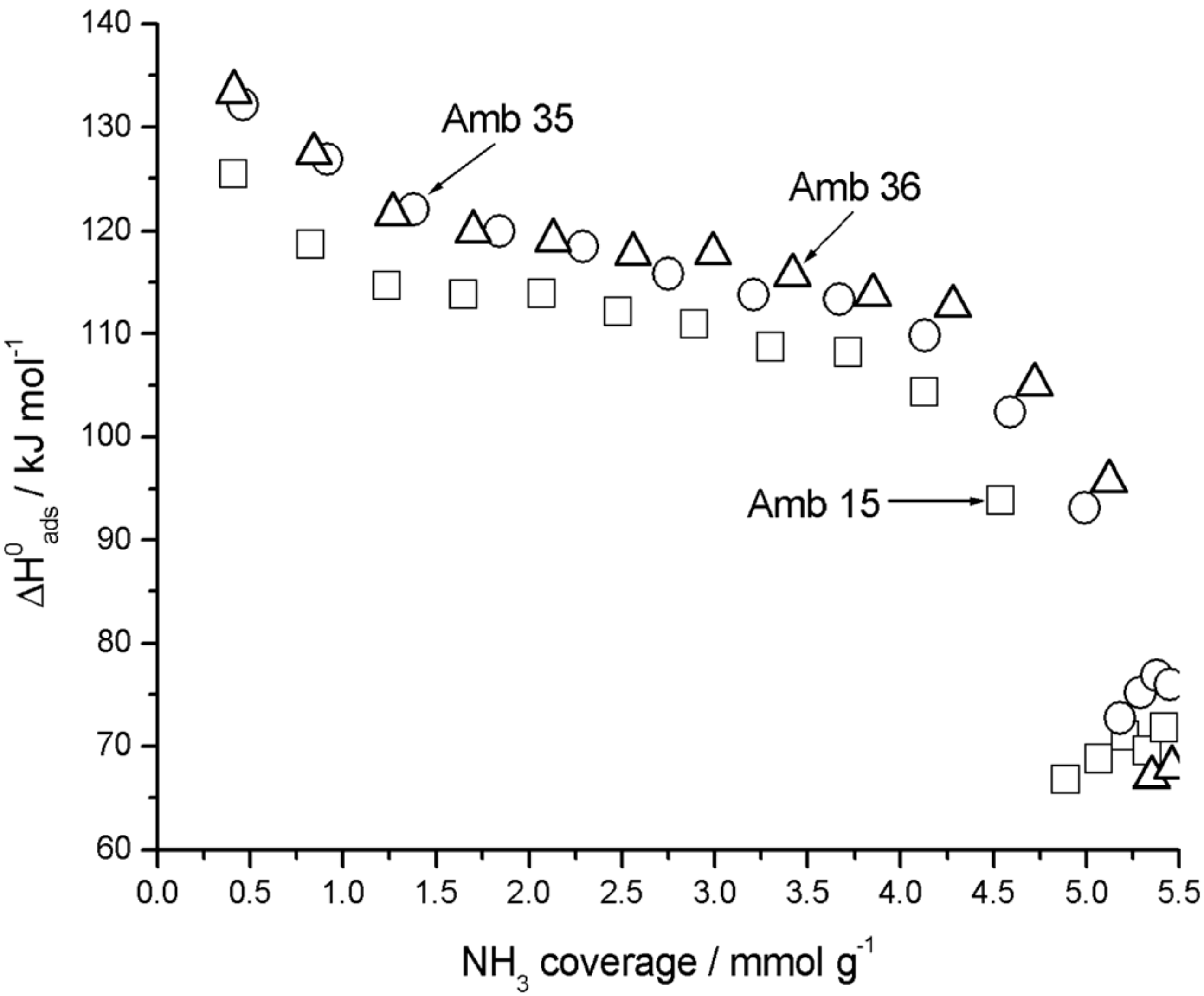
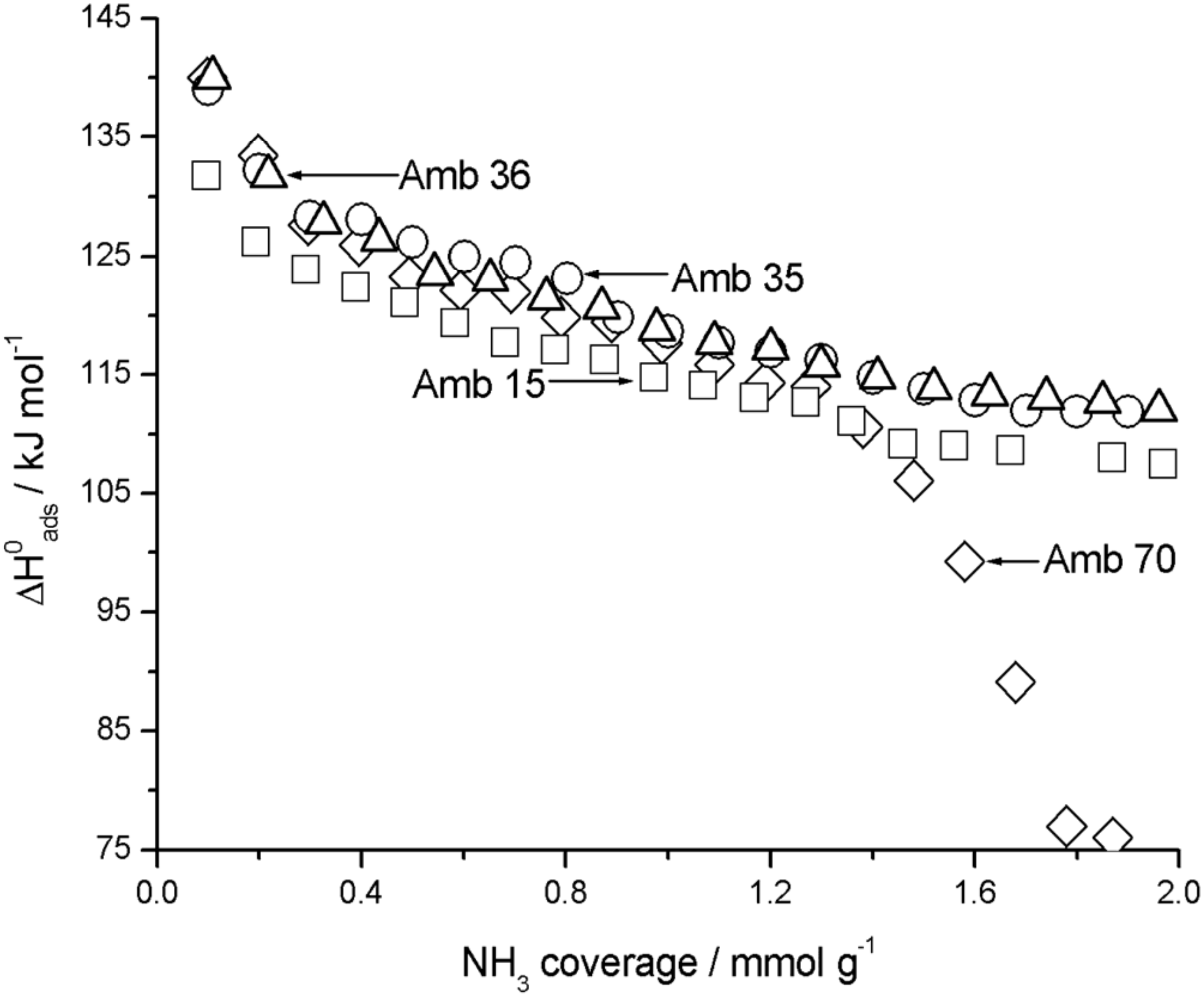
-ΔH^0_{ads}/adsorbed NH_3 for Amberlyst resins at 100 ^oC by adsorption calorimetry, sample size 5 mg



-ΔH^0_{ads}/adsorbed NH_3 for Amberlyst resins at 100 ^oC by adsorption calorimetry, sample size 20 mg



Acidity data by NH_3 adsorption calorimetry at 100 ^{o}C.

Sulfonated resin	Average $-\Delta H^0_{ads}$ [a] /kJ mol^{-1}	Total NH_3 adsorbed[b] /mmol g^{-1}	Cation exchange capacity[c] /mmol g^{-1}
Amberlyst 70	117 ± 2	1.65 ± 0.05	2.55
Amberlyst 15	110 ± 2	4.70 ± 0.10	4.7
Amberlyst 35	117 ± 2	5.20 ± 0.10	5.2
Nafion NR50	158 ± 4	0.85 ± 0.10	0.8

a Average up to coverage where ΔH^0_{ads} falls below -80 kJ mol^{-1}.
b coverage where ΔH^0_{ads} falls numerically below -80 kJ mol^{-1}.
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Acidity data by NH_3 adsorption calorimetry at 100 °C.

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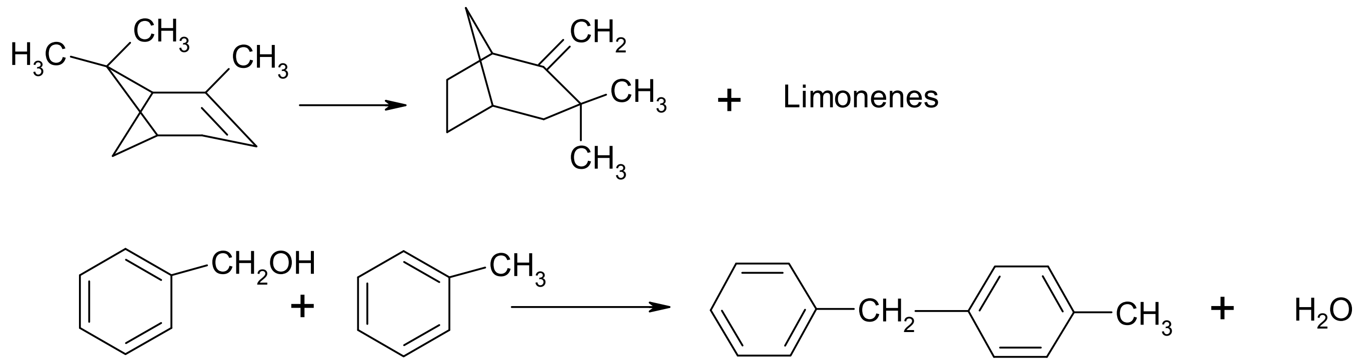
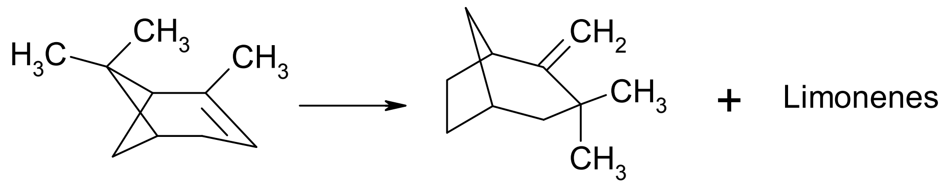
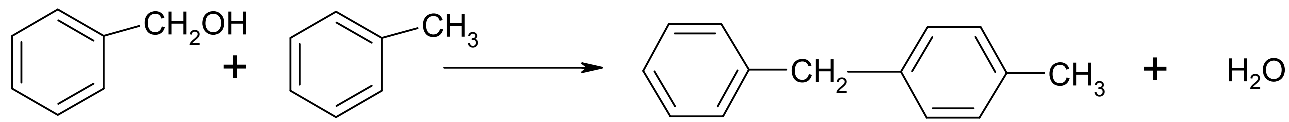


Reaction rate data

Catalyst	Isomerisation of α-pinene (conversion at 100 ^{o}C)	Benzylation of toluene (conversion of benzyl alcohol at 80 ^{o}C)
	Initial turnover frequency per acid site /h^{-1}	Initial turnover frequency per acid site /h^{-1}
Amberlyst 70	12	17
Amberlyst 15	47	13
Amberlyst 35	112	19
Nafion NR	1325	33





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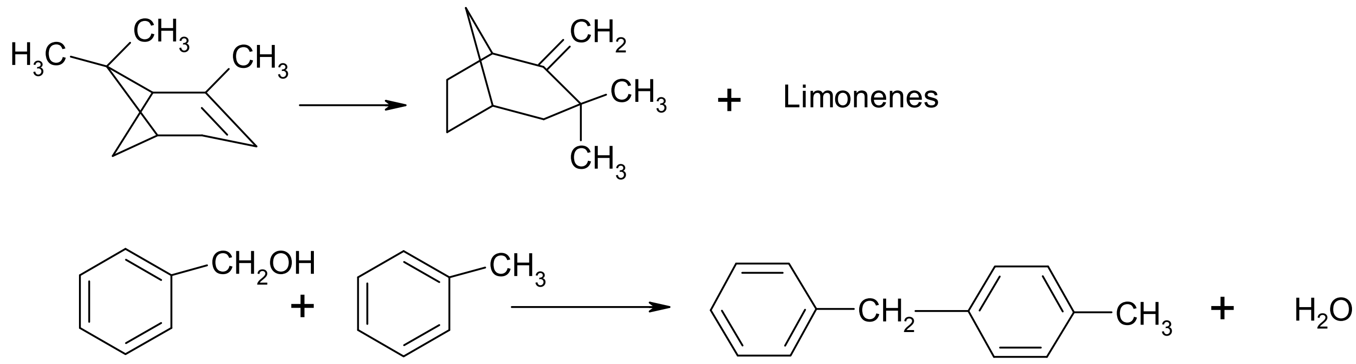

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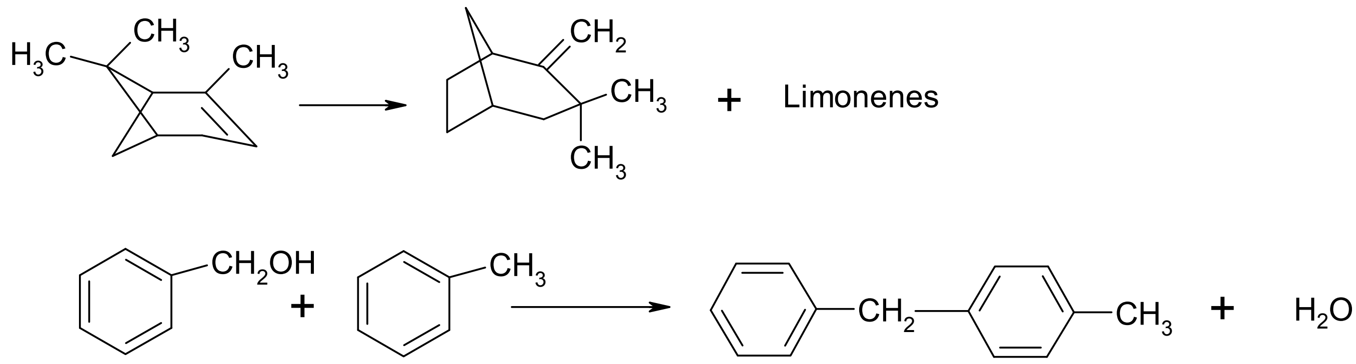

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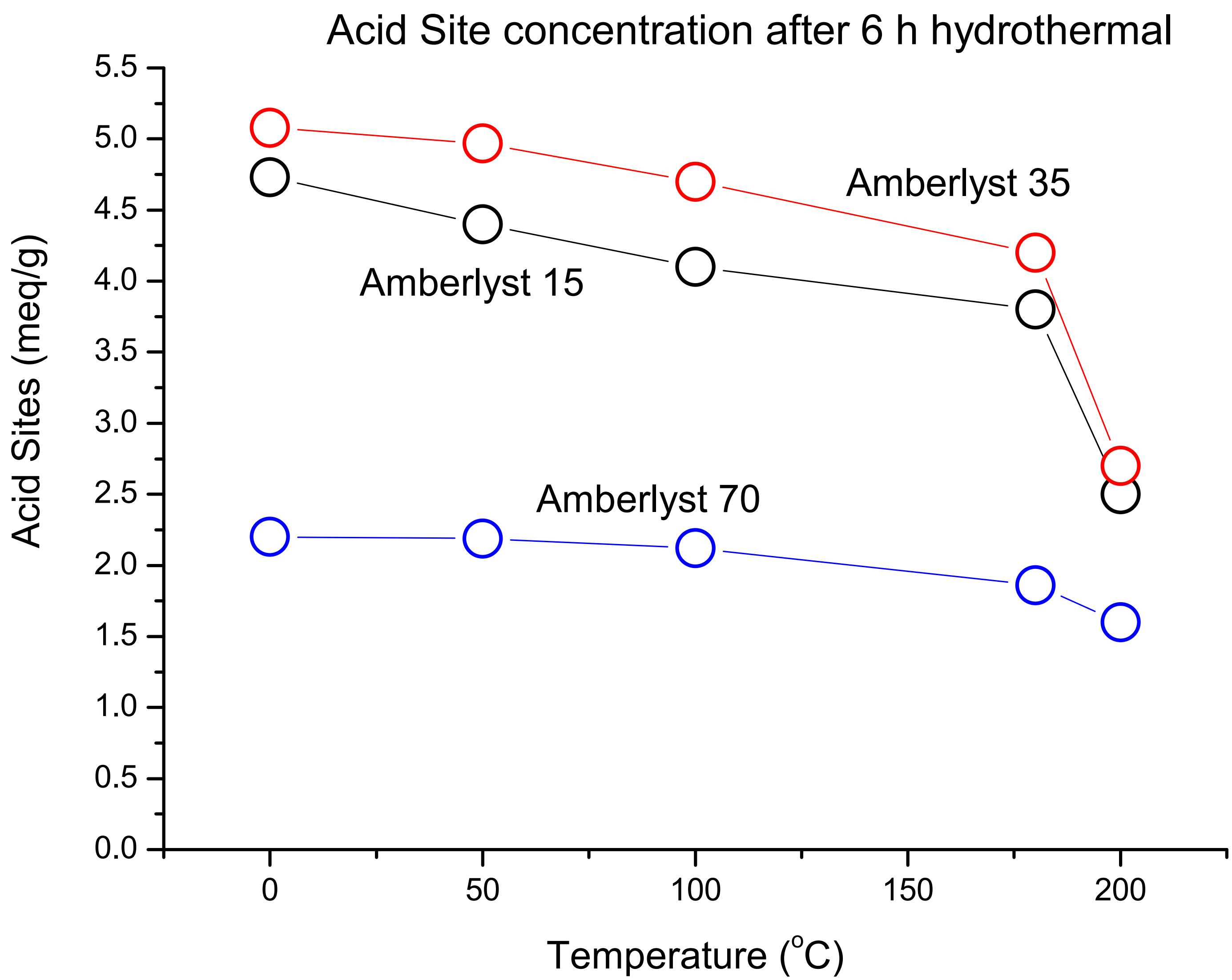
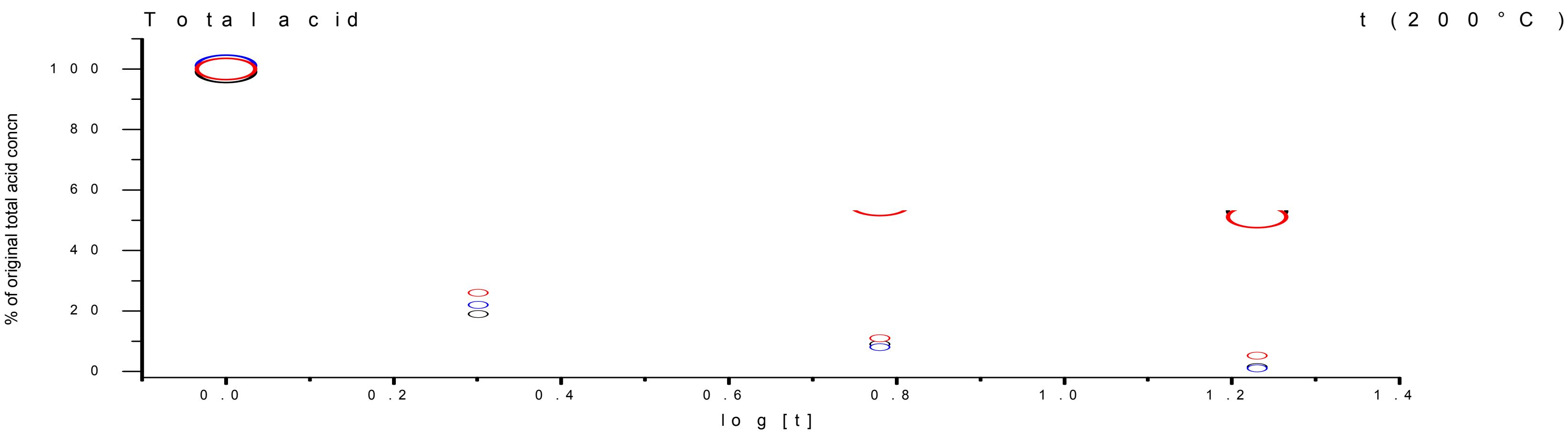
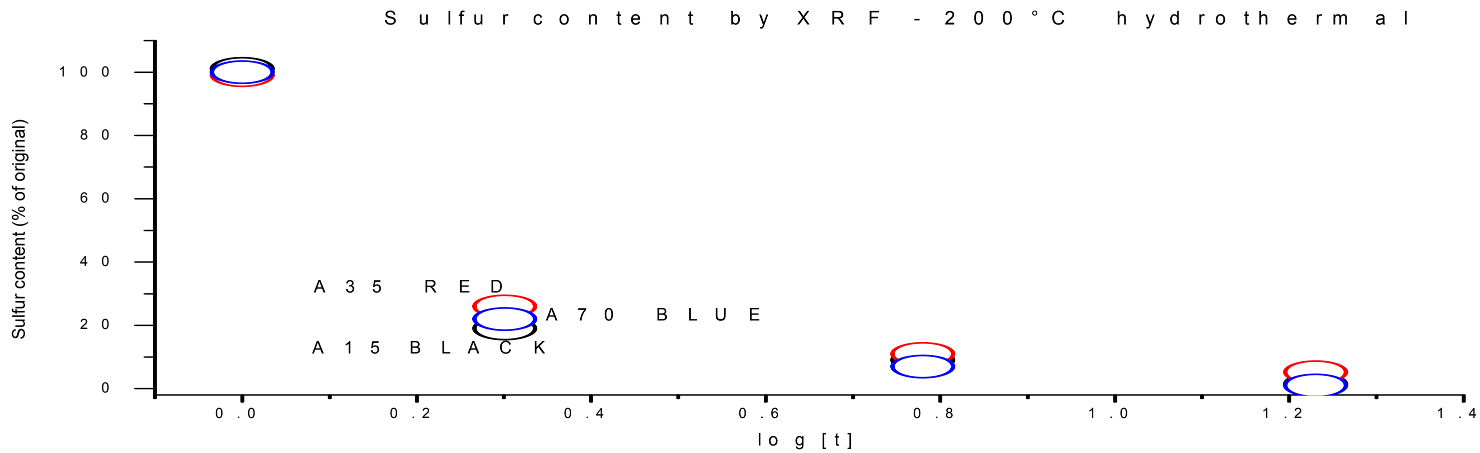
Hydrothermal stability of Amberlyst 70 compared to Amberlysts 15, 35 and 36




T o t a l a c id
t (2 0 0 ° C)
1 0 0
8 0
6 0
4 0
2 0
0
% of original total acid concn
0 . 0
0 . 2
0 . 4
0 . 6
0 . 8
1 . 0
1 . 2
1 . 4
lo g [t]



Sulfur content by XRF - 200°C hydrothermal
100
80
60
40
20
0
Sulfur content (% of original)
A35 RED
A70 BLUE
A15 BLACK
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
log[t]

Acknowledgements

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BP
University of Huddersfield

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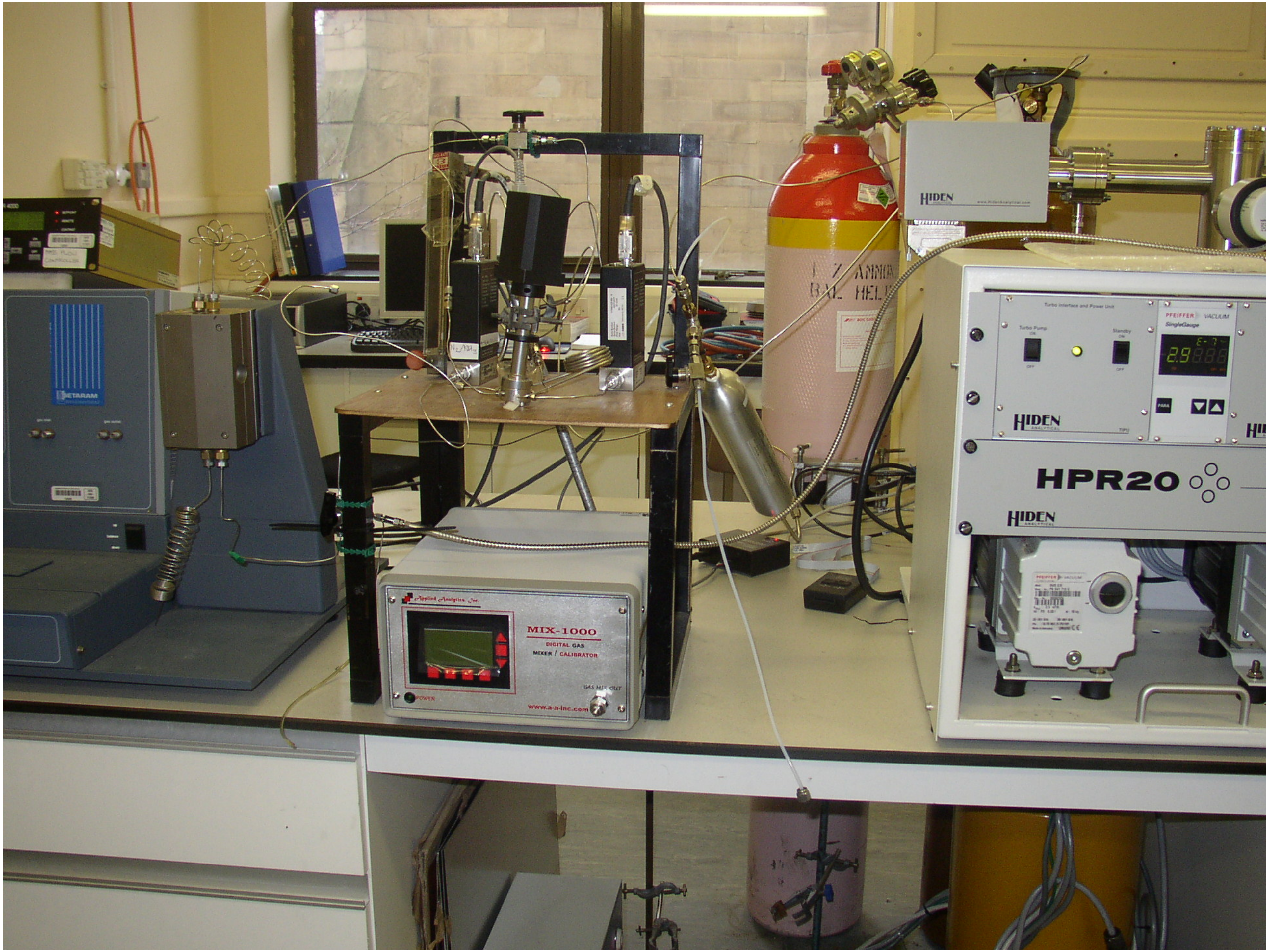
Hannah Cross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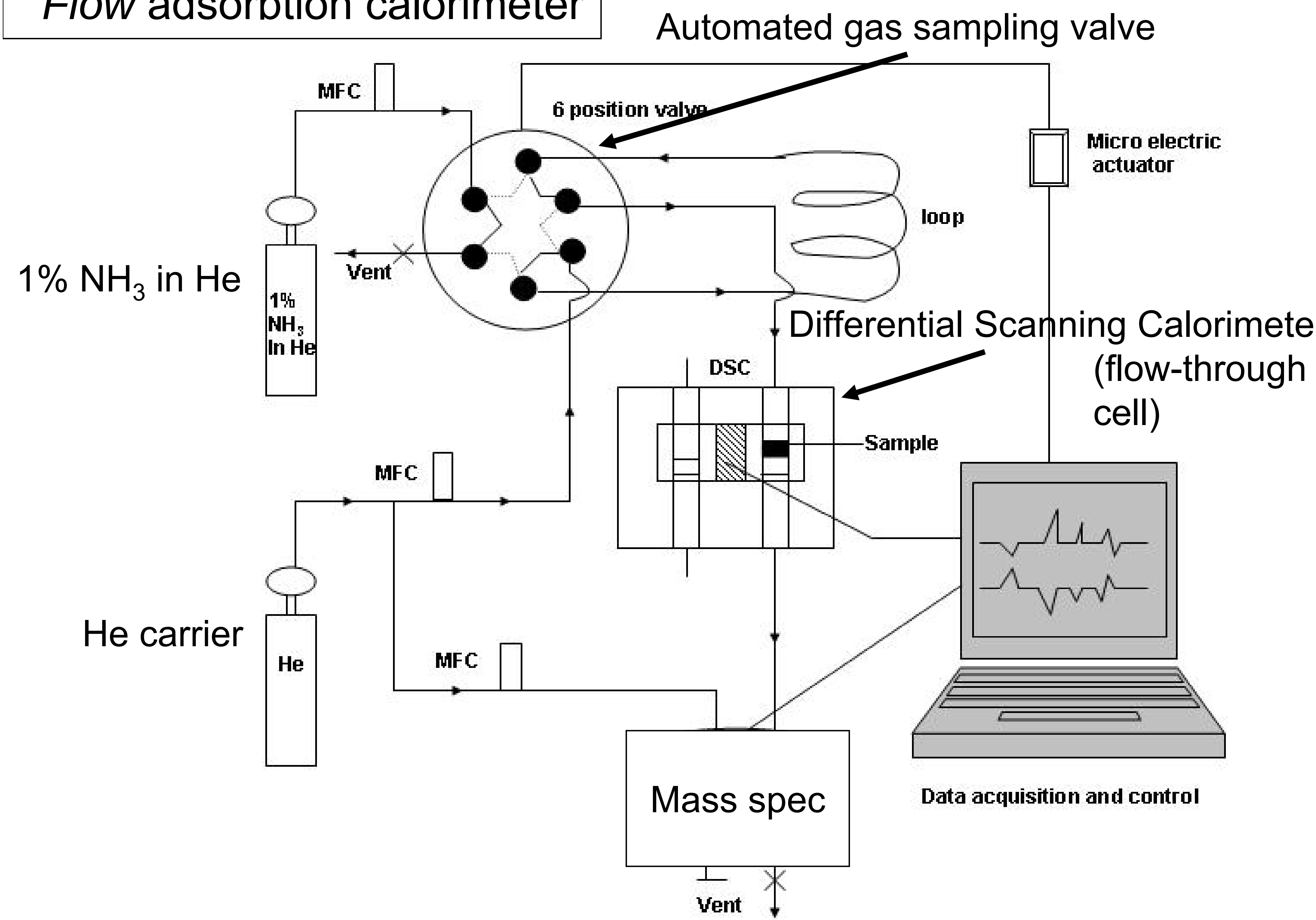
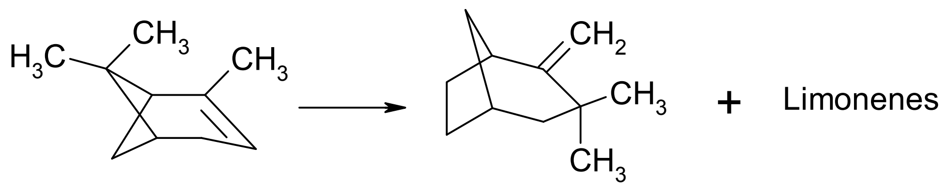
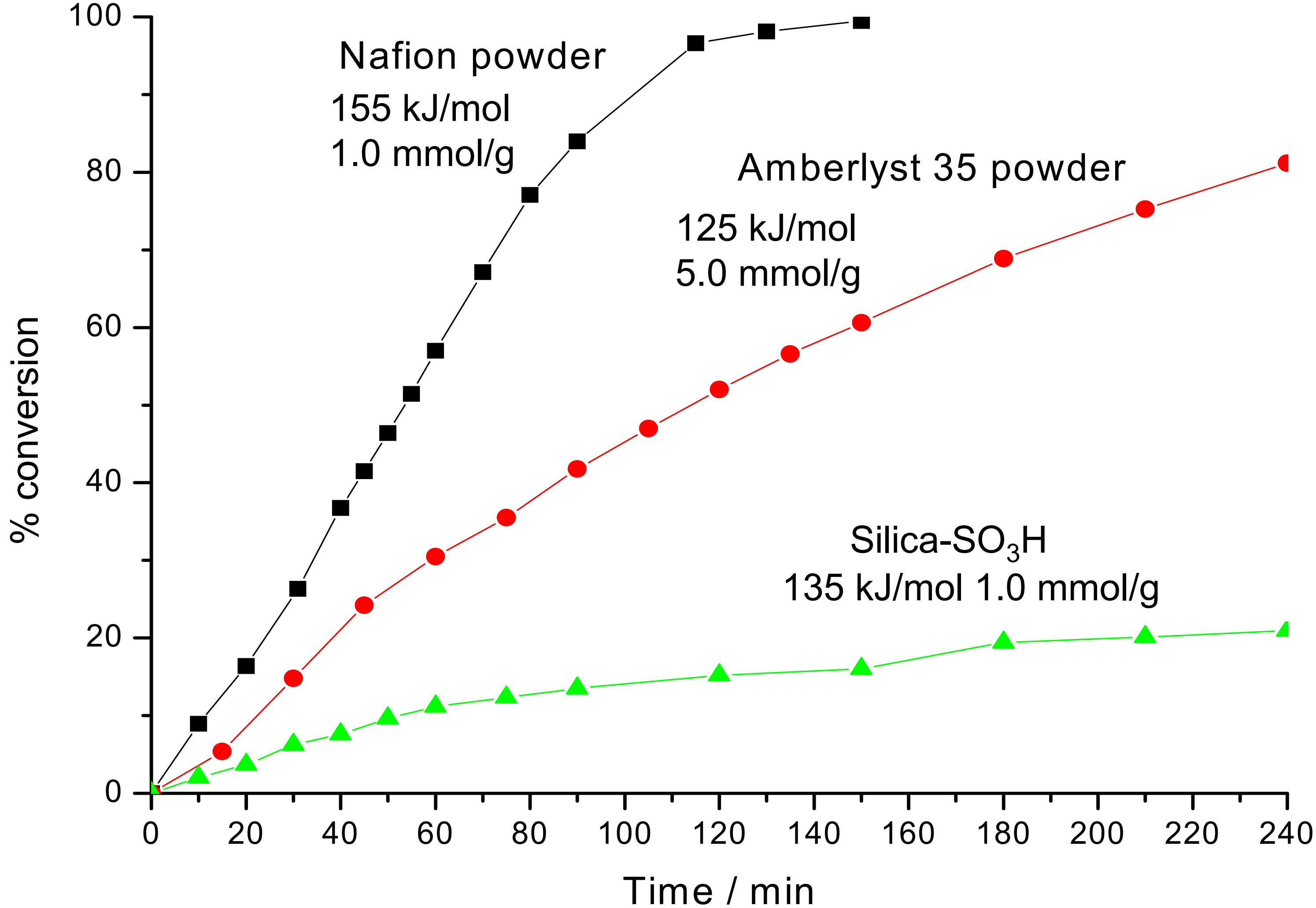
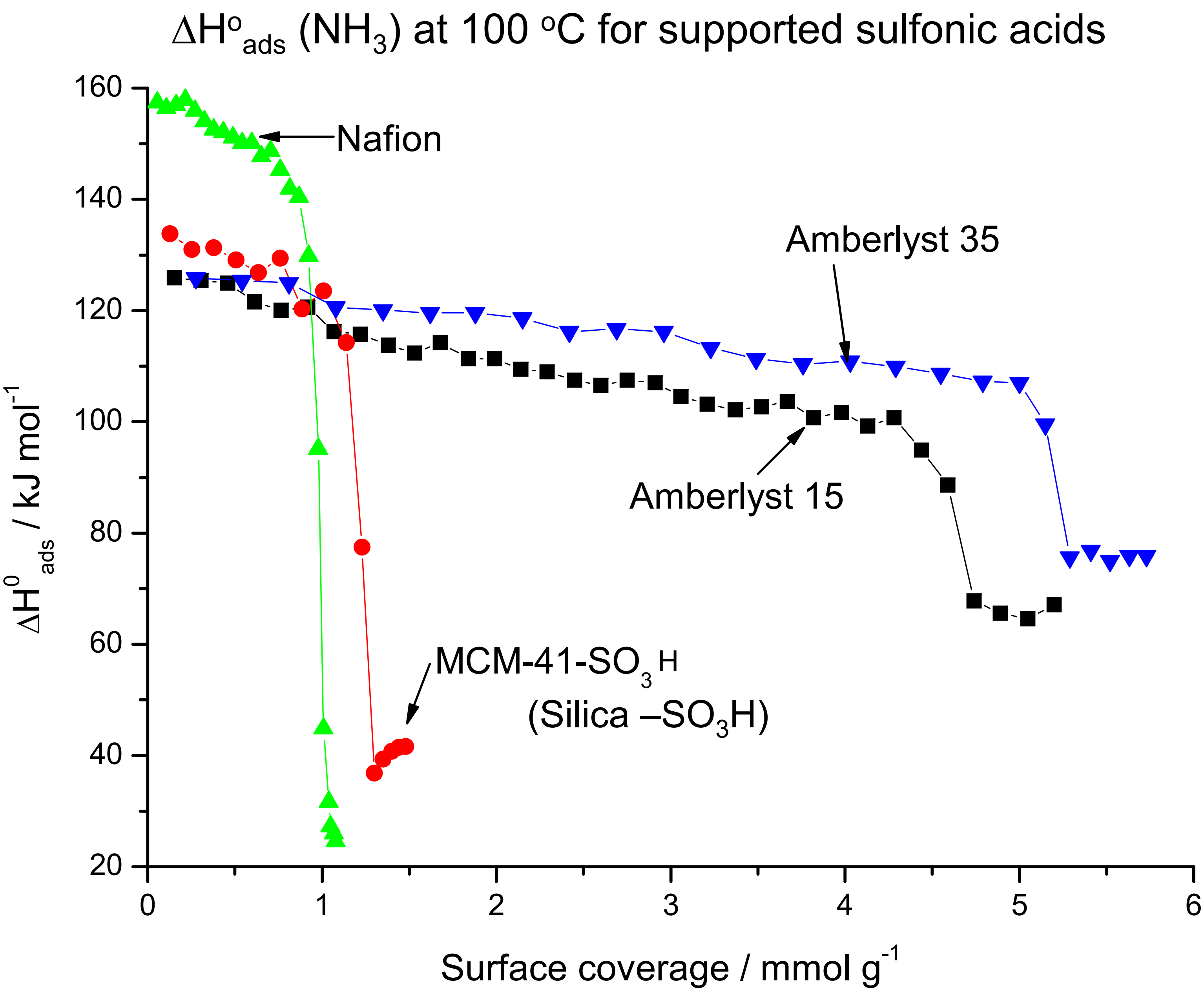
Flow adsorption calorimeter



α-pinene conversion to camphene at 100 °C

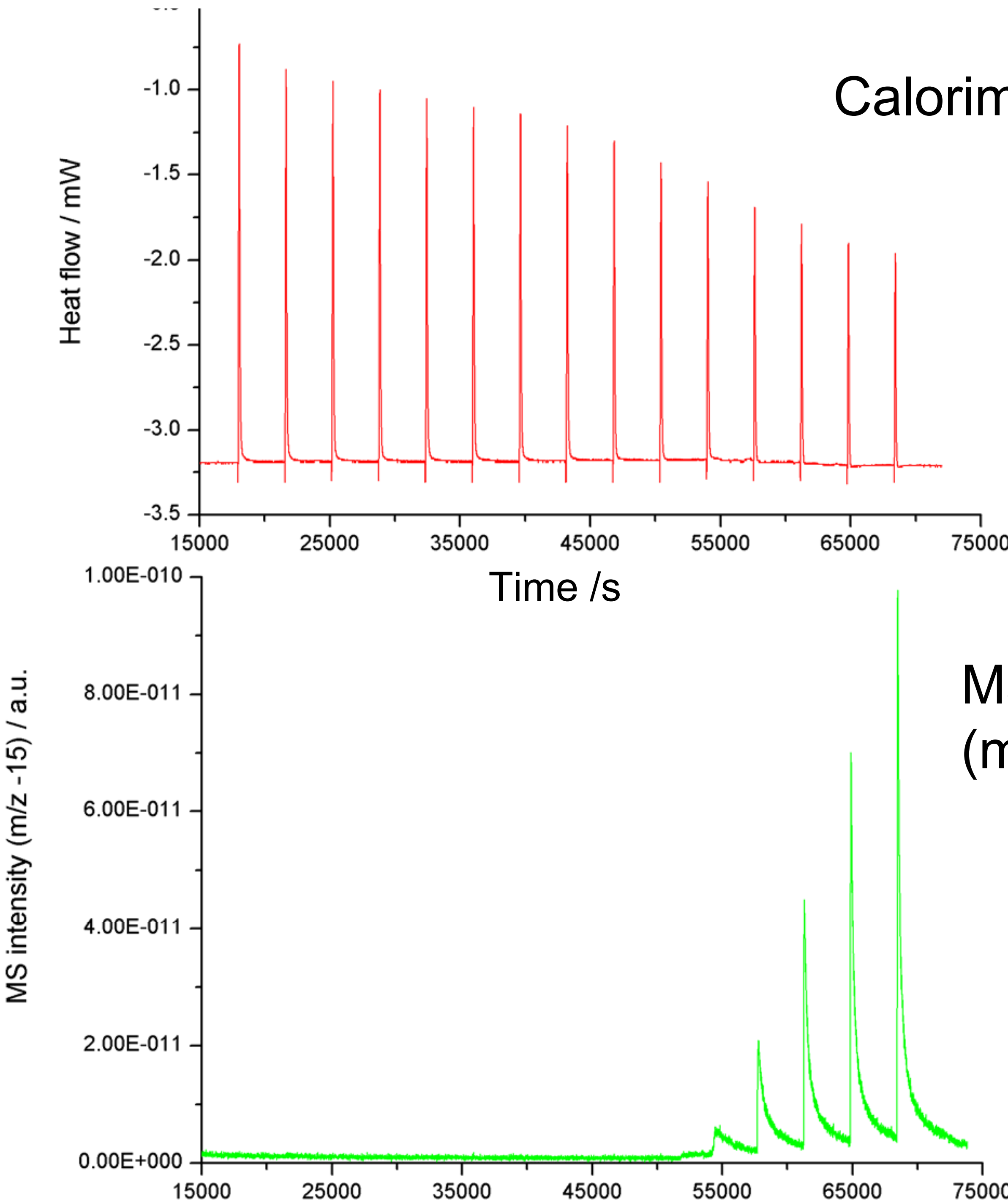




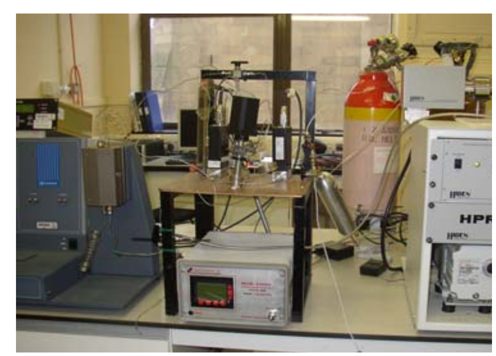


ΔH°ads (NH3) at 100 °C for supported sulfonic acids
Nafion
Amberlyst 35
Amberlyst 15
MCM-41-SO3H
(Silica –SO3H)
ΔH0ads / kJ mol-1
Surface coverage / mmol g-1
160
140
120
100
80
60
40
20
0
1
2
3
4
5
6

Calorimeter signal



Mass spec signal
(m/e 15)

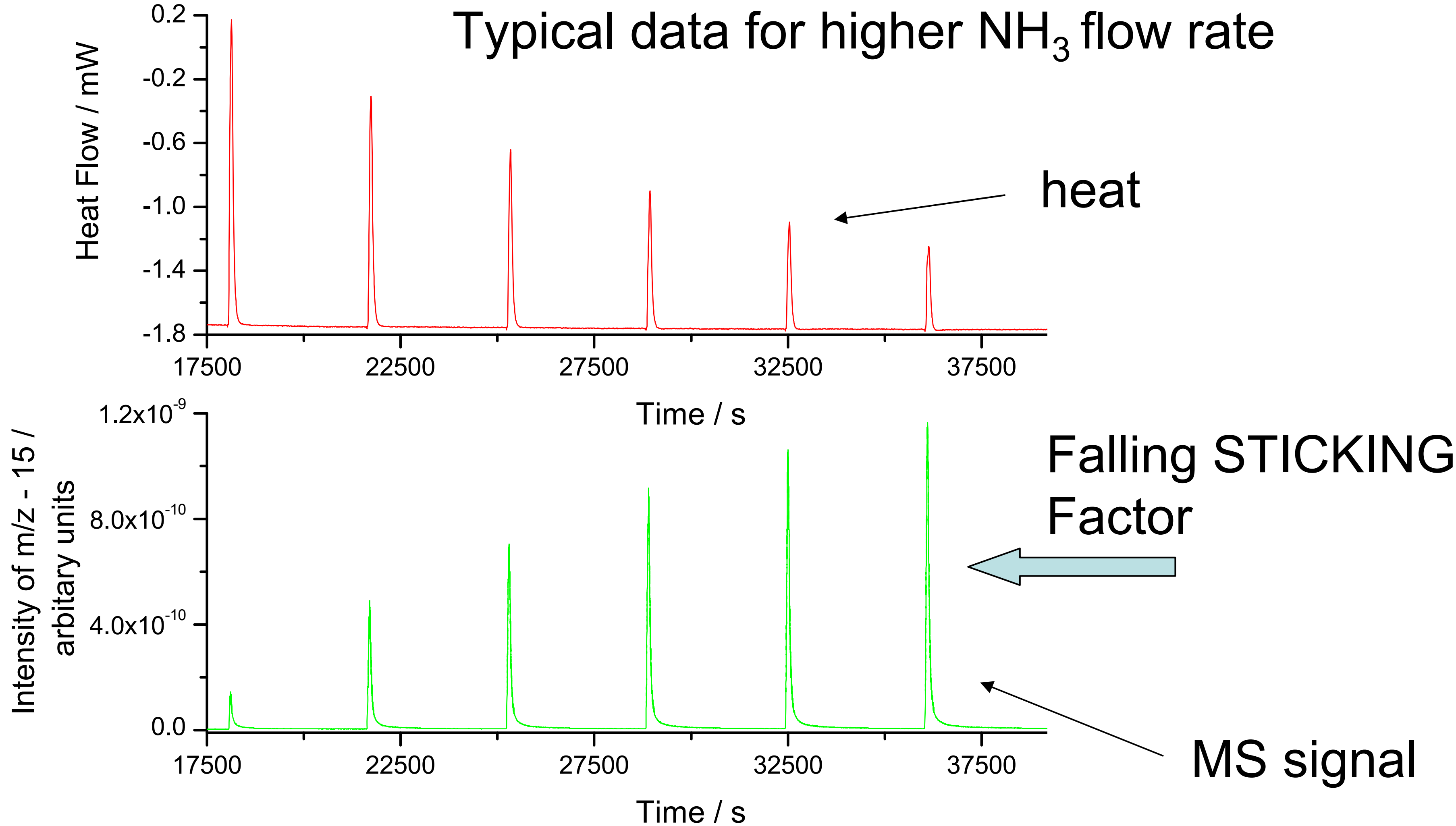


Output sensitive to the **RATE** of adsorption

Increased probe gas flow rate over sample

(reduced contact time)

Typical data for higher NH_3 flow rate



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Adsorption Calorimetry
Gas/Vapour on Solid

Capacities of adsorbent/catalysts

Adsorption enthalpies

Adsorption rates

Desorption

Adsorption Calorimetry
Gas/Vapour on Solid

Capacities of adsorbent/catalysts

Adsorption enthalpies

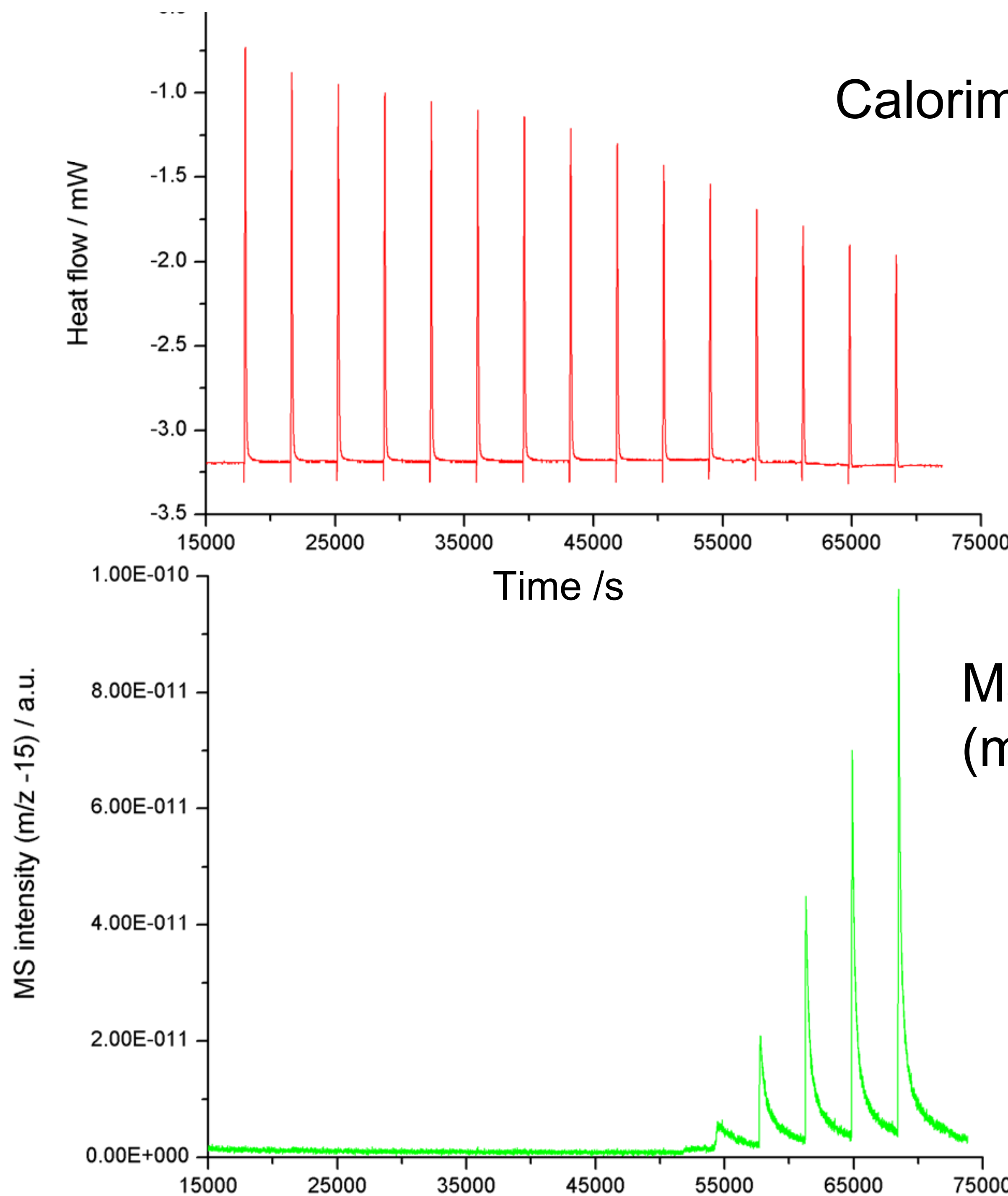
}

Strength/abundance of catalytic sites

→ Adsorption rates

Desorption

Calorimeter signal



Mass spec signal (m/e 15)