UOP, XPS, Synchrotrons and in situ

Simon R. Bare

International Workshop for New Opportunities in Hard X-ray Photoelectron Spectroscopy: HAXPES 2009

May 21, 2009

A Honeywell Company

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Variable Kinetic Energy XPS (VKE-XPS) Study of Y-Zeolites

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Outline

- XPS at UOP
- Zeolites
- Y zeolite
- Lab XPS (fixed KE) analysis of zeolites
- Variable kinetic energy XPS of zeolites
- Summary
- Outlook

X-ray Photoelectron Spectroscopy at UOP

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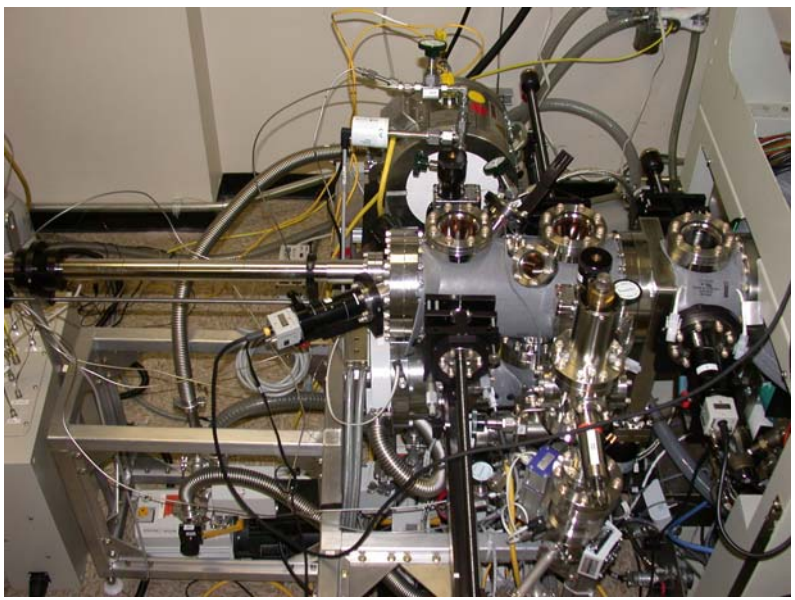
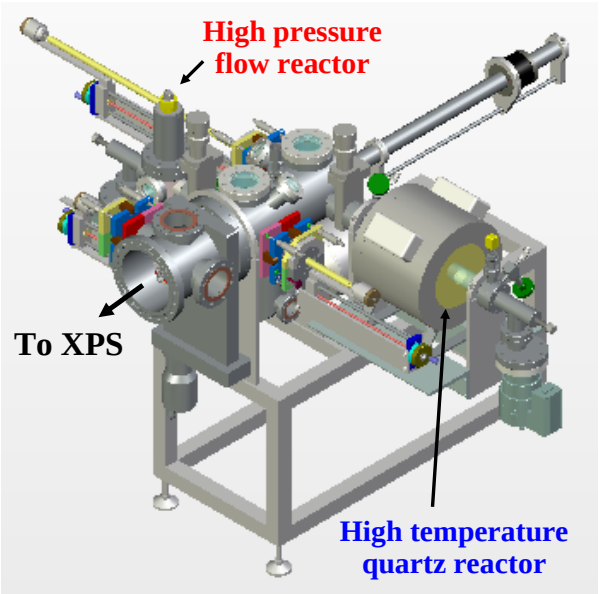
- X-ray Photoelectron Spectroscopy has always been a key catalyst characterization technique at UOP.
- Currently have two commercial spectrometers: Physical Electronics Quantum2000 and Physical Electronics Quantera.
- Used for surface analysis of catalysts, adsorbents and metallurgy: elemental concentration and oxidation states.
- Both instruments use micro-focused X-ray beams; analysis area 10 μm (spot) to 1.4 x 0.5 mm^2 rastered area.

X-ray Photoelectron Spectroscopy at UOP

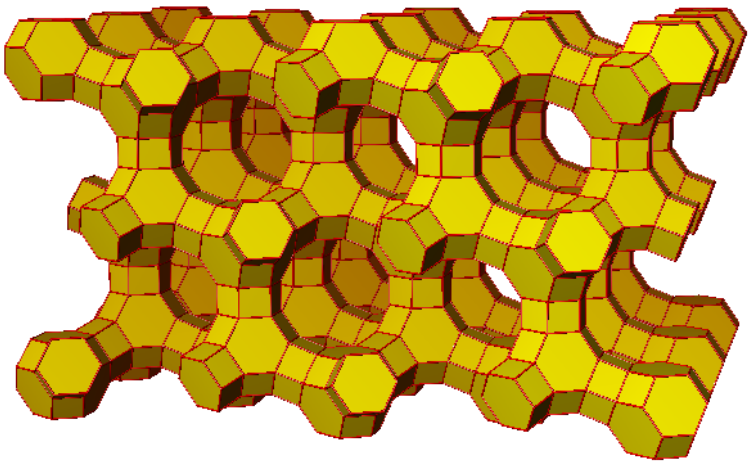
- **Two external catalytic reactors coupled to the Q2000 – allows the treatment of a sample prior to analysis.** Reduction, oxidation, reactions using gas phase hydrocarbon or a temperature controlled saturator for use with liquids.
  - Quartz Reactor for use at 1 bar & temperatures up to 700ºC
  - Cup Cell to use in pressures between mbar – 5 bar and temperatures up to 500ºC





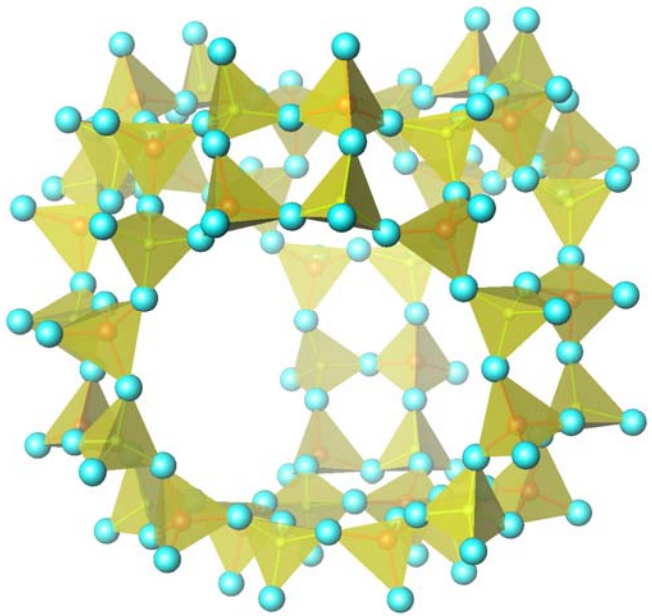
Limitation of Laboratory Instrument

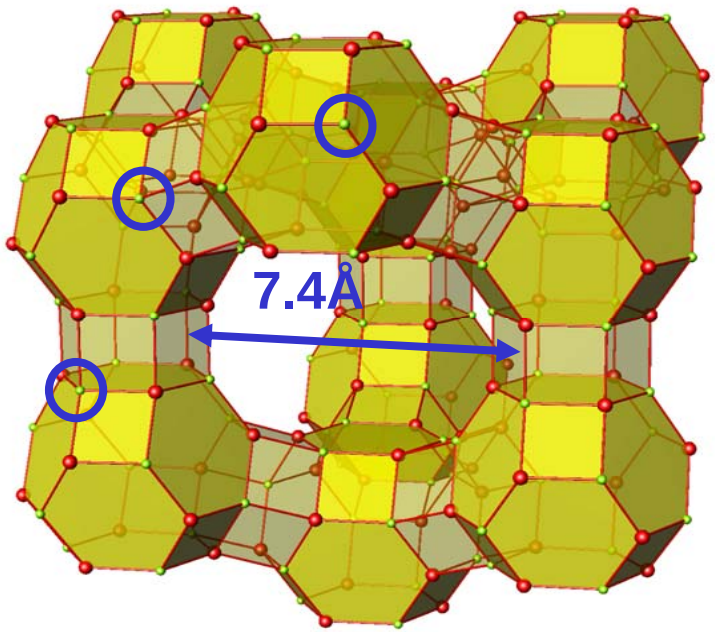
- Fixed photon energy: Al Kα 1486.6 eV
- Fixes the information depth (IMFP) that can be probed during the measurement
- Depth information determined using Ar^+ ion sputtering – sputter depth profiles
  - Destructive – changes sample
  - Preferential sputtering issues
  - Quantitative on powder samples?
- Often it would be useful to non-destructively probe the elemental surface concentration of a catalyst.
  - e.g. surface Si/Al ratio of a zeolite.



Zeolites: Solid acid catalysts

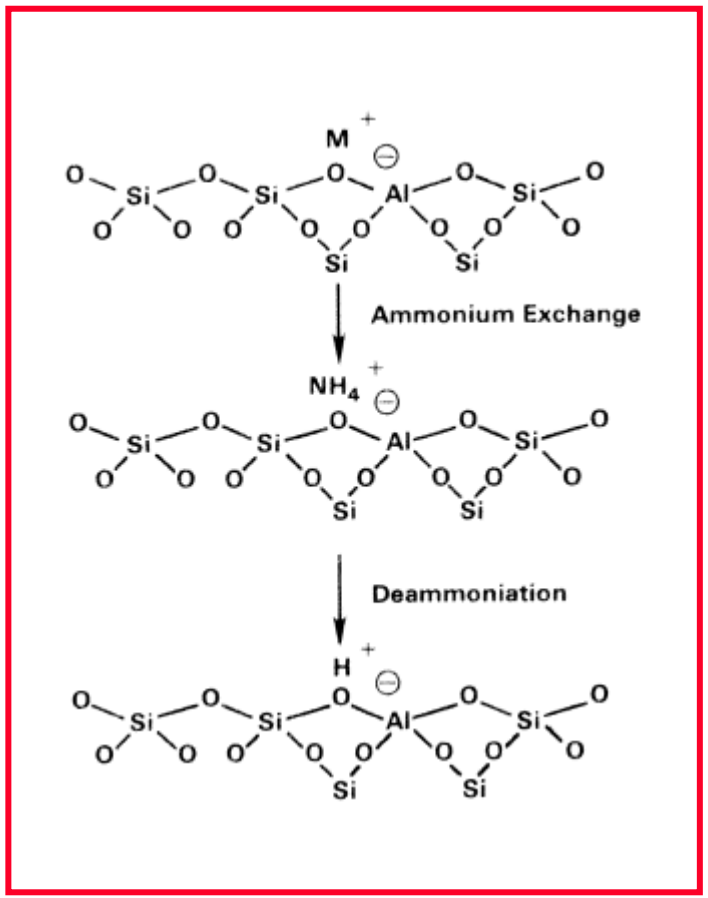
- Zeolite is crystalline aluminosilicate with a framework based on extensive 3D network of oxygen ions.
- Situated within the tetrahedral sites formed by the O can be either Si^{4+} or Al^{3+}. Charge balance achieved with cation.
- Pores of the framework are of molecular dimensions (molecular sieves).
- ~200 different zeolites have been synthesized with different 2D and3D framework structures.



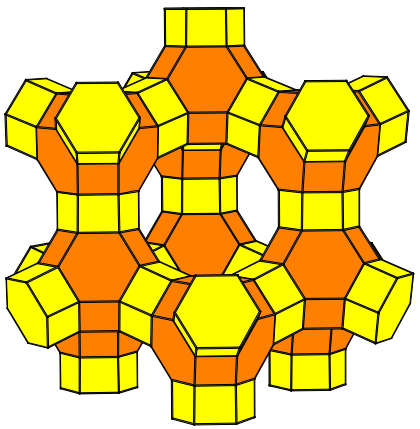


Zeolites: Solid acid catalysts

- **Acid sites in the zeolite are generated by exchanging the cation (Na) with ammonium, NH^{4+}, then thermal treatment to decompose ammonia to leave proton, H^+.**



Zeolite Y prepared in sodium form: one Na for each Al to balance charge.
To generate acid sites the Na must be exchanged with NH_4^+, then steam calcined to convert the NH_4^+ to H^+.



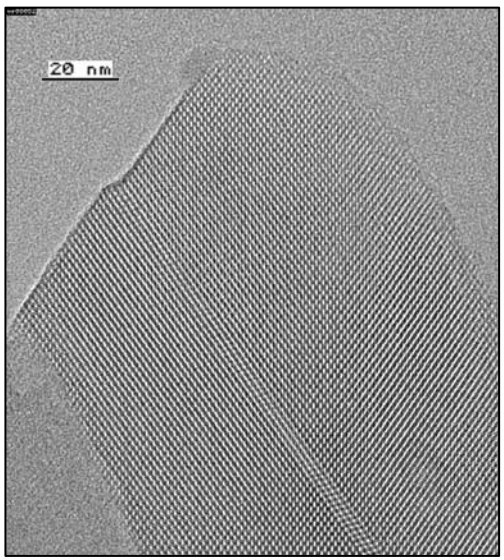
Y Zeolite (Faujasite, FAU)

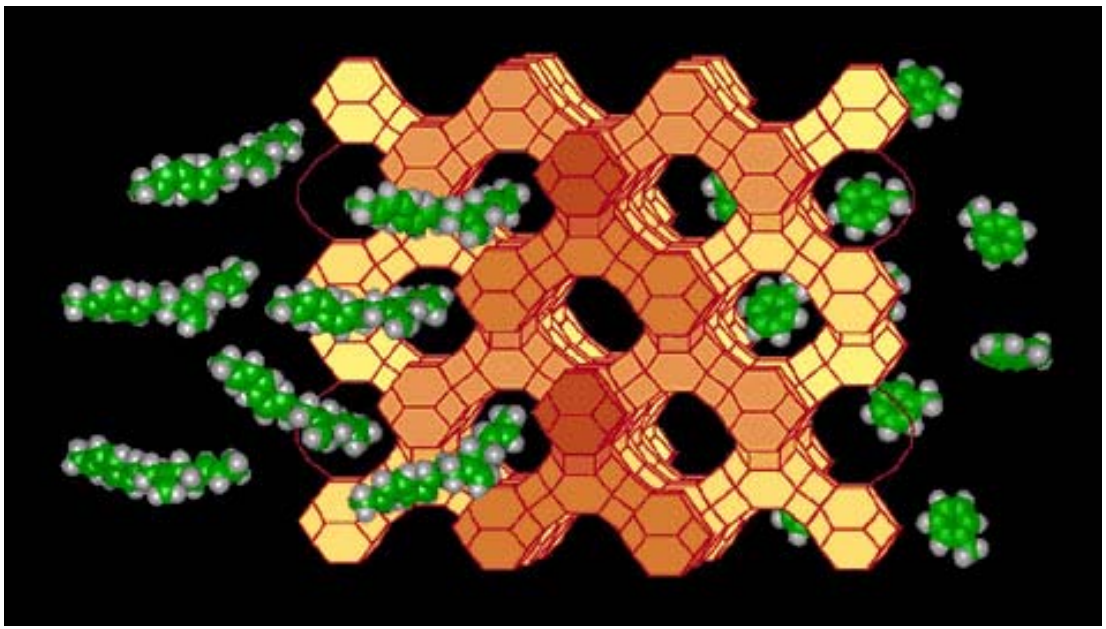
- Zeolite Y used in Fluid Catalytic Cracking (FCC)
  - to convert high molecular weight hydrocarbons into gasoline
  - >50% world's gasoline produced via FCC process

- The strength, number, and distribution of the acid sites in the Y zeolite can be controlled by varying the degree of ion exchange, the calcination temperature/time, steaming temperature/time, etc.
- These treatments will affect the activity of the zeolite.

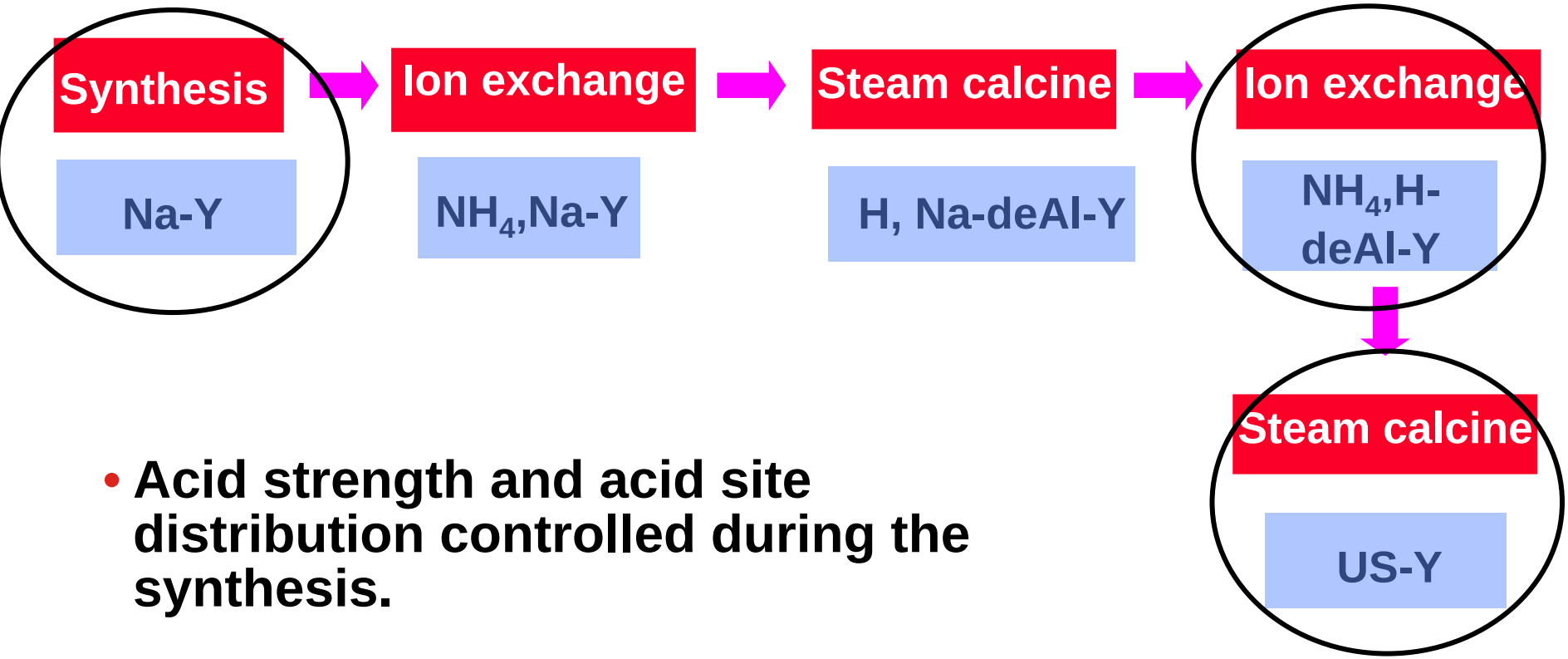
Y zeolite

- **Diffusional constraints for large molecular weight hydrocarbons in the catalyst an important issue**
  - **Location of Al (acid sites) in the zeolite is critically important.**
  - **Is the Al located near pore mouths or uniformly in zeolite channels?**





Y Zeolites: Preparation

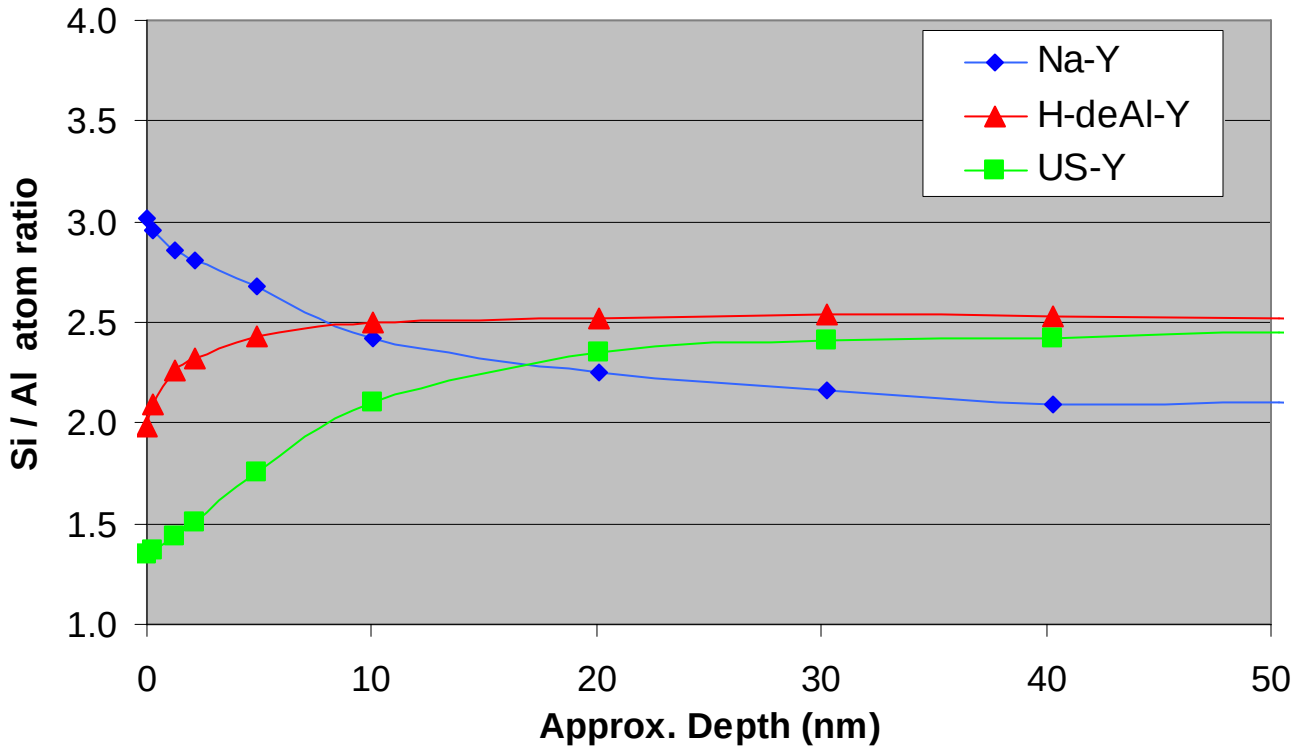


- **Acid strength and acid site distribution controlled during the synthesis.**

Lab XPS Data on Y Zeolites

- **Surface Si/Al ratio different from the bulk value of 2.6**
- **Data imply:**
  - **Na-Y is depleted in Al at surface**
  - **NH_4,H-deAl-Y is enriched in Al at surface**
  - **US-Y is strongly enriched in Al at surface**

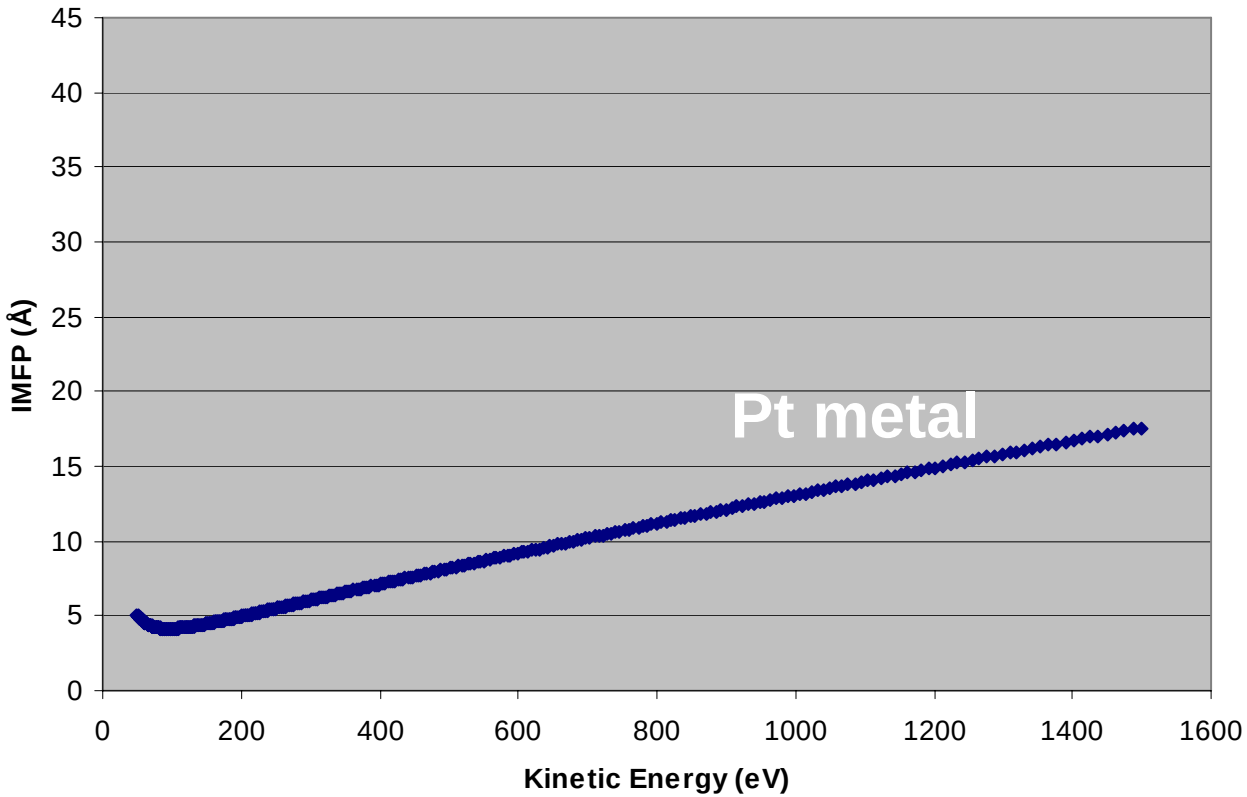
Sample	Si/Al rato
Na-Y	**3.0**
NH_4,H-deAl-Y	**2.0**
US-Y	**1.3**



- **SDP indicates concentration gradient that approaches the bulk value.**

Depth information in XPS: Mean Free Path

- **The mean free path calculated using TPP-2M***

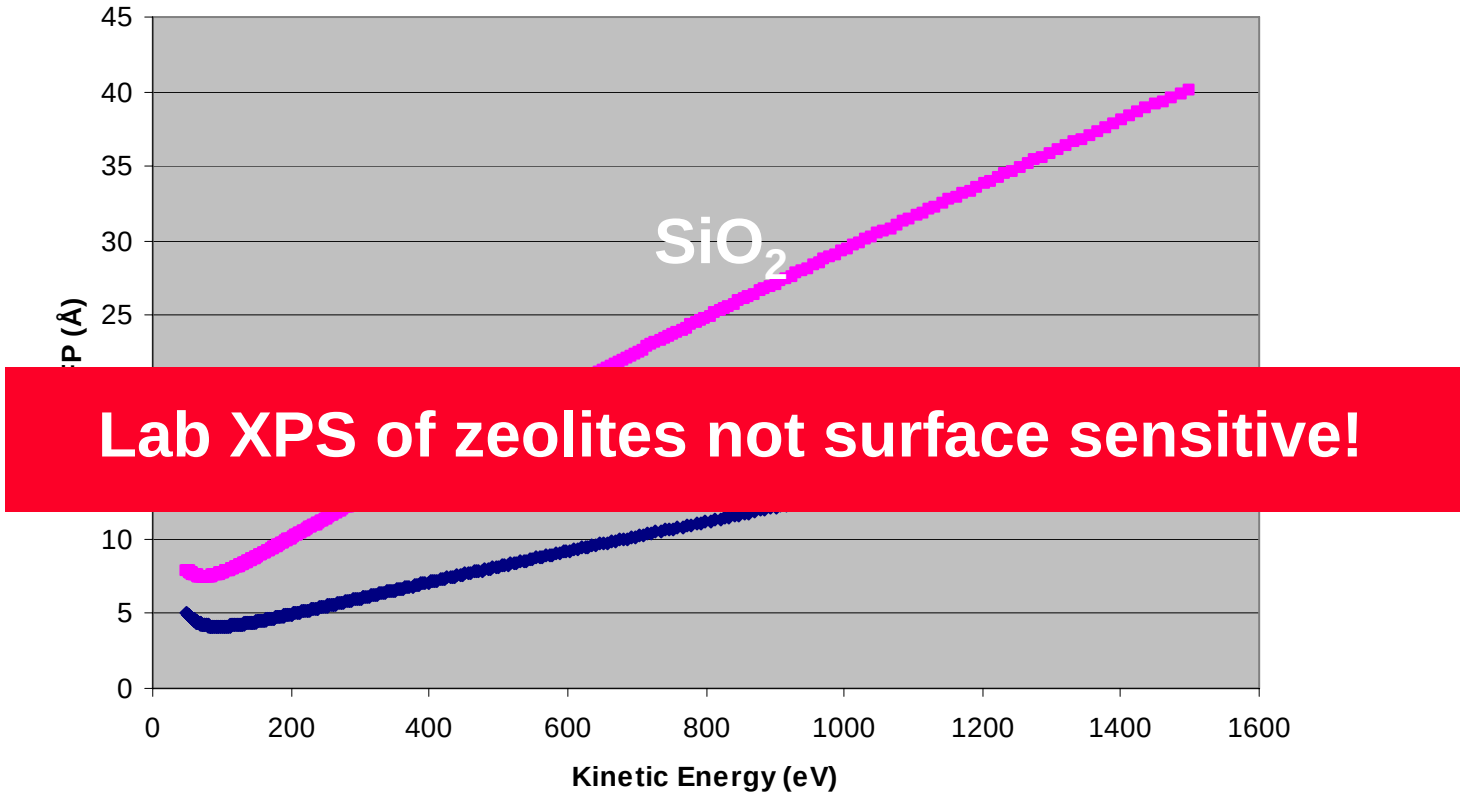


- **Using AlKα, Pt4f has KE ~1415 eV, so signal from 15-45Å: near surface being probed**

***Tanuma, Powell & Penn, TPP=2M, (Surf. Interface Anal. 17 (1991) 927)**

Depth information in XPS: Mean Free Path

- **The mean free path calculated using TPP-2M***

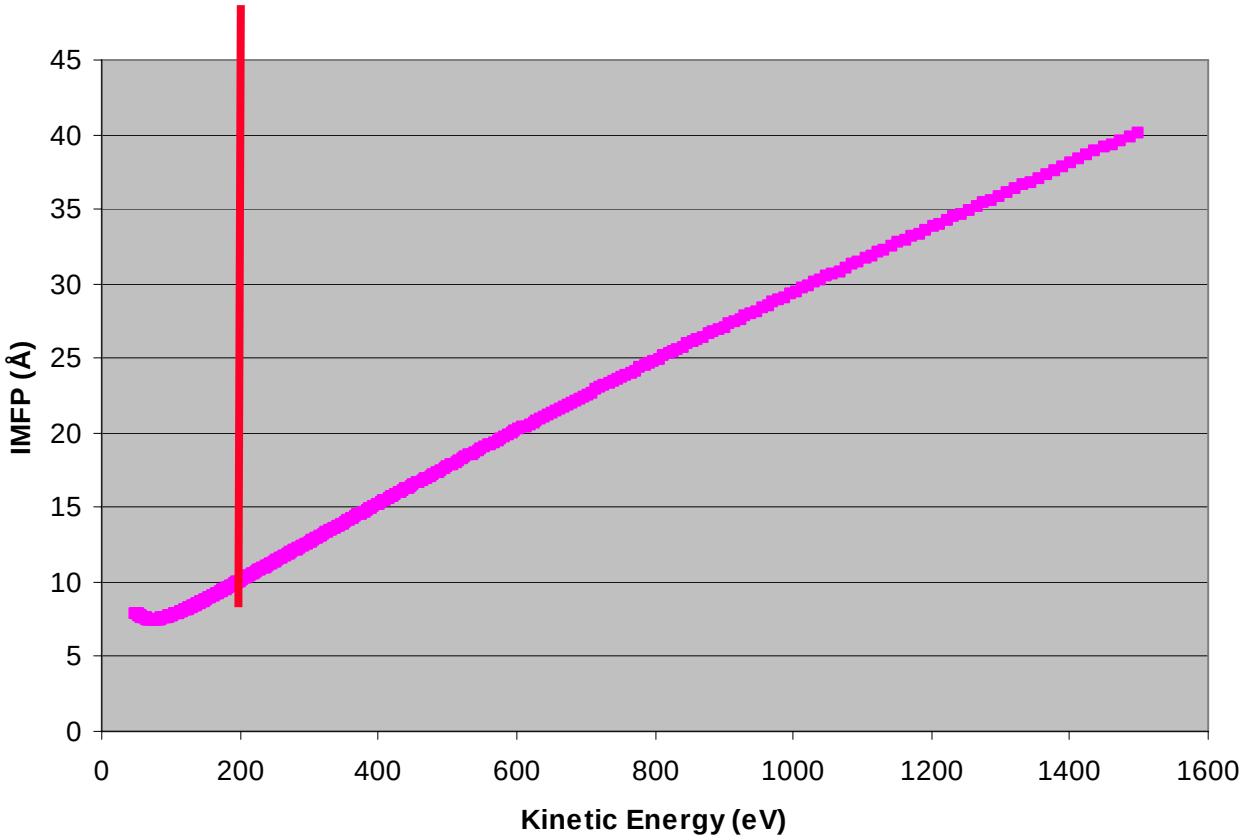


- **Using AlKα, Si2p has KE ~1386 eV, so signal from 38-114Å!**
- **Can this truly be called surface analysis?**

***Tanuma, Powell & Penn, TPP=2M, (Surf. Interface Anal. 17 (1991) 927)**

Variable Photon Energy XPS

- **Use a synchrotron beamline to vary the photon energy so that signal is more representative of the external surface region of the zeolite.**
- **But XPS is never the true surface for zeolites – need low energy ion scattering (LEIS).**



Experimental

- **XPS data collected at BESSY using the ambient pressure XPS spectrometer of the Dept. Inorganic Chemistry at the Fritz-Haber-Institut der Max-Planck-Gesellschaft.**
- **Beamline ISISS.**

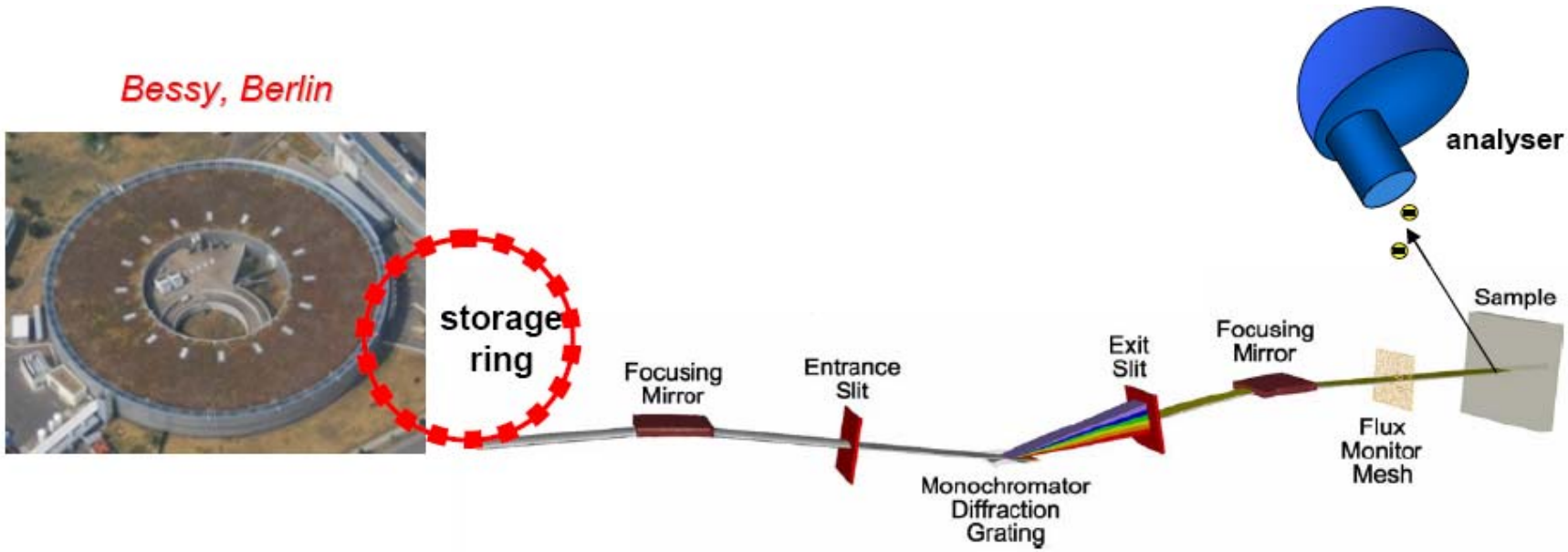
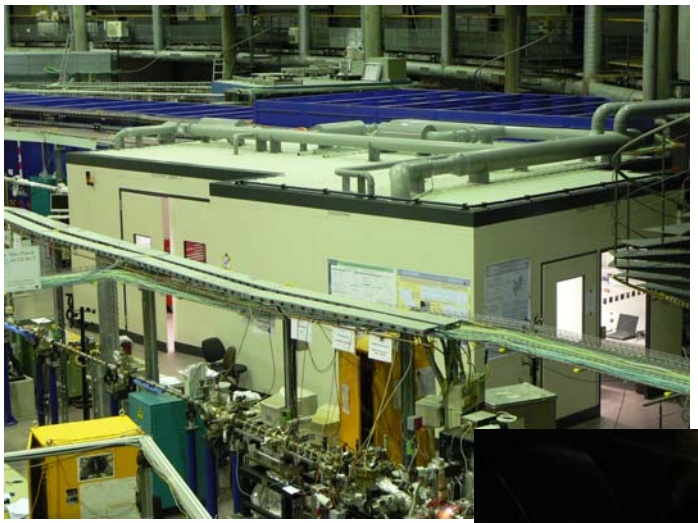
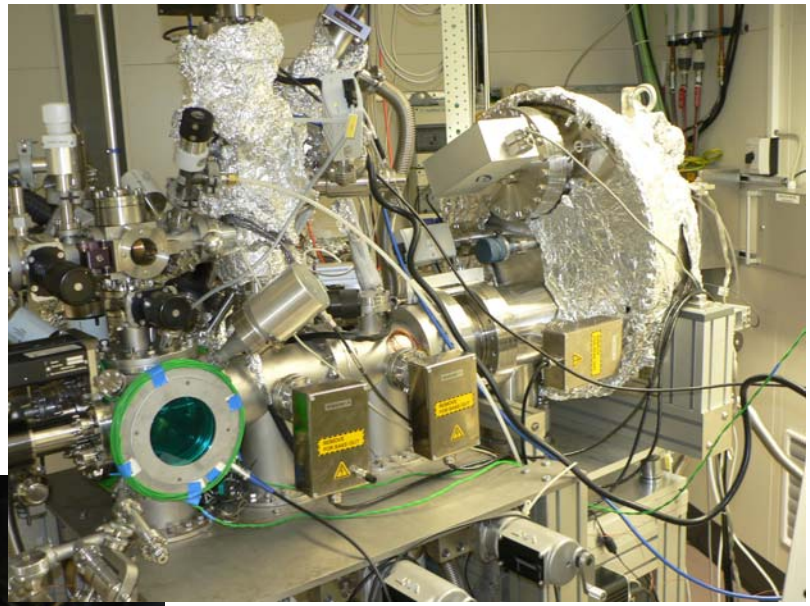


Figure adapted from Dr. Christian Linsmeier, Max-Planck-Institut fur Plasmaphysik

Experimental

- Usable photon energy range 210-1400 eV (limited by photon flux from monochromator) and transmission through analyzer)
- Zeolite samples dispersed on a Au foil and mounted in spectrometer.





Experimental

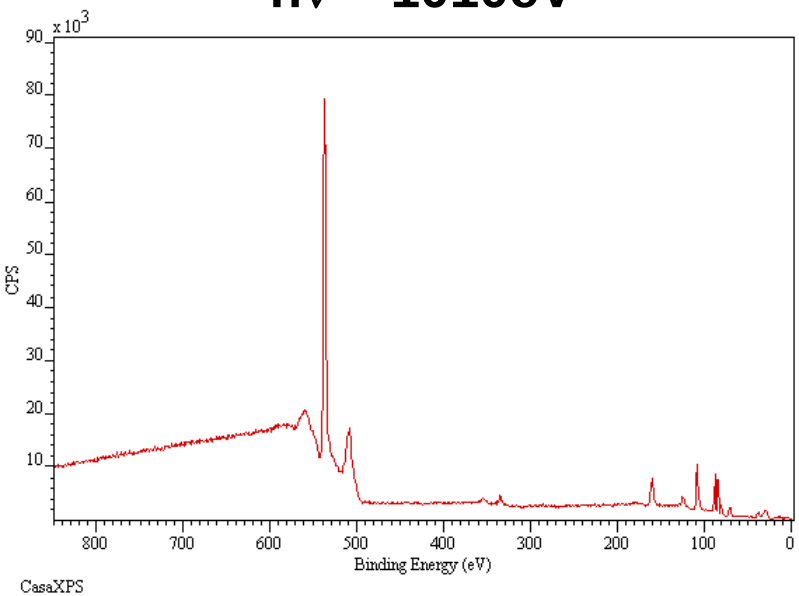
- XPS spectra collected on series of Y zeolites – at reaction temperature (225°C), and in the presence of moisture (0.5 mbar H_2O)
  - pseudo in situ!
- Integrated intensity of Si2p and Al2p corrected for cross-section as a function of photon energy, flux as function of energy, and beam current.
- Data shown as atomic Si/Al ratio.

XPS Survey Scans: Na-Y zeolite

- **Comparison with lab data:**
  - **Spectra on insulating powdered solid (zeolite) with good s/n data can be recorded.**
  - **XPS data from beamline and lab similar.**

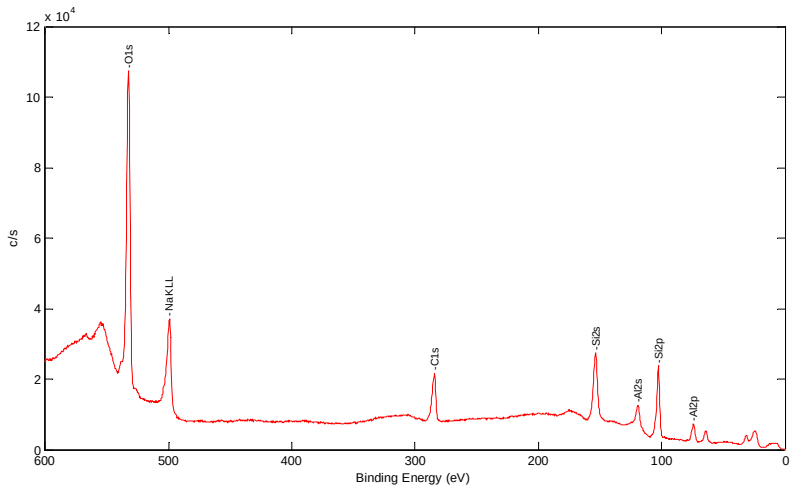
BESSY XPS data

hν = 1010eV



Lab XPS data

hν = 1486.6eV



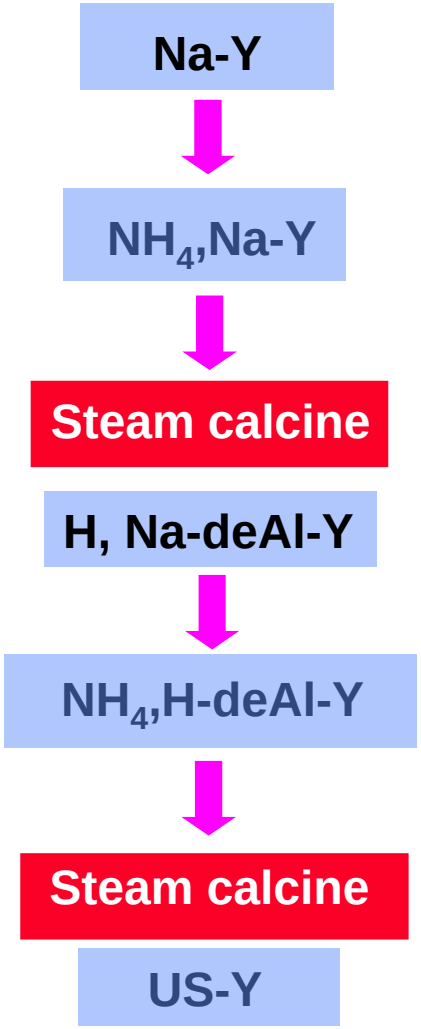
Si/Al ratio: comparison with lab XPS

Si/Al ratio		
Sample	Lab XPS (1486.6 eV)	Synchrotron XPS (1210 eV)
Na-Y	3.0	2.77
NH_4,H-deAl-Y	2.0	2.3
US-Y	1.3	1.83

- **Same trend in Si/Al ratio for the Y-zeolites for lab and synchrotron XPS data.**
  - Na-Y is depleted in Al at surface
  - NH_4,H-deAl-Y is enriched in Al at surface
  - US-Y is strongly enriched in Al at surface

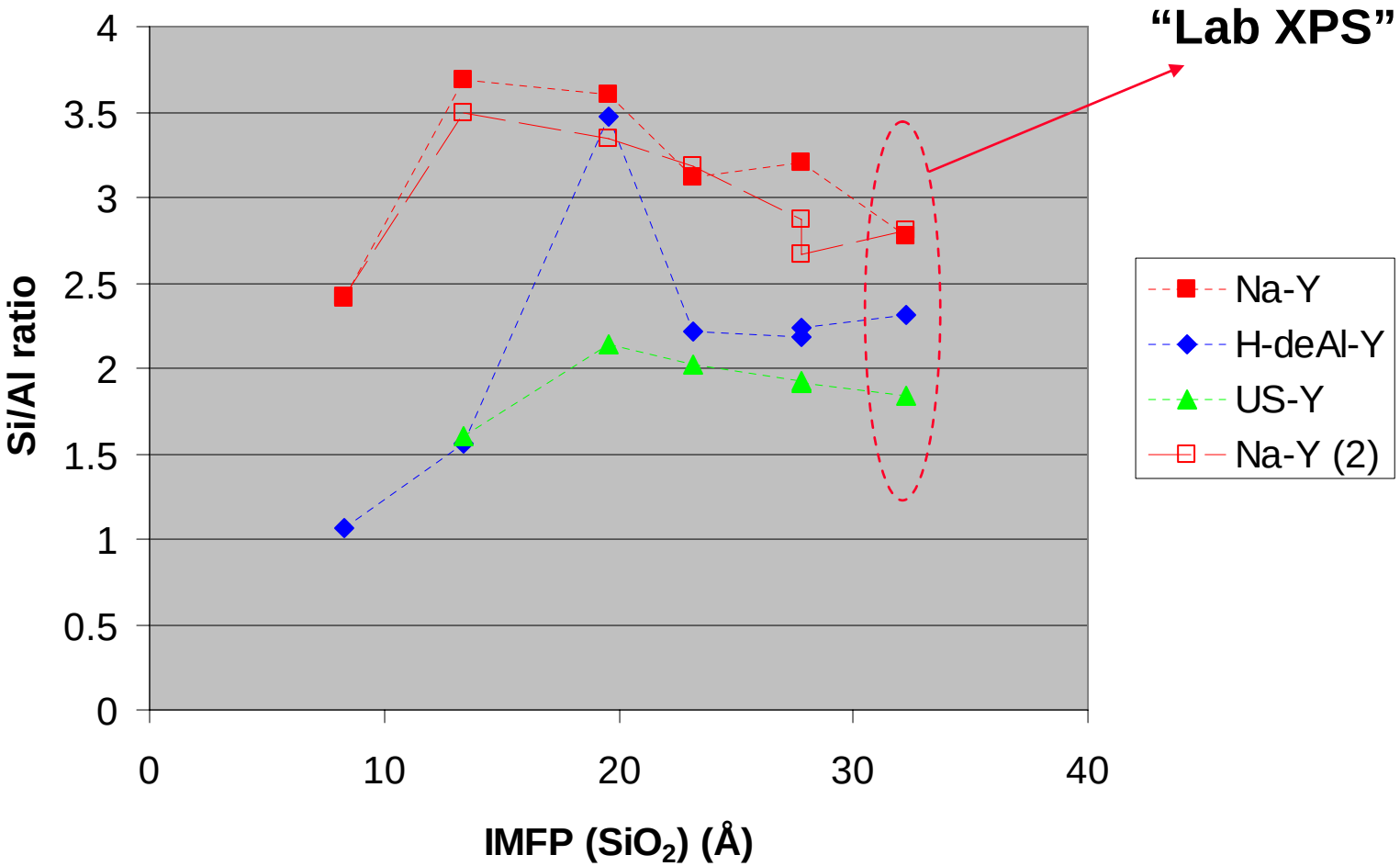
- **Absolute differences due to ΔE of 200eV kinetic energy.**

- **Bulk Si/Al for all samples ratio is 2.6.**



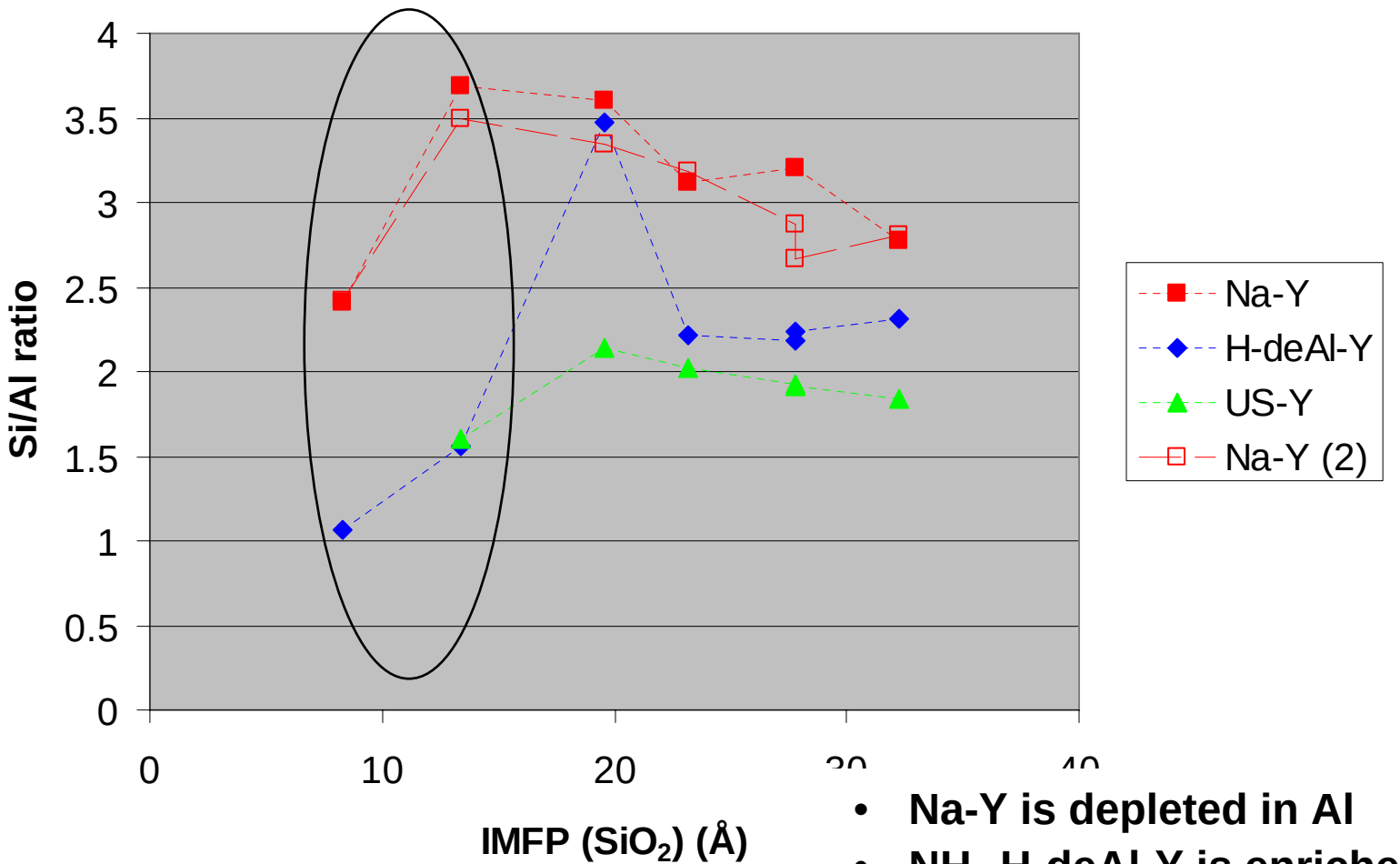
Results: Si/Al ratio as f(IMFP)

- Data points at 32Å correspond approx to the lab XPS IMFP (1210 eV (32Å) vs. 1486 eV (40Å) photon energy).
- All data at lower IMFP are new information.



Results: Si/Al ratio as f(IMFP)

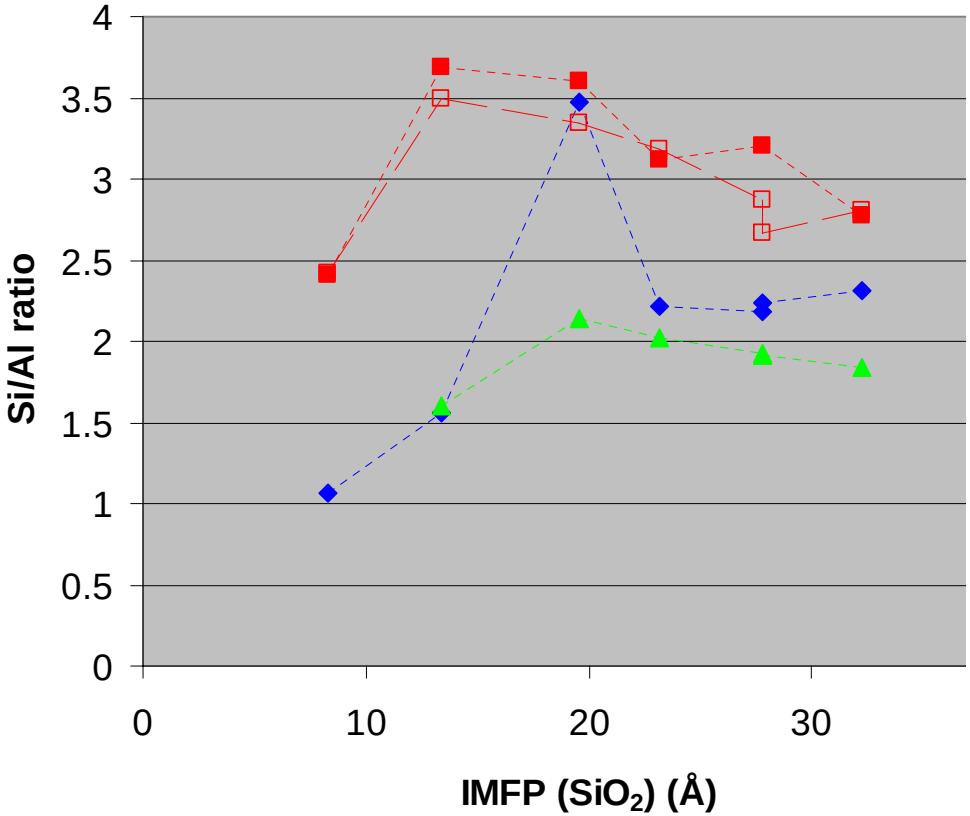
Outer surface enriched in Al relative to immediate sub-surface.

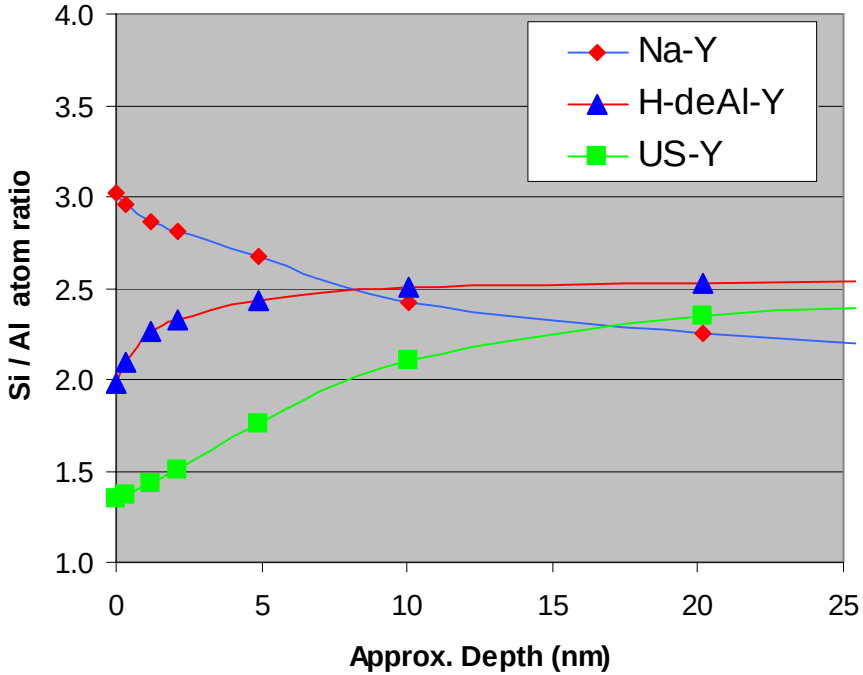


- **Na-Y is depleted in Al**
- **NH_4,H-deAl-Y is enriched in Al**
- **US-Y is strongly enriched in Al**

Combine Sputter Depth Profiling

- **The SDP begins where the synchrotron XPS data ends**
- **General trends from SDP continue to the outer surface region – but then change to Al enrichment at extreme surface.**





Summary

- Varying the photon energy from 200-1200 eV allows non-destructive quantitative depth profile of Si/Al ratio of an industrially-relevant zeolite: Y zeolite.
- Data show that for the first time the outer surface of the zeolite can be analyzed using XPS.
- Data show Al enrichment at the outer surface
  - What is the acid strength of this Al?
  - Is this framework or extra-framework?
  - Does it play a role in acid-catalyzed chemistry?
- Complementary low energy ion scattering (LEIS) confirms that extreme outer surface is strongly enriched in Al (Si/Al = 0.8 for Na-Y).

HAXPES: Opportunities for Catalysis

- **Catalysis occurs on the surface of a material – so why do HAXPES?**

HAXPES: Opportunities for Catalysis

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- Surface properties influenced by the sub-surface and bulk
- If see changes in surface will be able to compare directly to bulk
- Will be able to extend this zeolite work to non-destructively probe deeper into the zeolite – correlate with sputter depth profiles
- Ability to access wider range of transitions: core & valance e.g. Al 1s and Al 2p, Si 1s and Si 2p.
- Complementary to XAFS: filled states vs. empty states
- Segregation in alloys
- Spent catalysts often covered by a coke overlayer – want to probe beneath the coke
- Metallurgy – ability to probe deeper into the outer layers of treated stainless steel
- In situ – able to operate at higher pressures than ISISS
- Liquid-solid interface

Acknowledgements

- Norma Kahn
- Ally Chan
- Laszlo Nemeth
- Mike Gatter
- Steve Wilson
- Wharton Sinkler

- Robert Schlögl
- Axel Knop-Gericke
- Detre Teschner
- Michael Hävacker
- Raoul Blume
- Tulio Rocha

- Staff at BESSY