Facility for Adsorbent Characterization and Testing (FACT)

Laura Espinal, Martin L. Green, Roger D. van Zee

Brad Boyerinas, Matthias Thommes, Jarod Horn, and Ford Scott

Key collaborator: Phil Parilla (NREL)

http://nist.gov/mml/fact/

November 2014

Outline

1. Motivation
2. Capabilities
3. Ongoing project
4. Future work

Outline

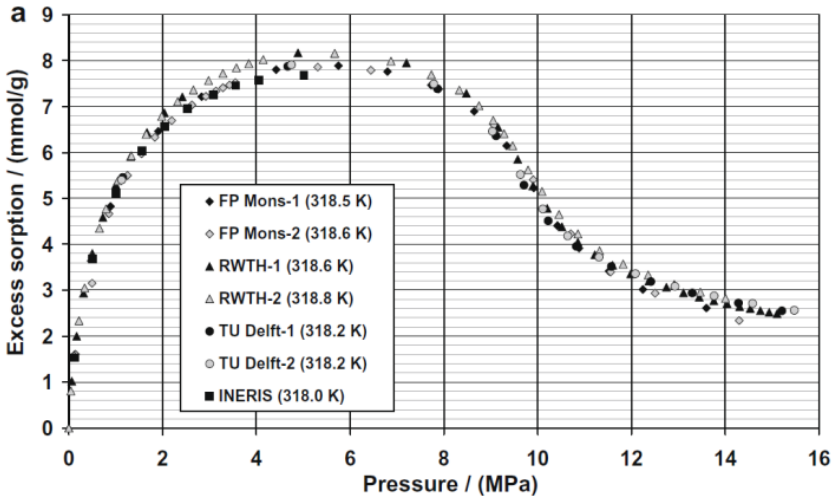
1. **Motivation**
2. Capabilities
3. Ongoing project
4. Future work

High pressure sorption data

Literature data

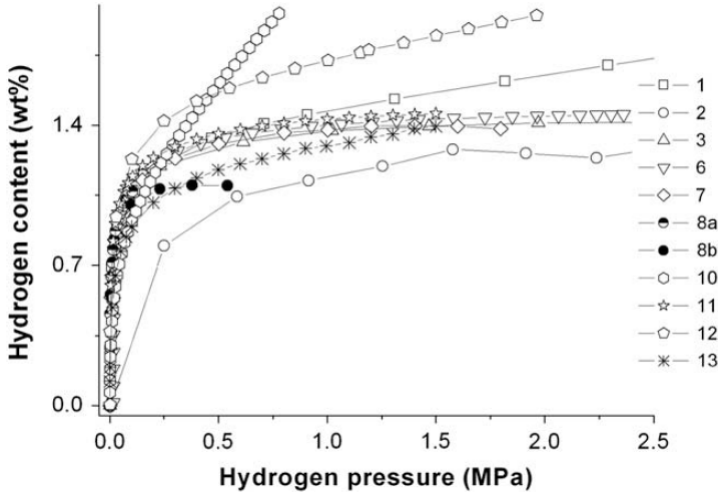
Round robin tests:

High pressure CO_2 sorption isotherms on porous carbon at 318 K



Gensterblum et al., *Carbon* **2009**

High pressure H_2 sorption isotherms on porous carbon at 77 K



Zlotea et al., *Int. J. Hydrogen Energy* **2009**

Outline

1. Motivation
2. **Capabilities**
3. Ongoing project
4. Future work

Capabilities: parameter space

Instrument		P range	T range	AST***	Static	Flow
Volumetric	Ch1*	0 bar – 200 bar	78 K – 780 K	Yes	Yes	-
	Ch2	0 bar – 80 bar	20 K – 670 K	Yes	Yes	-
	Ch3*	0 bar – 1 bar	LN_2, LAr, RT – 670 K	Yes	Yes	-
	Ch4*	0 bar – 100 bar	RT – 670 K	Yes	Yes	-
Gravimetric*		0 bar – 20 bar	273 K – 773 K	Yes	Yes	Yes
Volumetric & Gravimetric		0 bar – 90 bar**	LN_2, LAr, 273 K – 423 K	-	Yes	-
Volumetric with chromatography		0 bar – 90 bar**	283 K – 670 K / 283 K – 323 K	Yes	Yes	-
Pore size analyzer (volumetric)		0 bar – 1 bar	RT – 670 K / LN_2, LAr, 253 K – 373 K	Yes	Yes	-
Gravimetric*		0 bar – 50 bar	278 K – 1073 K	-	Yes	Yes
Gravimetric		0 bar – 1 bar	278 K – 423 K	-	-	Yes

*: Mass spectrometry available for gas analysis.
**: Higher pressure measurements are possible for single gas sorption isotherms.
***: Air-less sample transfer capability.
Complementary instruments highlighted in red.

Capabilities: parameter space

High pressures

Instrument		P range	T range	AST***	Static	Flow
Volumetric	Ch1*	0 bar – 200 bar	78 K – 780 K	Yes	Yes	-
	Ch2	0 bar – 80 bar	20 K – 670 K	Yes	Yes	-
	Ch3*	0 bar – 1 bar	LN_2, LAr, RT – 670 K	Yes	Yes	-
	Ch4*	0 bar – 100 bar	RT – 670 K	Yes	Yes	-
Gravimetric*		0 bar – 20 bar	273 K – 773 K	Yes	Yes	Yes
Volumetric & Gravimetric		0 bar – 90 bar**	LN_2, LAr, 273 K – 423 K	-	Yes	-
Volumetric with chromatography		0 bar – 90 bar**	283 K – 670 K / 283 K – 323 K	Yes	Yes	-
Pore size analyzer (volumetric)		0 bar – 1 bar	RT – 670 K / LN_2, LAr, 253 K – 373 K	Yes	Yes	-
Gravimetric*		0 bar – 50 bar	278 K – 1073 K	-	Yes	Yes
Gravimetric		0 bar – 1 bar	278 K – 423 K	-	-	Yes

*: Mass spectrometry available for gas analysis.
**: Higher pressure measurements are possible for single gas sorption isotherms.
***: Air-less sample transfer capability.
Complementary instruments highlighted in red.

Capabilities: parameter space

Cryogenic temperatures

Instrument		P range	T range	AST***	Static	Flow
Volumetric	Ch1*	0 bar – 200 bar	78 K – 780 K	Yes	Yes	-
	Ch2	0 bar – 80 bar	20 K – 670 K	Yes	Yes	-
	Ch3*	0 bar – 1 bar	LN_2, LAr, RT – 670 K	Yes	Yes	-
	Ch4*	0 bar – 100 bar	RT – 670 K	Yes	Yes	-
Gravimetric*		0 bar – 20 bar	273 K – 773 K	Yes	Yes	Yes
Volumetric & Gravimetric		0 bar – 90 bar**	LN_2, LAr, 273 K – 423 K	-	Yes	-
Volumetric with chromatography		0 bar – 90 bar**	283 K – 670 K / 283 K – 323 K	Yes	Yes	-
Pore size analyzer (volumetric)		0 bar – 1 bar	RT – 670 K / LN_2, LAr, 253 K – 373 K	Yes	Yes	-
Gravimetric*		0 bar – 50 bar	278 K – 1073 K	-	Yes	Yes
Gravimetric		0 bar – 1 bar	278 K – 423 K	-	-	Yes

*: Mass spectrometry available for gas analysis.
**: Higher pressure measurements are possible for single gas sorption isotherms.
***: Air-less sample transfer capability.
Complementary instruments highlighted in red.

Capabilities: parameter space

Gas mixtures

Instrument		P range	T range	AST***	Static	Flow
Volumetric	Ch1*	0 bar – 200 bar	78 K – 780 K	Yes	Yes	-
	Ch2	0 bar – 80 bar	20 K – 670 K	Yes	Yes	-
	Ch3*	0 bar – 1 bar	LN_2, LAr, RT – 670 K	Yes	Yes	-
	Ch4*	0 bar – 100 bar	RT – 670 K	Yes	Yes	-
Gravimetric*		0 bar – 20 bar	273 K – 773 K	Yes	Yes	Yes
Volumetric & Gravimetric		0 bar – 90 bar**	LN_2, LAr, 273 K – 423 K	-	Yes	-
Volumetric with chromatography		0 bar – 90 bar**	283 K – 670 K / 283 K – 323 K	Yes	Yes	-
Pore size analyzer (volumetric)		0 bar – 1 bar	RT – 670 K / LN_2, LAr, 253 K – 373 K	Yes	Yes	-
Gravimetric*		0 bar – 50 bar	278 K – 1073 K	-	Yes	Yes
Gravimetric		0 bar – 1 bar	278 K – 423 K	-	-	Yes

*: Mass spectrometry available for gas analysis.
**: Higher pressure measurements are possible for single gas sorption isotherms.
***: Air-less sample transfer capability.
Complementary instruments highlighted in red.

Capabilities: parameter space

Airless sample transfer

Instrument		P range	T range	AST***	Static	Flow
Volumetric	Ch1*	0 bar – 200 bar	78 K – 780 K	Yes	Yes	-
	Ch2	0 bar – 80 bar	20 K – 670 K	Yes	Yes	-
	Ch3*	0 bar – 1 bar	LN_2, LAr, RT – 670 K	Yes	Yes	-
	Ch4*	0 bar – 100 bar	RT – 670 K	Yes	Yes	-
Gravimetric*		0 bar – 20 bar	273 K – 773 K	Yes	Yes	Yes
Volumetric & Gravimetric		0 bar – 90 bar**	LN_2, LAr, 273 K – 423 K	-	Yes	-
Volumetric with chromatography		0 bar – 90 bar**	283 K – 670 K / 283 K – 323 K	Yes	Yes	-
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Gravimetric*		0 bar – 50 bar	278 K – 1073 K	-	Yes	Yes
Gravimetric		0 bar – 1 bar	278 K – 423 K	-	-	Yes

*: Mass spectrometry available for gas analysis.
**: Higher pressure measurements are possible for single gas sorption isotherms.
***: Air-less sample transfer capability.
Complementary instruments highlighted in red.

Capabilities: parameter space

Adsorptives: CO_2, CH_4, H_2, N_2, He, H_2O, Toluene, other vapors.

Instrument		P range	T range	AST***	Static	Flow
Volumetric	Ch1*	0 bar – 200 bar	78 K – 780 K	Yes	Yes	-
	Ch2	0 bar – 80 bar	20 K – 670 K	Yes	Yes	-
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Gravimetric		0 bar – 1 bar	278 K – 423 K	-	-	Yes

*: Mass spectrometry available for gas analysis.
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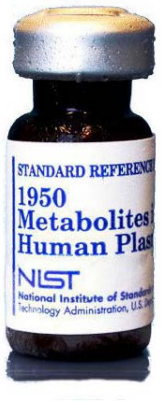
Complementary instruments highlighted in red.

Capabilities: competencies

Example of Measurement

Example of Data



Define the measurement or data need

↓

Design and work on approach

↓

Deliver product or solution

Capabilities: competencies

Example of Measurement

Example of Data

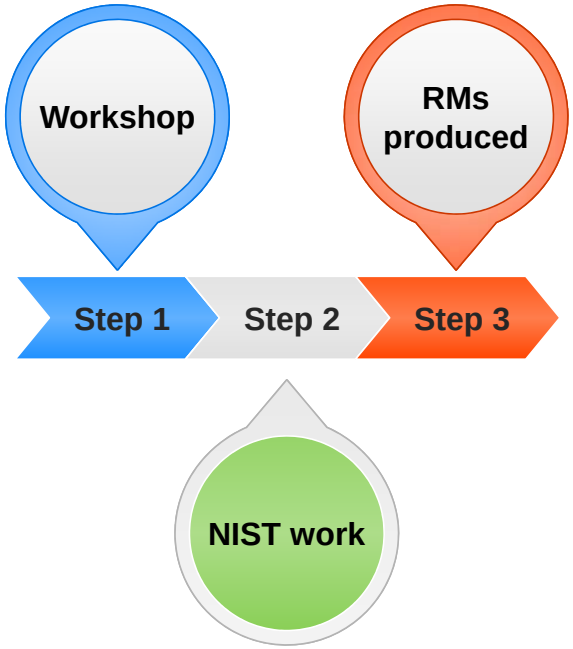
Define the measurement or data need

Design and work on approach

Deliver product or solution

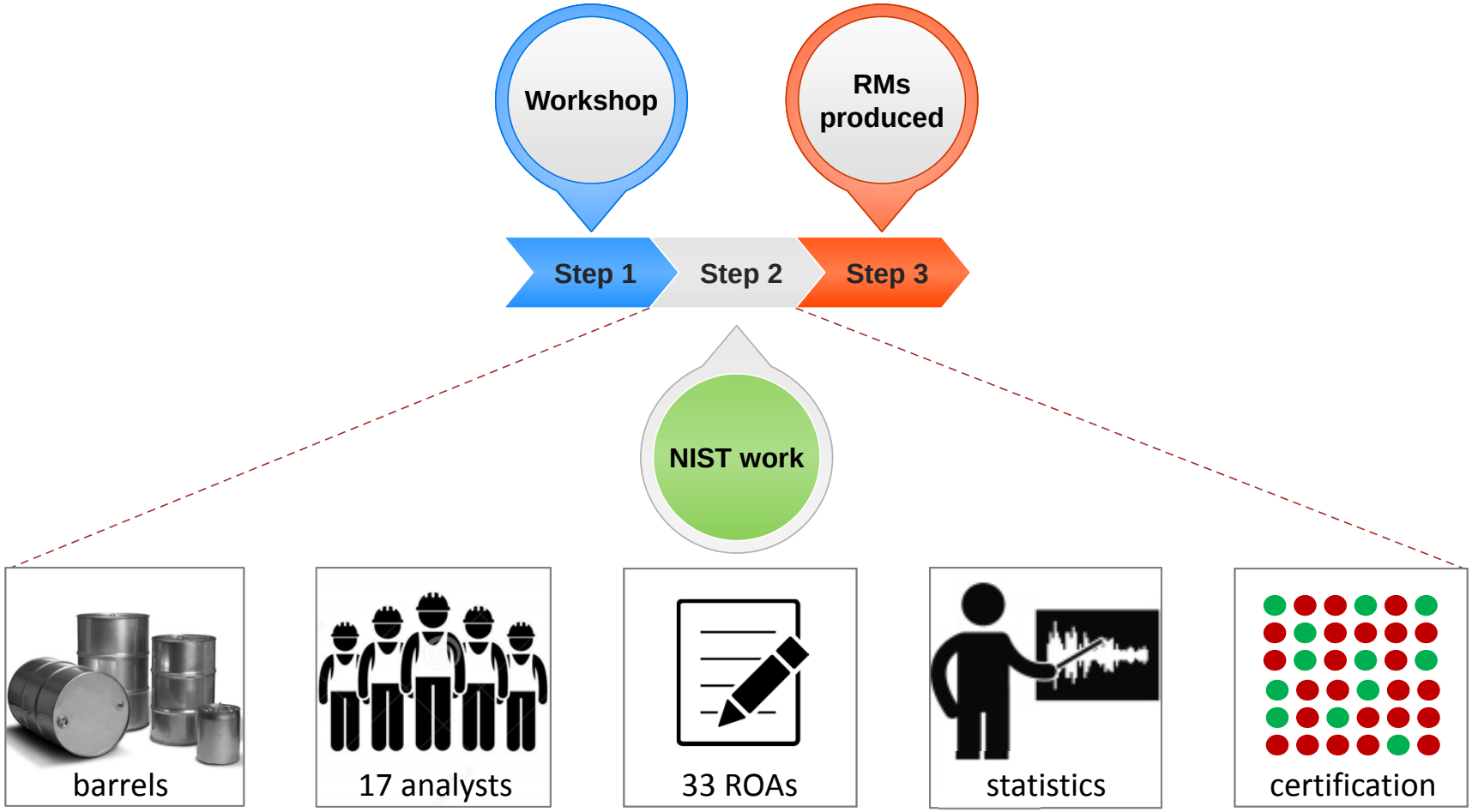
Capabilities: competencies

Example of Measurement



Capabilities: competencies

Example of Measurement



Capabilities: competencies

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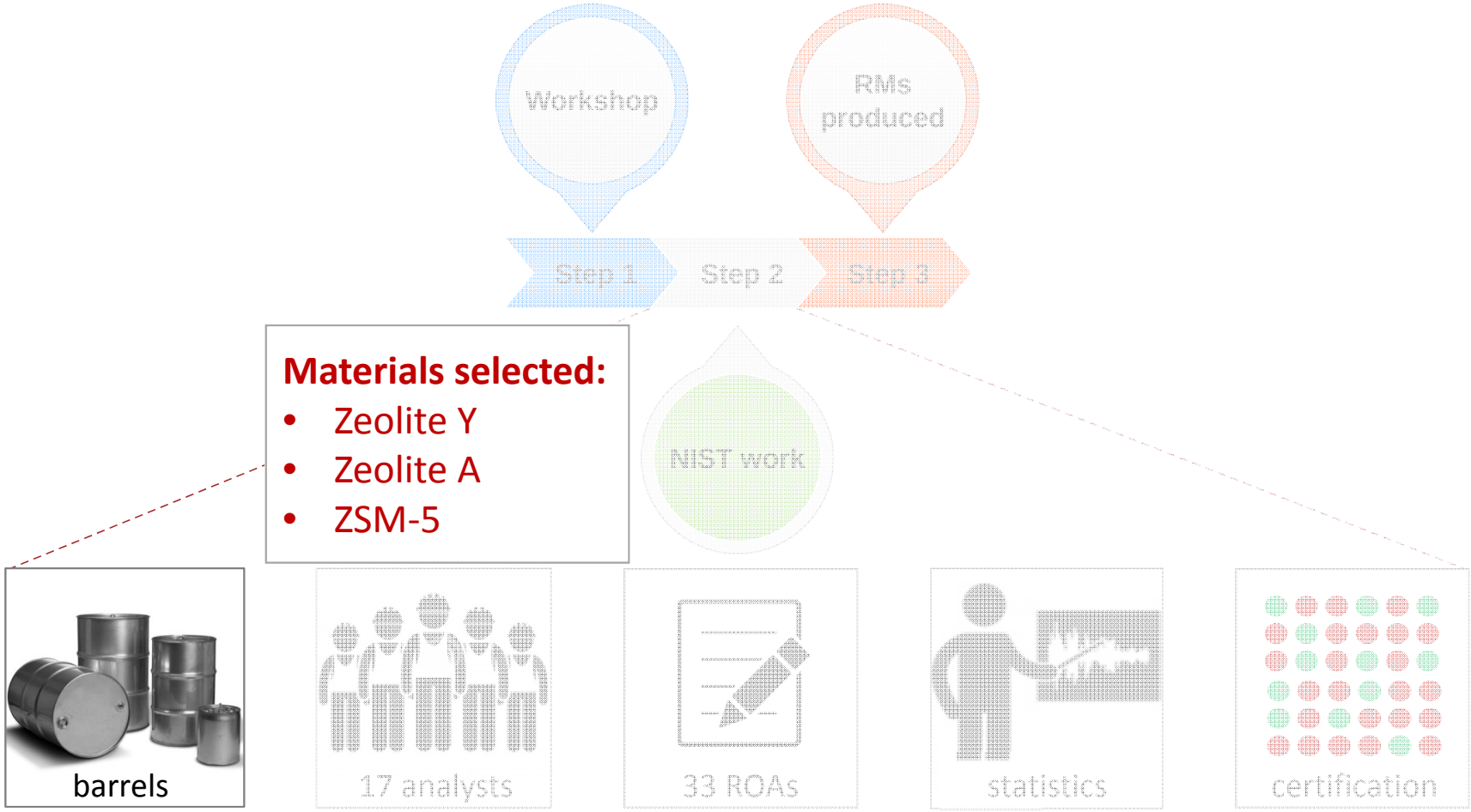
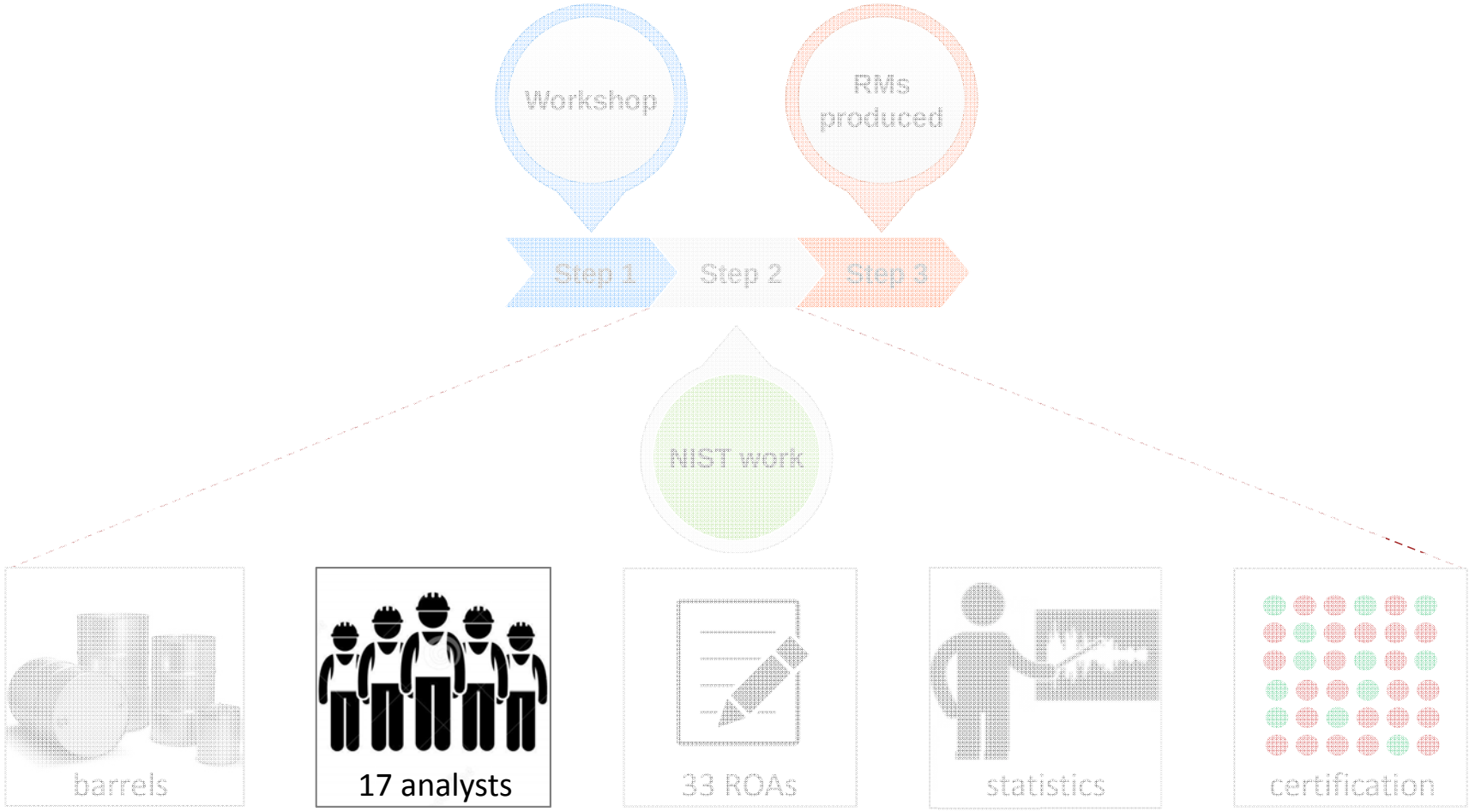


Capabilities: competencies

Example of Measurement



Capabilities: competencies

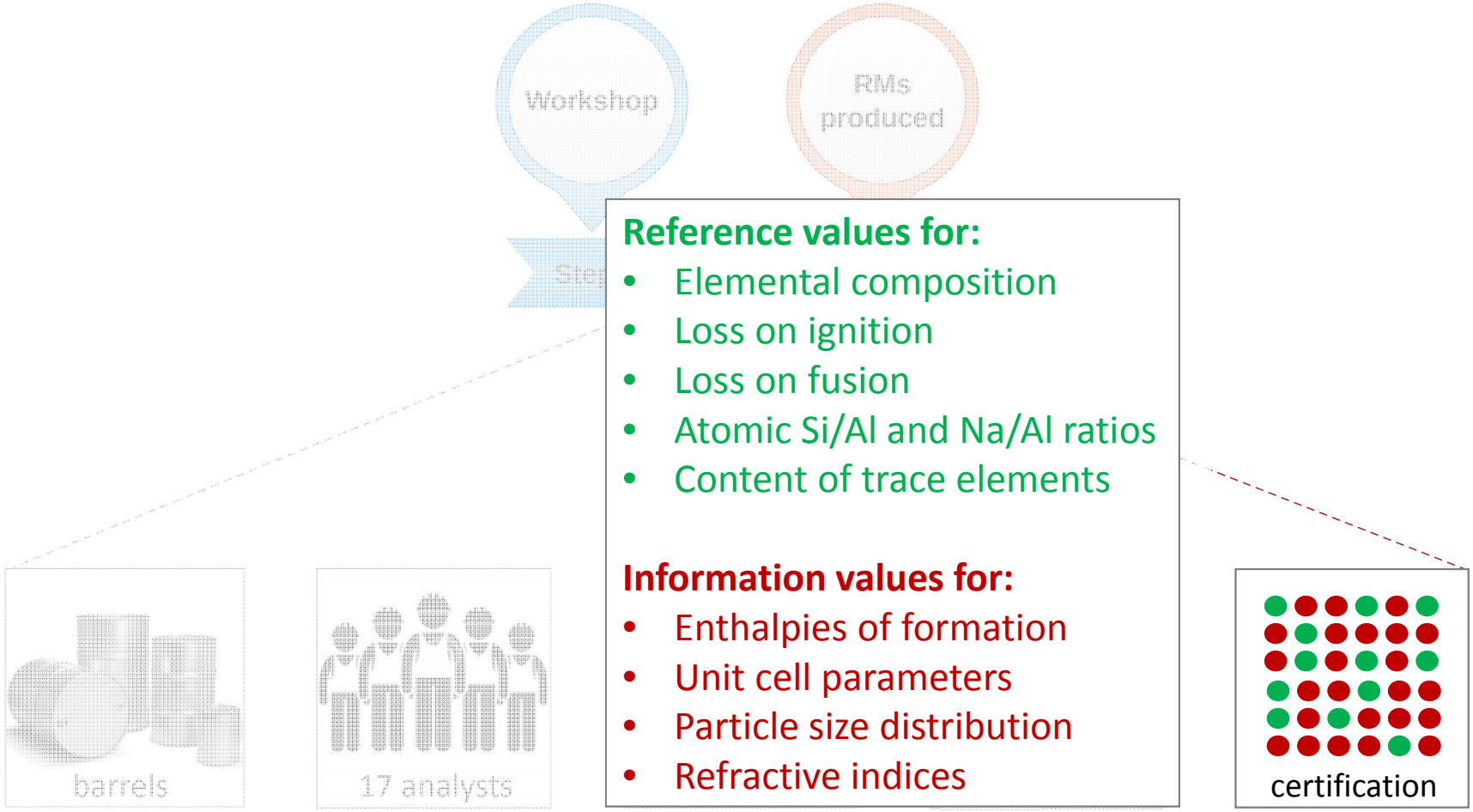
Example of Measurement

Capabilities: competencies

Example of Measurement

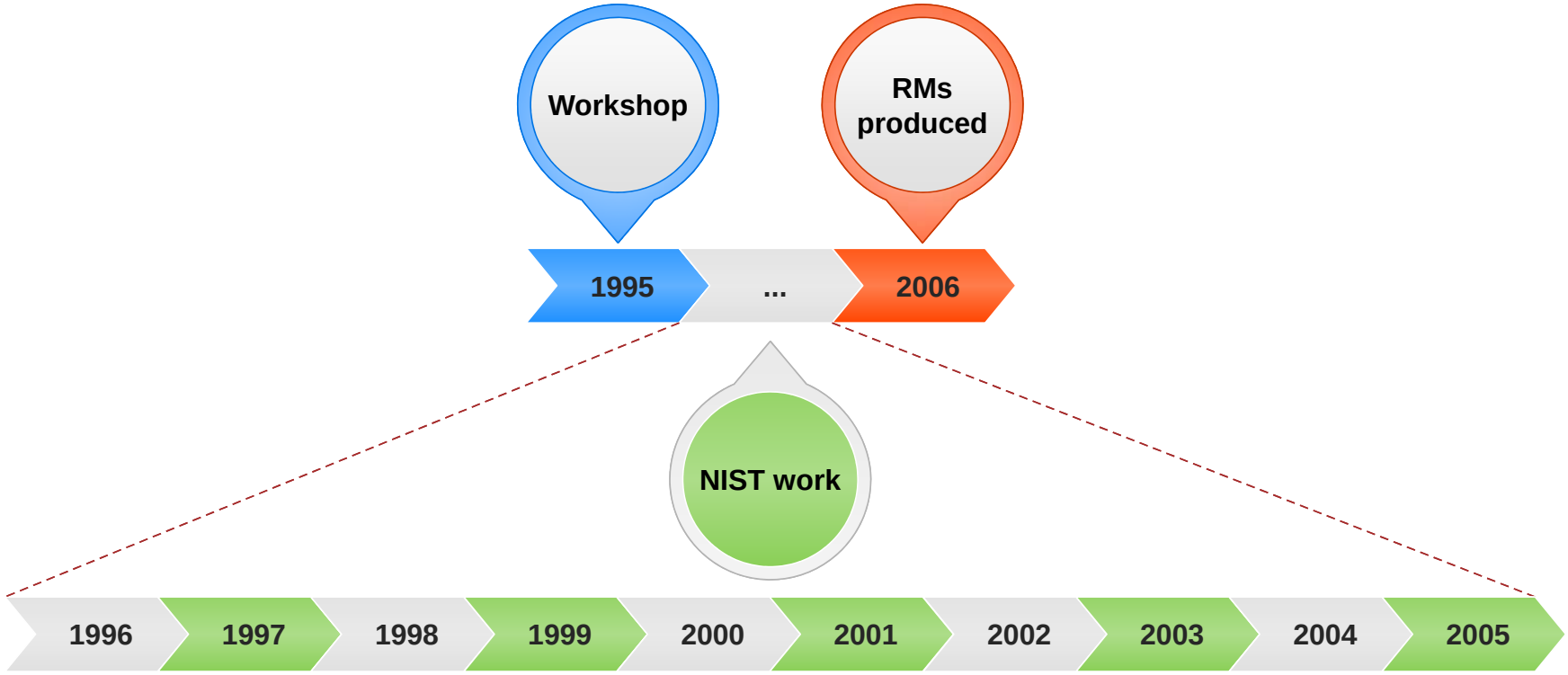
Capabilities: competencies

Example of Measurement



Capabilities: competencies

Example of Measurement

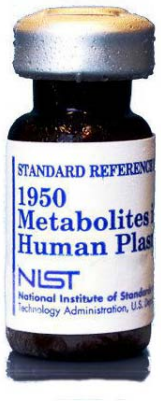


10 years

Capabilities: competencies

Example of Measurement

Example of Data



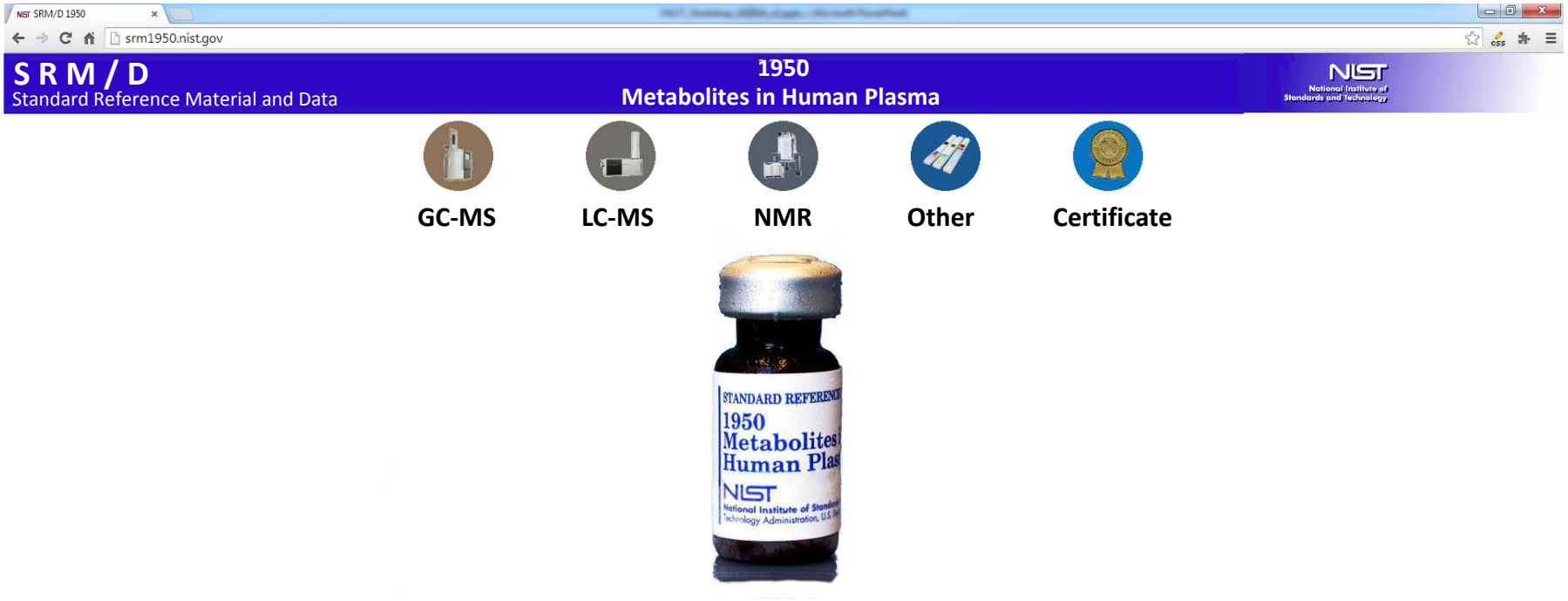
Define the measurement or data need

Design and work on approach

Deliver product or solution

Standard Reference Materials and Data (RMD)

Example of Data



High-quality data are obtained and critically assessed on a material certified for amount-of-substance.

Outline

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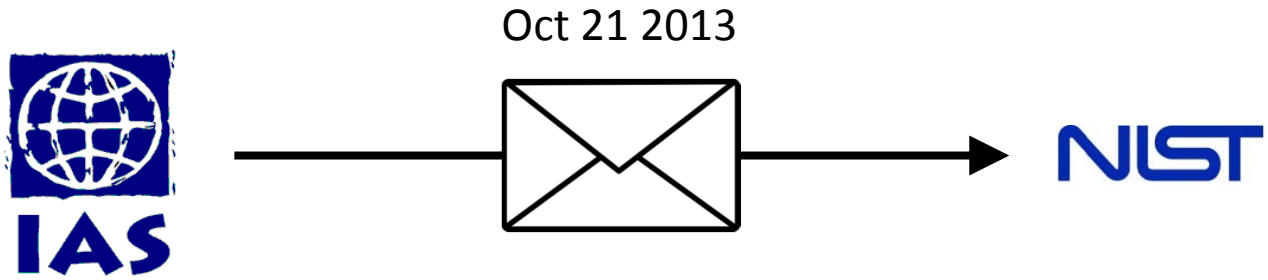
3. **Ongoing project**
4. Future work

Request from the International Adsorption Society

IAS sends a Memo to NIST



…"develop of (certified) reference materials with (certified) reference gas adsorption isotherms, with priority given to reference materials for industrial adsorption applications over a wide pressure range (e.g. up to ca. 100 bar)."…

…"availability of such reference materials will allow for calibration of gas adsorption analytical equipment appropriate to high pressure conditions, which will enable reliable comparison and evaluation of adsorbent materials between independent laboratories."…

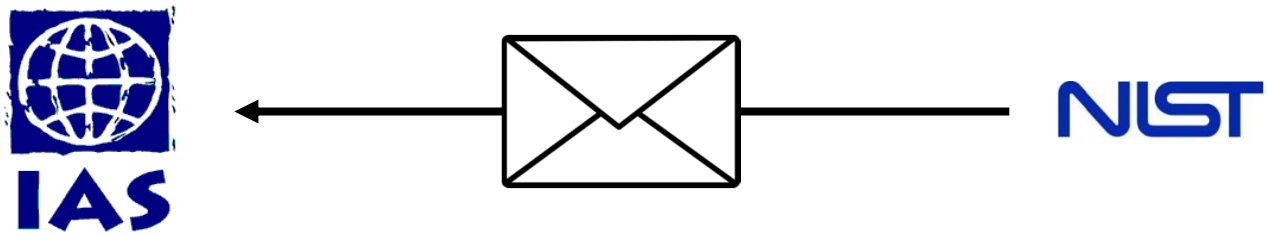
Data of interest

Adsorbate	T	P	Existing CRMs	Suggested candidates
CO_2	0 °C - 70 °C	1 bar - 100 bar	None	Zeolite 5A, Zeolite 13X, BPL Carbon, Filtrasorb 400, ZSM5/ Silicalite
CO_2	0 °C - 20 °C	0 bar - Psat	None	Zeolite 5A, Zeolite 13X, BPL Carbon, Filtrasorb 400, ZSM5/ Silicalite
CH_4	0 °C - 70 °C	1 bar - 100 bar	None	Zeolite 5A, Zeolite 13X, BPL Carbon, Filtrasorb 400, ZSM5/ Silicalite
H_2	0 °C - 70 °C	1 bar - 100 bar	None	Zeolite 5A, Zeolite 13X, BPL Carbon, Filtrasorb 400, ZSM5/ Silicalite
SF_6	0 °C - 70 °C	1 bar - 100 bar	None	Zeolite 5A, Zeolite 13X, BPL Carbon, Filtrasorb 400, ZSM5/ Silicalite
Ar	87 K	0 bar - Psat	BCR-704, BCR-705	Zeolite 5A, Zeolite 13X
H_2O	20 °C - 30 °C	0 bar - Psat	None	Zeolite 5A, Zeolite 13X, BPL Carbon, Filtrasorb 400, ZSM5/ Silicalite

Request from the International Adsorption Society

NIST sends a response Memo to IAS

Nov 11 2013

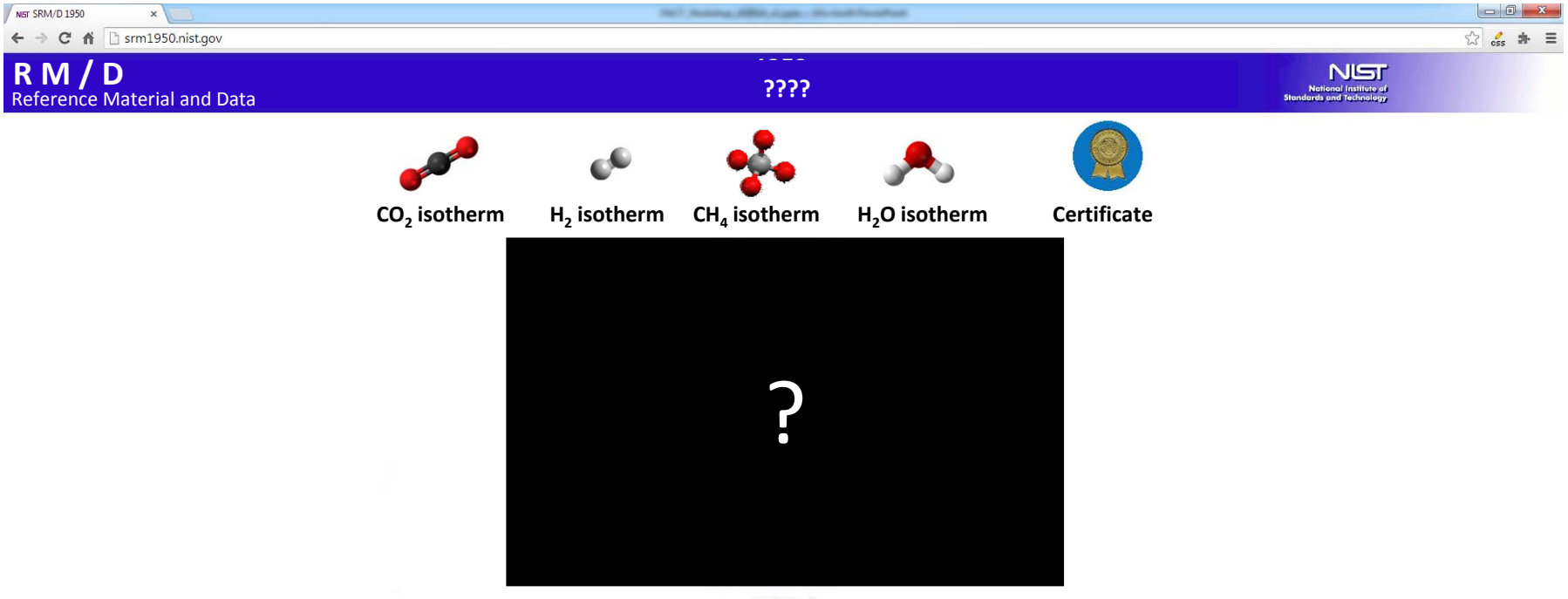


…*"[NIST] proposes measuring high pressure isotherms for CO_2 and CH_4 using one of our existing RM zeolite materials, both at NIST and other laboratories as part of a round robin."…*

…*"inclusion of other adsorption scientists, with IAS participation, would give greater credibility to the effort."…*

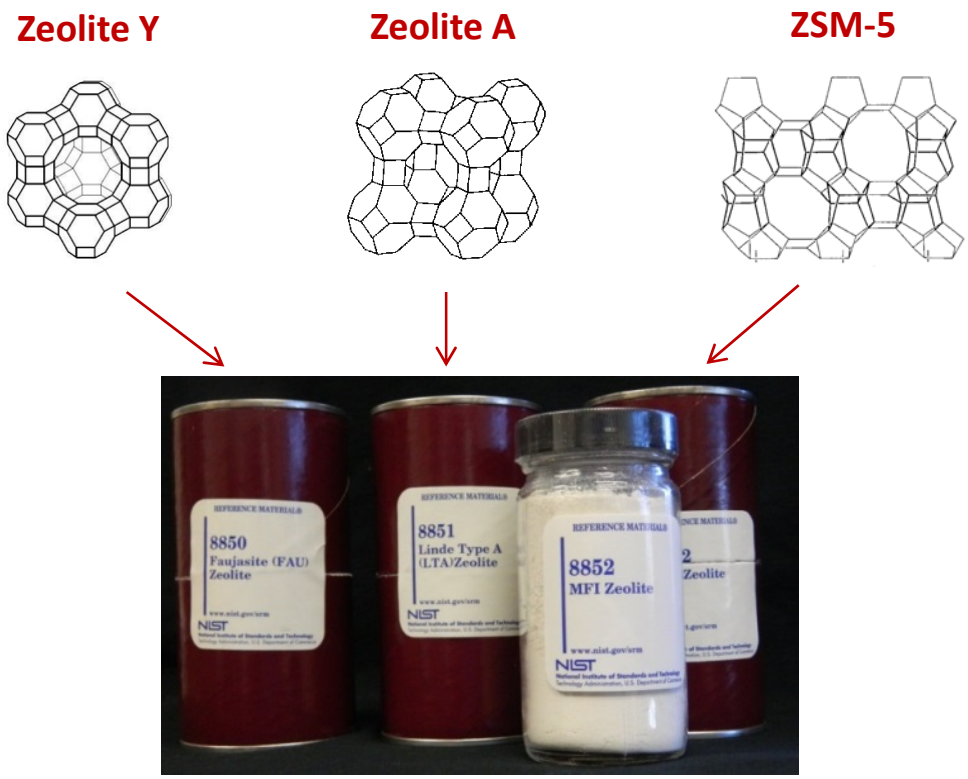
…*"the resulting isotherm data would not be, in the strict sense used here at NIST, 'certified values', but would have considerable credibility in the adsorption science community."…*

Reference Materials and Data (RM/D)



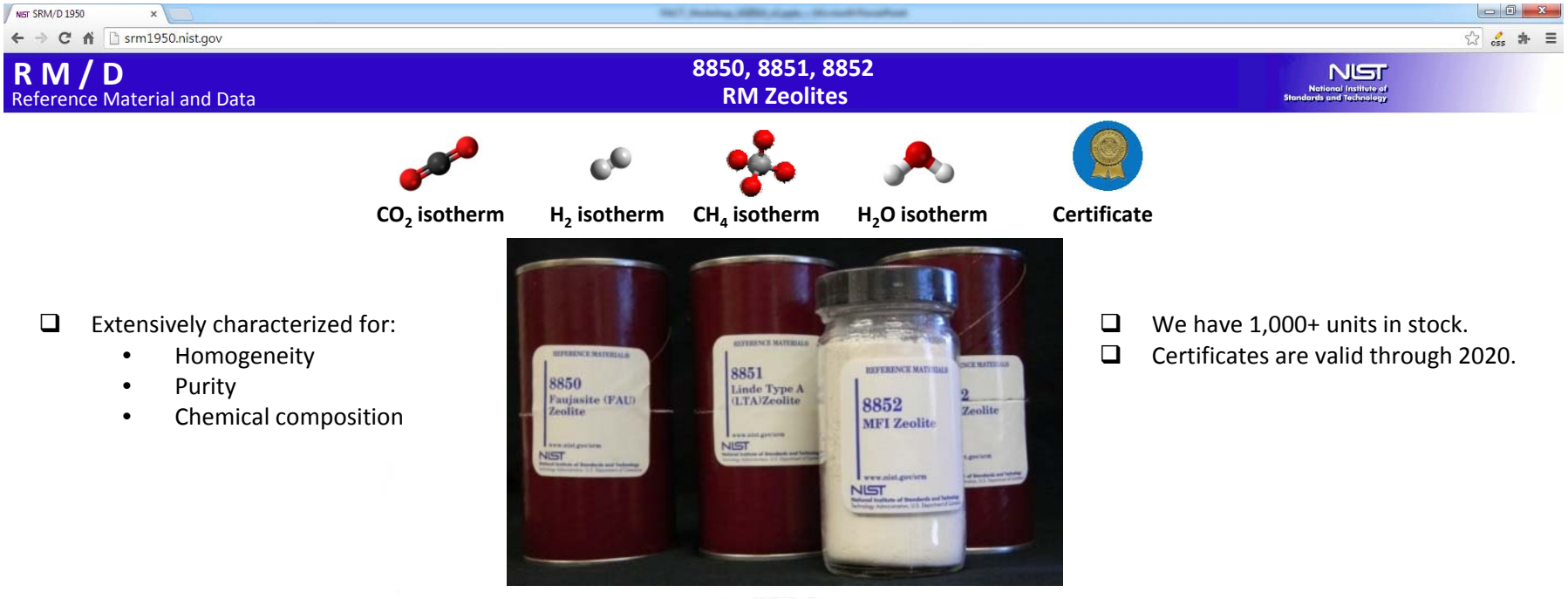
High-quality gas adsorption isotherm data on a material certified for amount-of-substance.

Reference Materials and Data (RM/D)



High-quality gas adsorption isotherm data on one of the NIST RM zeolites certified for chemical composition.

Reference Materials and Data (RM/D)



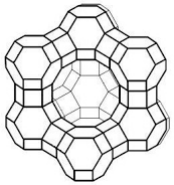
- Extensively characterized for:
  - Homogeneity
  - Purity
  - Chemical composition

- We have 1,000+ units in stock.
- Certificates are valid through 2020.

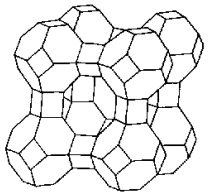
High-quality gas adsorption isotherm data on one of the NIST RM zeolites certified for chemical composition.

The RM zeolites

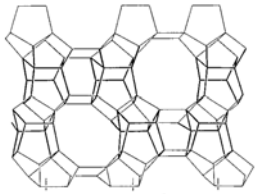
Zeolite Y



Zeolite A



ZSM-5



Elem. ratio	Zeolite Y	Zeolite A	ZSM-5
Si/Al	2.55	0.99	28.34
Na/Al	0.99	1.01	-

Available online at www.sciencedirect.com
ScienceDirect
Microporous and Mesoporous Materials 107 (2008) 252–267
MICROPOROUS AND MESOPOROUS MATERIALS
www.elsevier.com/locate/micromeso
ELSEVIER

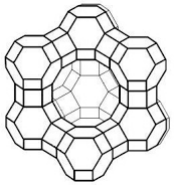
Characterization of chemical properties, unit cell parameters and particle size distribution of three zeolite reference materials: RM 8850 – zeolite Y, RM 8851 – zeolite A and RM 8852 – ammonium ZSM-5 zeolite

S. Turner [a,*], J.R. Sieber [a], T.W. Vetter [a], R. Zeisler [a], A.F. Marlow [a], M.G. Moreno-Ramirez [a,1], M.E. Davis [b], G.J. Kennedy [c], W.G. Borghard [c], S. Yang [d,2], A. Navrotsky [d], B.H. Toby [e,3], J.F. Kelly [f], R.A. Fletcher [a], E.S. Windsor [a], J.R. Verkouteren [a], S.D. Leigh [g]

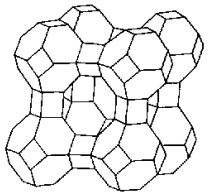
Turner *et al.*, Micropor. Mesopor. Mat. 2008

The RM zeolites

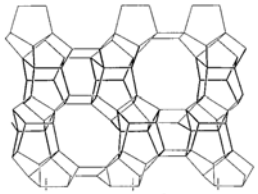
Zeolite Y



Zeolite A



ZSM-5



Elem. ratio	Zeolite Y	Zeolite A	ZSM-5
Si/Al	2.55	0.99	28.34
Na/Al	0.99	1.01	-

least hydrophilic

Available online at www.sciencedirect.com
ScienceDirect
Microporous and Mesoporous Materials 107 (2008) 252–267
MICROPOROUS AND MESOPOROUS MATERIALS
www.elsevier.com/locate/micromeso
ELSEVIER

Characterization of chemical properties, unit cell parameters and particle size distribution of three zeolite reference materials: RM 8850 – zeolite Y, RM 8851 – zeolite A and RM 8852 – ammonium ZSM-5 zeolite

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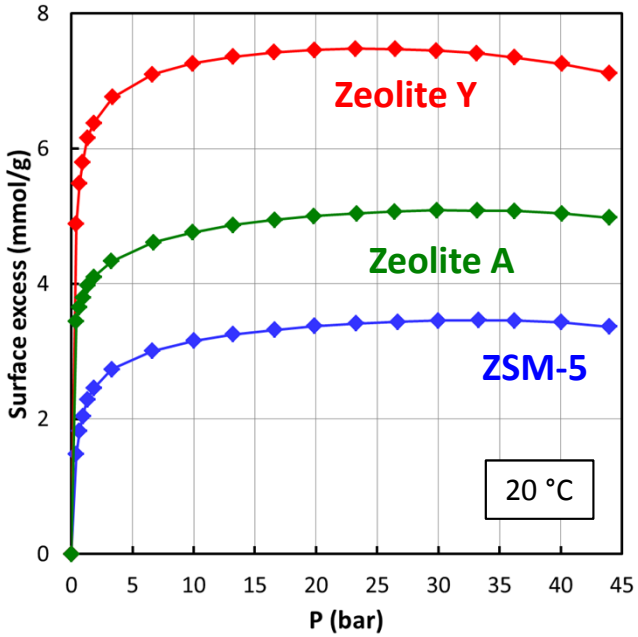
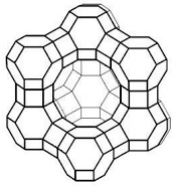
Turner *et al.*, Micropor. Mesopor. Mat. 2008

Preliminary CO_2 adsorption data

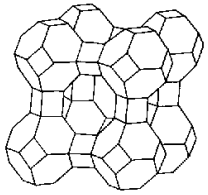
CO_2



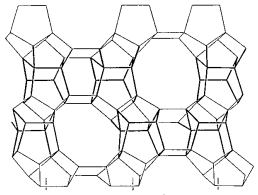
Zeolite Y



Zeolite A

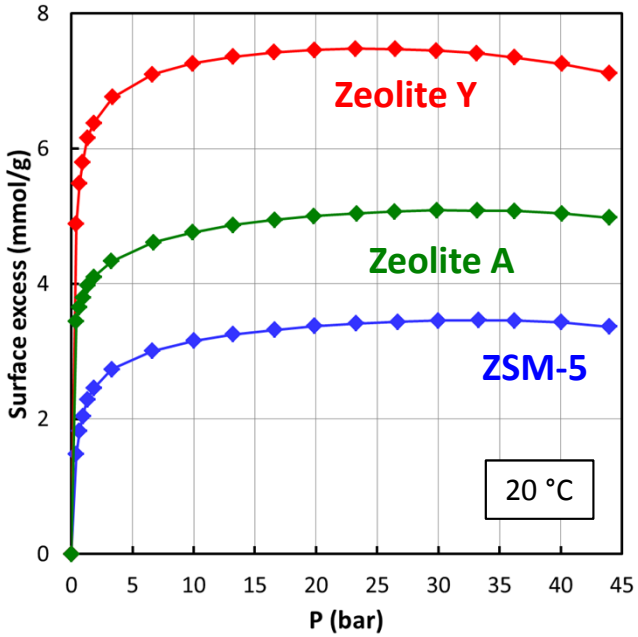


ZSM-5

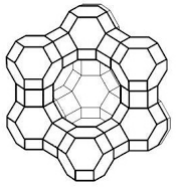


Preliminary CO_2 adsorption data

CO_2



Zeolite Y



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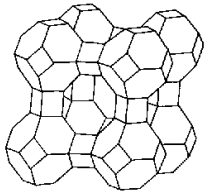
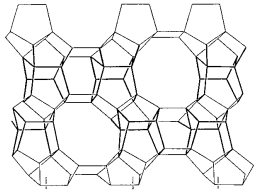
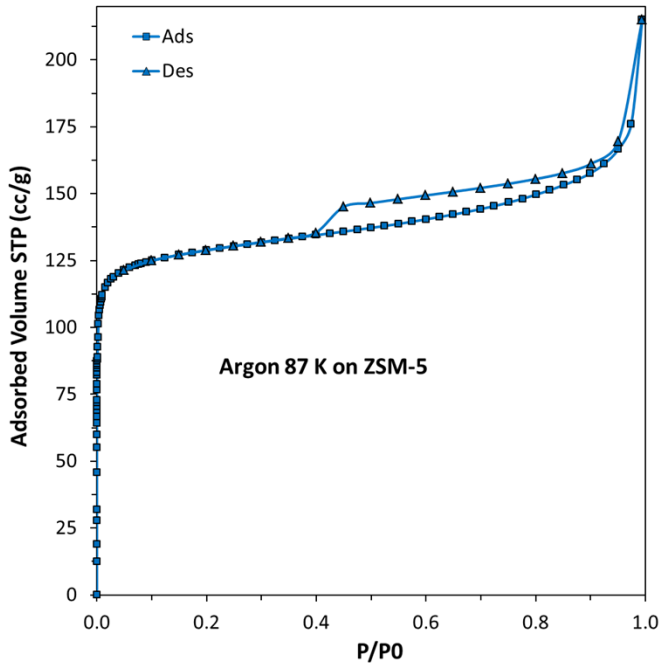


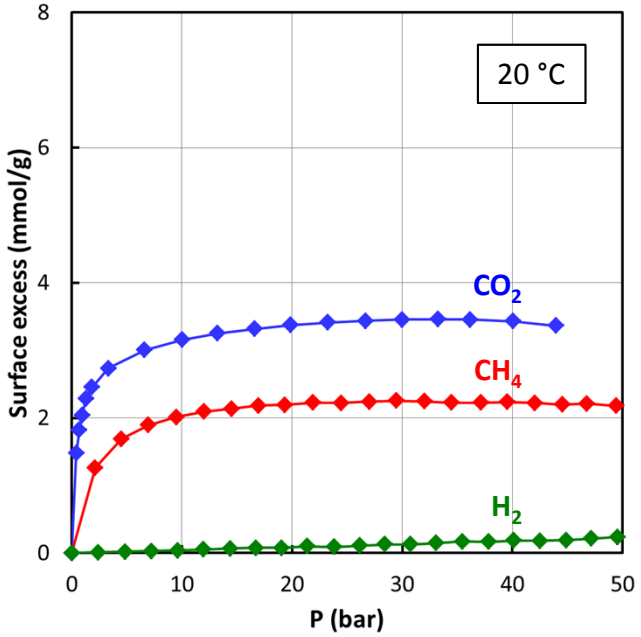
ZSM-5



Preliminary CO_2 , CH_4, and H_2 adsorption data

ZSM-5

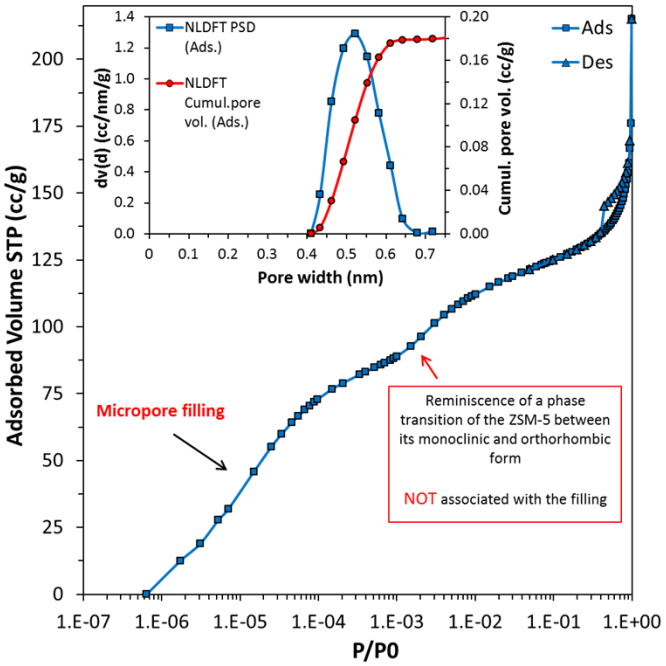


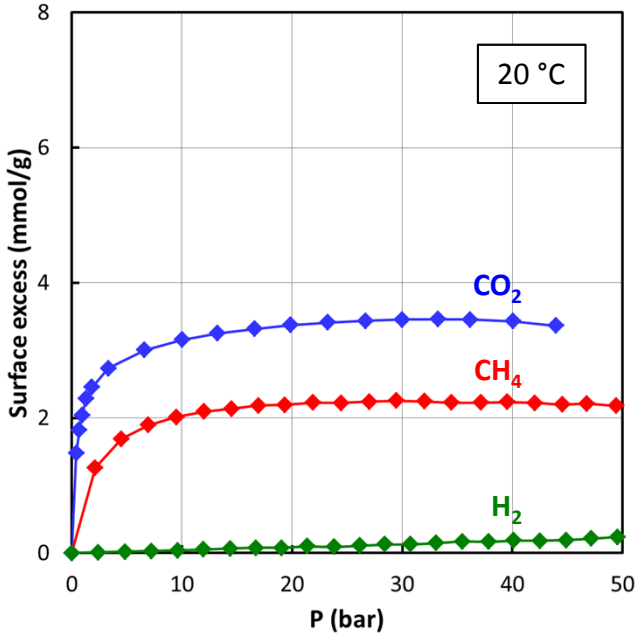


CO_2: T/Tc = 0.9
CH_4: T/Tc = 1.5
H_2: T/Tc = 8.8

Preliminary CO_2 , CH_4, and H_2 adsorption data

ZSM-5

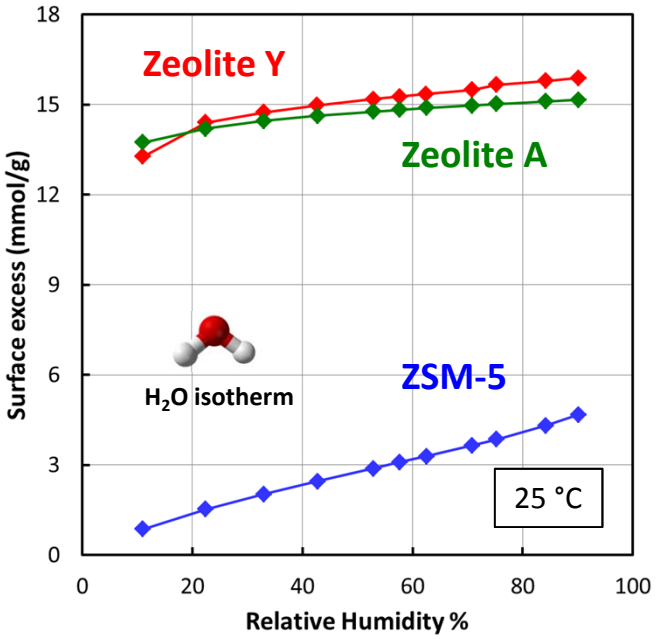




CO_2: T/Tc = 0.9
CH_4: T/Tc = 1.5
H_2: T/Tc = 8.8

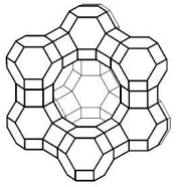
Preliminary H_2O adsorption data

H_2O

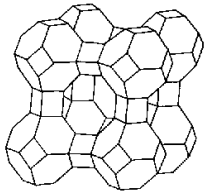


Psat = 0.032 bar

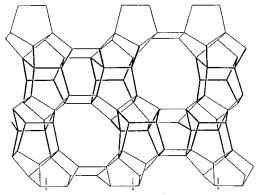
Zeolite Y



Zeolite A



ZSM-5



Next step

- **Round robin of CO_2 adsorption isotherm measurements on NIST RM8852 (ZSM-5) at 20 °C up to 45 bar, with assistance from:**
  - International Adsorption Society (IAS)
  - Versailles Project on Advanced Materials and Standards (VAMAS)

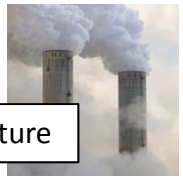
- **Prioritize other measurements:**
  - H_2 and CH_4 adsorption isotherm measurements on NIST RM8852 (ZSM-5).
  - H_2O adsorption isotherm measurements on NIST RM8850 (Zeolite Y), RM8851 (Zeolite A), and RM8852 (ZSM-5).

Outline

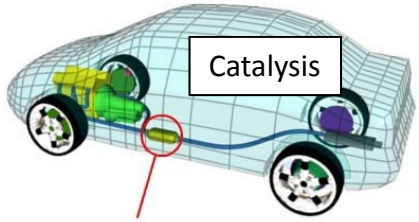
1. Motivation
2. Capabilities
3. Ongoing project
4. **Future work**

Future work

Environmental remediation



CO_2 capture



Catalysis

Natural gas purification

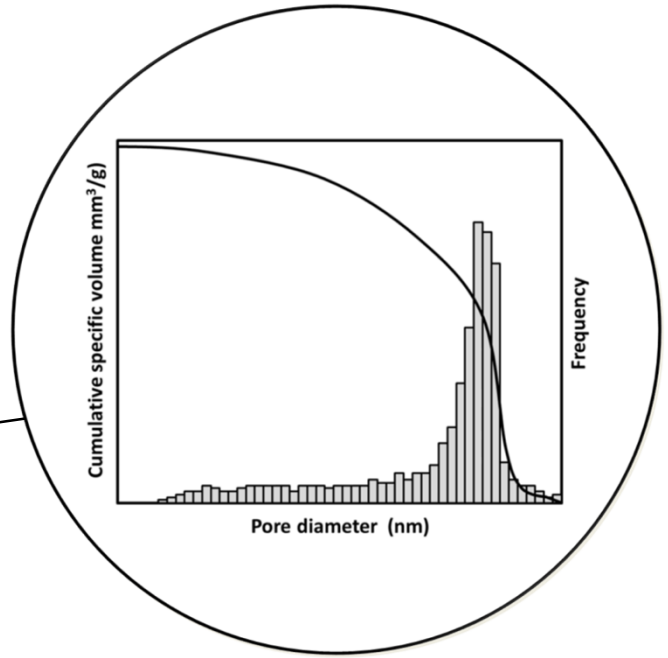
Cleaner fuels

Fuel storage

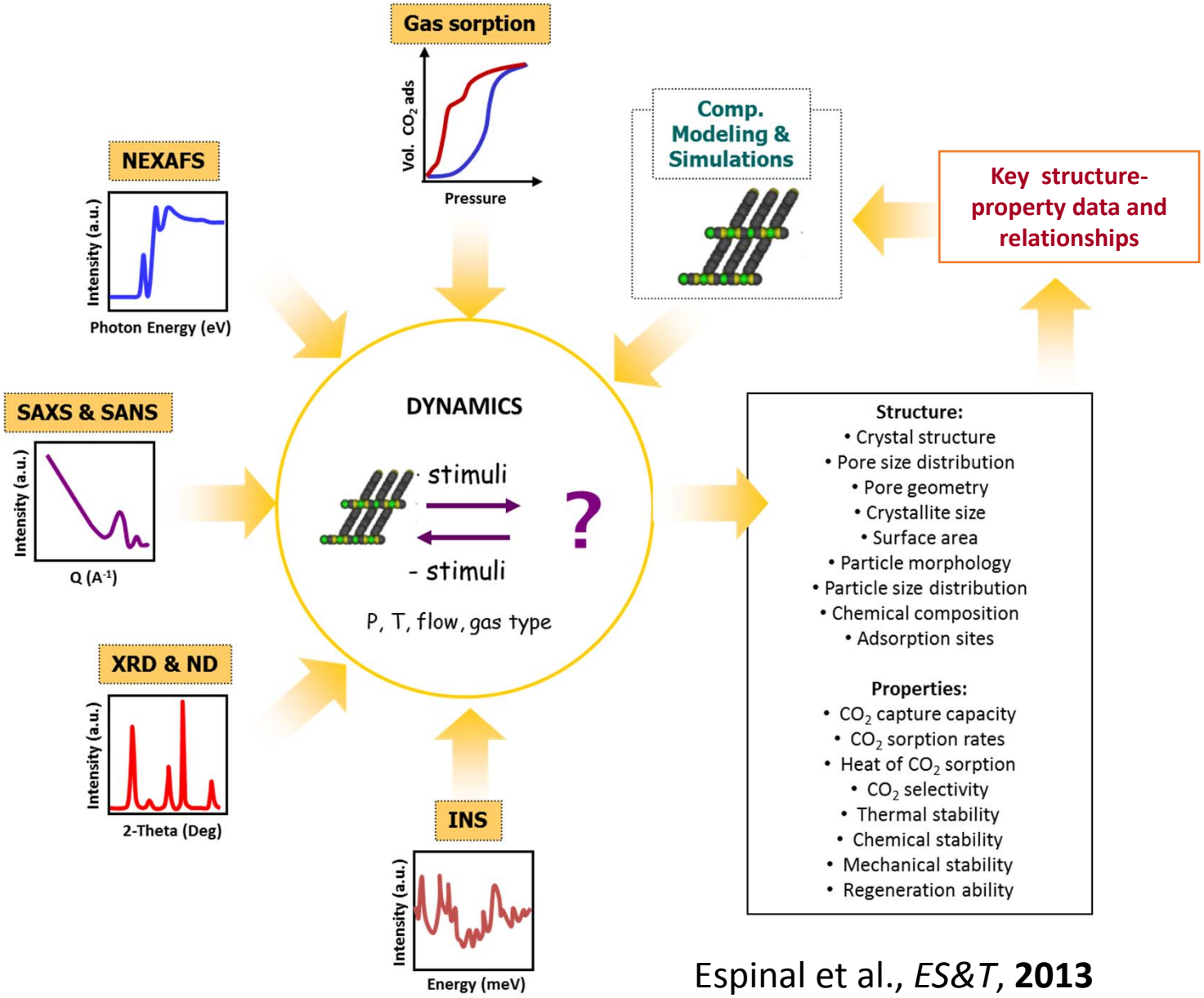
LET'S WORK TOGETHER

GRACE
NETL
BASF
The Chemical Company
NREL
ATMI
Black Pak
ExxonMobil
Johnson Matthey
U.S. DEPARTMENT OF ENERGY
Carleton College
GORE
Creative Technologies Worldwide
VCU
Virginia Commonwealth University
Georgia Institute of Technology
THE UNIVERSITY OF SYDNEY
BOISE STATE UNIVERSITY
UNLV
UMASS
RICE
CORNING
arpa·e
AIR LIQUIDE
University of Connecticut
AIR PRODUCTS
U.S. Department of Energy EERE
Aramco
UNIVERSITY OF SOUTH ALABAMA
BOSE
Schlumberger
UNIVERSITY OF MARYLAND
DU PONT
bp
UNIVERSITY OF DELAWARE
ASU ARIZONA STATE UNIVERSITY
UNIVERSITY OF MINNESOTA
SRNL SAVANNAH RIVER NATIONAL LABORATORY
UNIVERSITY OF SOUTH CAROLINA
NORTHWESTERN UNIVERSITY
Cleveland State University
THE STATE UNIVERSITY OF NEW JERSEY RUTGERS
STANFORD UNIVERSITY

Characterization of shale gas?

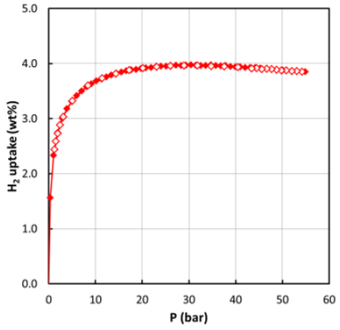


Complement *in-situ* characterization?

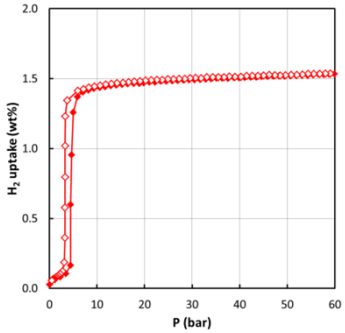


Espinal et al., *ES&T*, **2013**

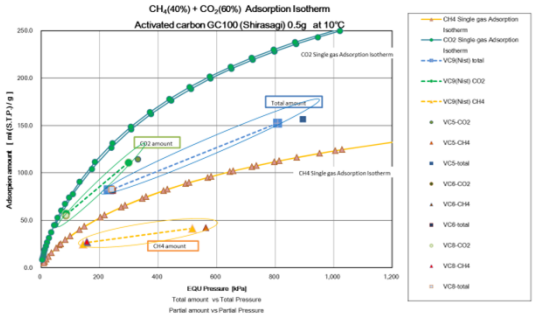
Storage and separations?



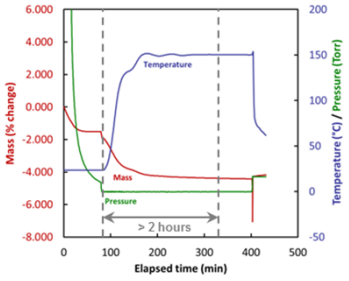
H_2 ads. on Cu-BTC at 77K

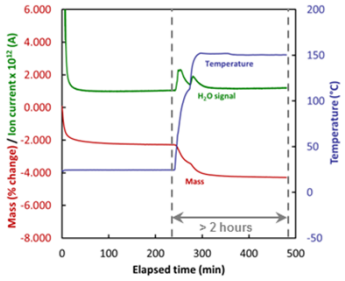


H_2 abs. on LaNi5 at 40 °C

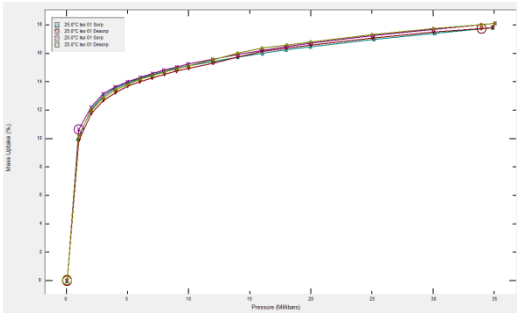


CO_2/CH_4 adsorption on porous carbon at 10 °C





Monitoring H_2O evolution during outgassing of molecules sieves



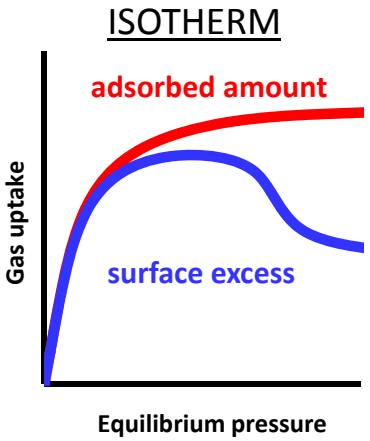
Toluene adsorption on F400 at 25 °C

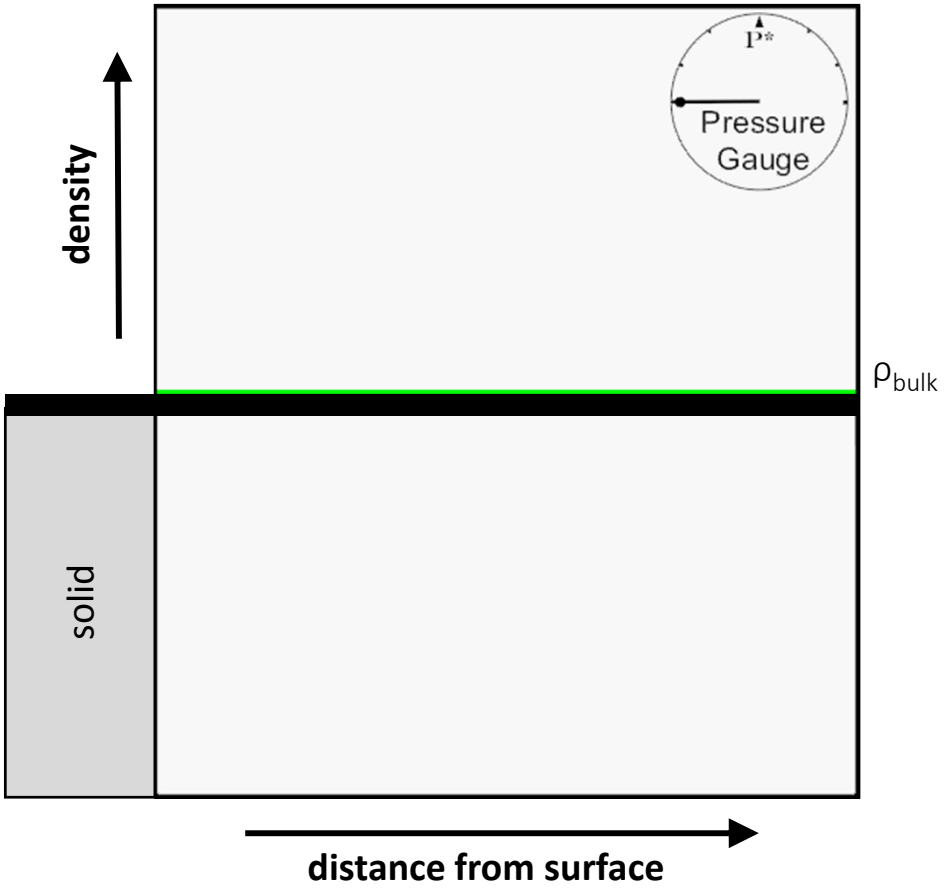
QUESTIONS?

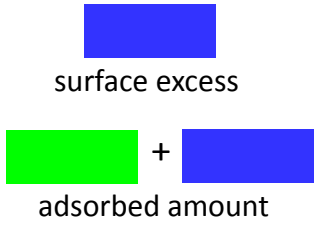
EXTRA SLIDES

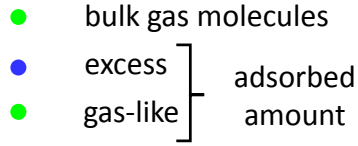
Clarification on nomenclature

surface excess vs. adsorbed amount



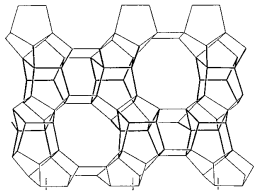


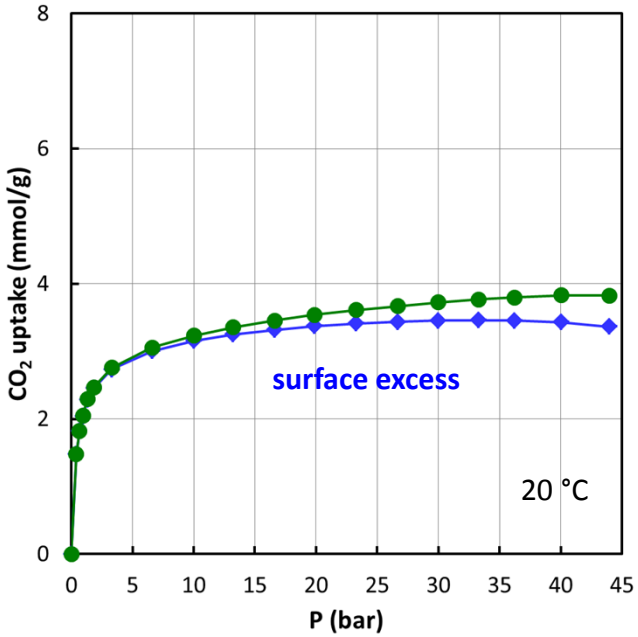




CO_2 adsorption data

ZSM-5





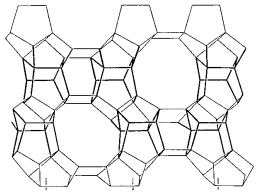
adsorbed amount

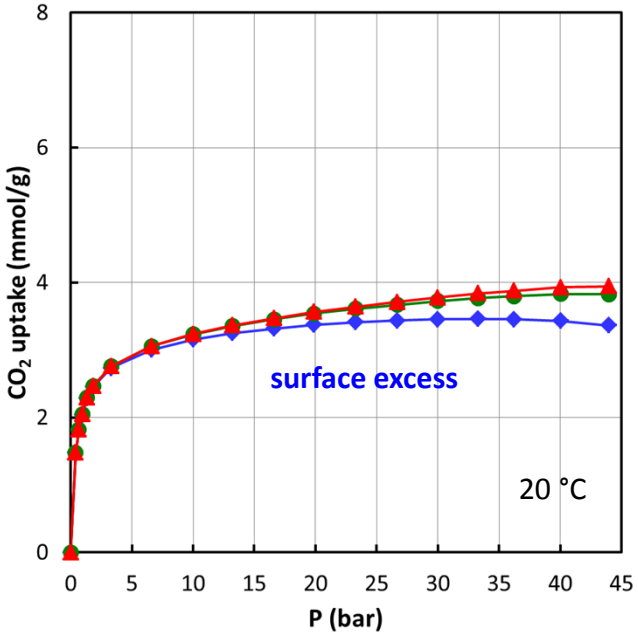
$$n_A = n^\sigma + \rho_g V_p$$

V_p: pore volume

CO_2 adsorption data

ZSM-5





adsorbed amount

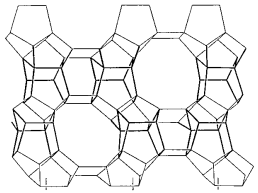
$$n_A = n^{\sigma} + \rho_g V_p$$

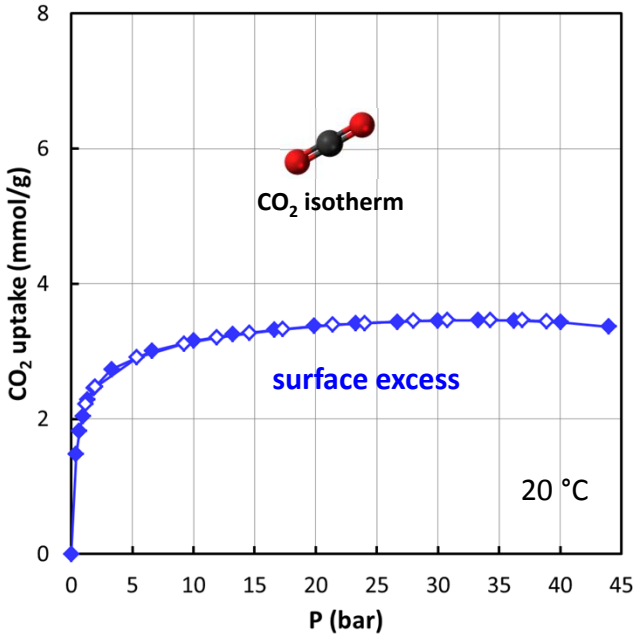
$$n_A = \frac{n^{\sigma}}{\left(1 - \frac{\rho_g}{\rho_{liq}}\right)}$$

Psat = 57.29 bar

CO_2 adsorption data

ZSM-5





T/Tc = 0.9 (subcritical temperature)