Gas adsorption microcalorimetry: probing energetics of oxide surfaces

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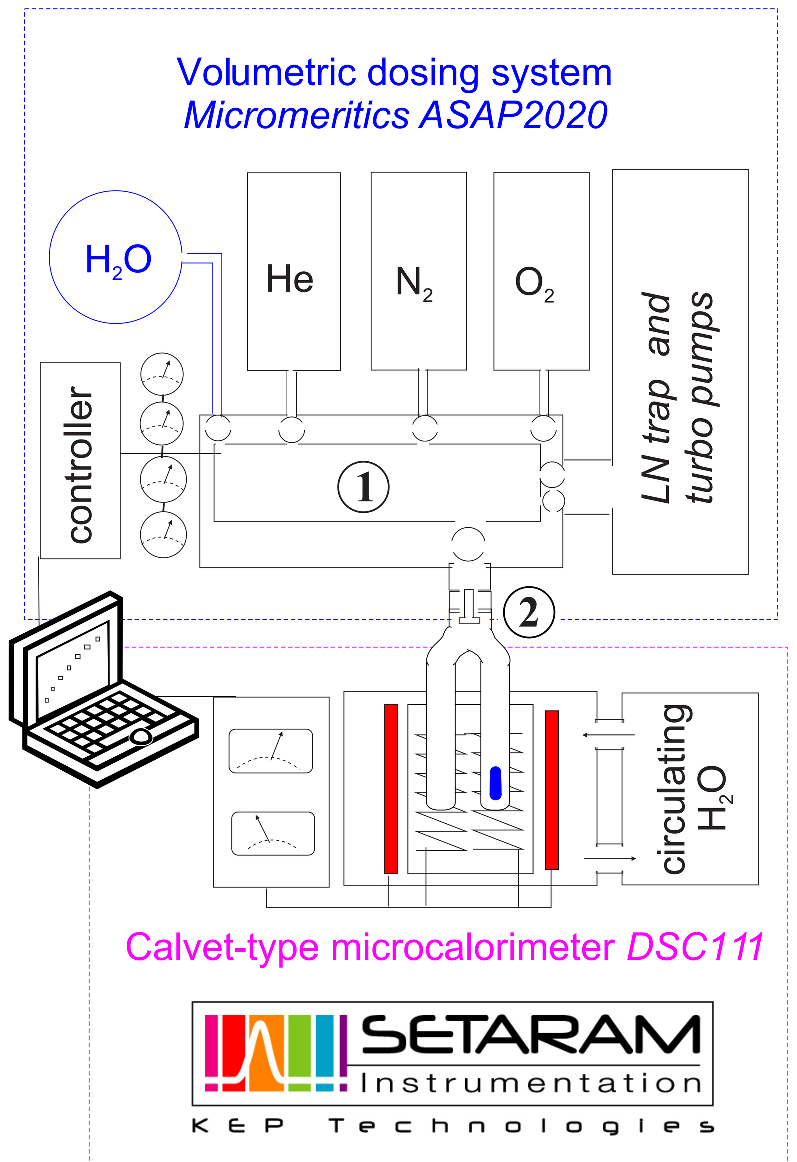
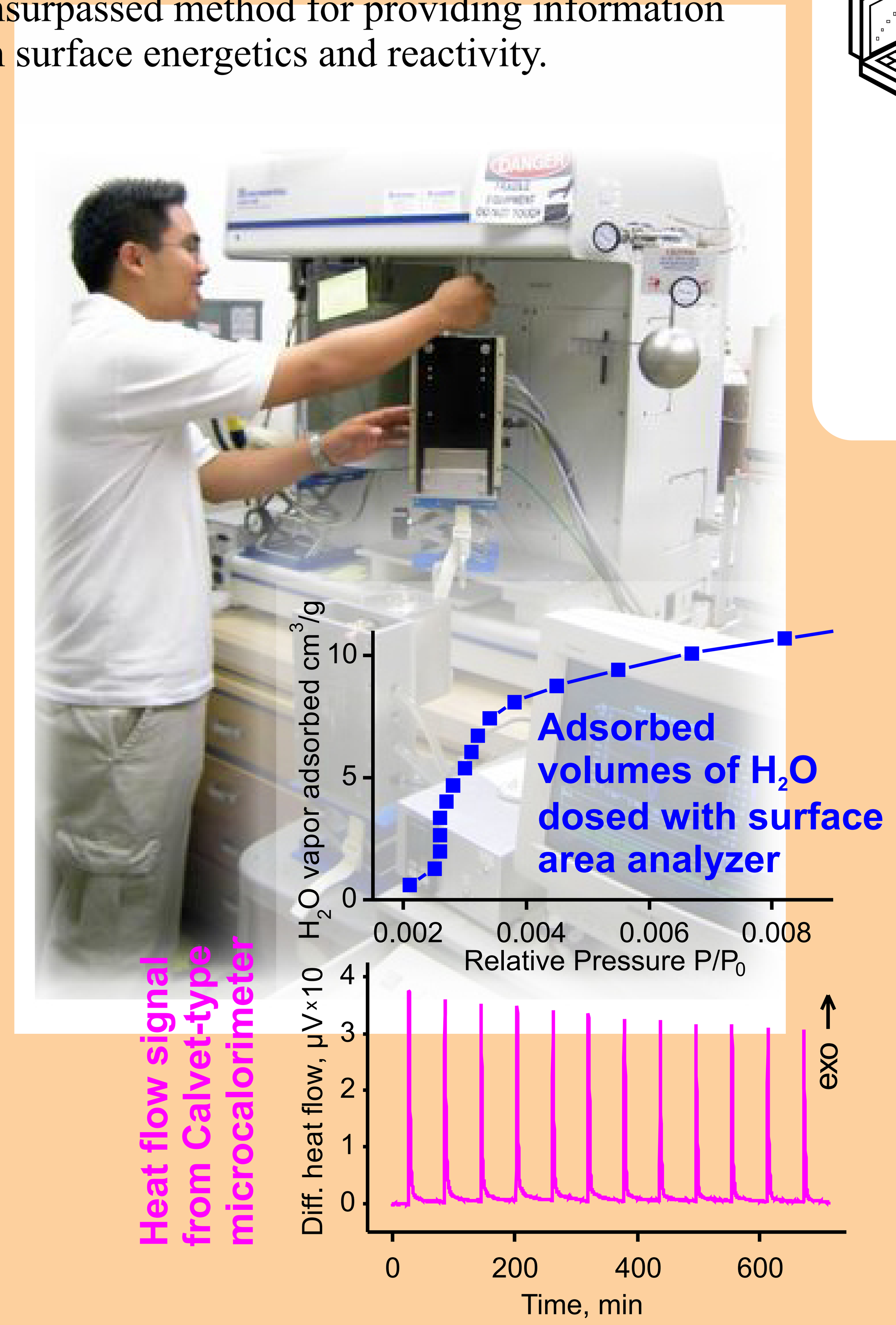
Method

As the dimensions decrease, surface properties become an overriding feature controlling reactivity and phase transformations in nanophases. The control of properties of solid surfaces is of paramount importance in a number of fields ranging from heterogeneous catalysis and fuel cells to microchip fabrication and corrosion-resistive coatings.

Gas adsorption microcalorimetry is an unsurpassed method for providing information on surface energetics and reactivity.



S.V. Ushakov and A. Navrotsky, Applied Physics Letters 87, 164103 (2005)



Micromeritics ASAP2020 is used as a dosing system. Setaram Calvet-DSC 111 operated in isoperibol mode used as calorimetric detector for heat of adsorption. The adsorbent is placed into one side of the quartz fork-type sample tube, which fits into the twin calorimeter cells. The other side is left empty and serves as a reference. In these conditions, measured experimental heats are in fact enthalpies of adsorption. Experiments include three steps:

i) sample degassing in vacuum at the desired temperature;

ii) measurement of free volume of the sample tube with helium and measurement of BET surface area of the sample by nitrogen adsorption;

iii) final evacuation of the system and measurement of the heats of adsorption in a series of small dosing steps with the calorimeter at 25 °C. Dose amounts and equilibration times are set up with the surface analyzer controls and the adsorption isotherm is measured simultaneously.

Novel setup for gas adsorption microcalorimetry, unique to UC Davis Thermochemistry Facility.

- **It uses well established technology for volumetric dosing implemented in BET instruments.**
- **Small total volume of the system allows fast equilibration.**
- **High sensitivity of Calvet-type microcalorimeter allows small samples: enthalpies of adsorption were measured on samples with total surface area less than 0.5 m^2.**
- **The temperature range of the microcalorimeter allows one to study a wide range of gas-solid interactions from -100 to about 800 °C.**

S.V. Ushakov and A. Navrotsky, Applied Physics Letters 87, 164103 (2005)

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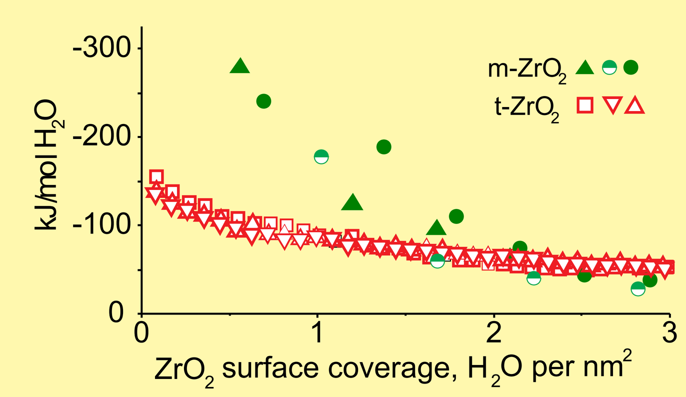
Applications examples

Determination of the surface site energy distribution

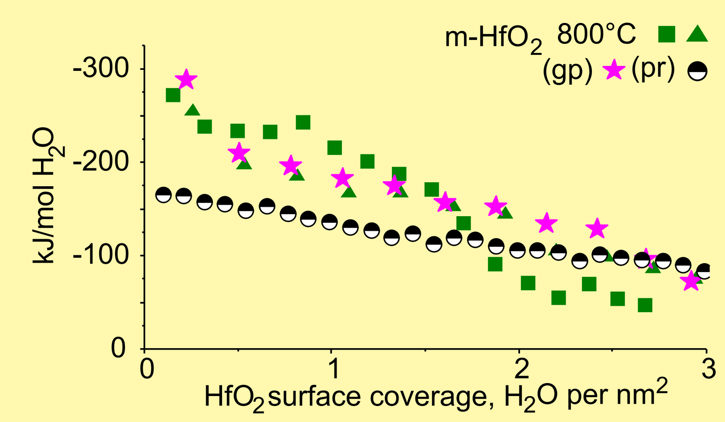
Bulk phase dependence



Differential enthalpies of water adsorption on monoclinic and tetragonal zirconia phases after degassing at 800 °C.

S.V. Ushakov and A. Navrotsky, Applied Physics Letters 87, 164103 (2005)

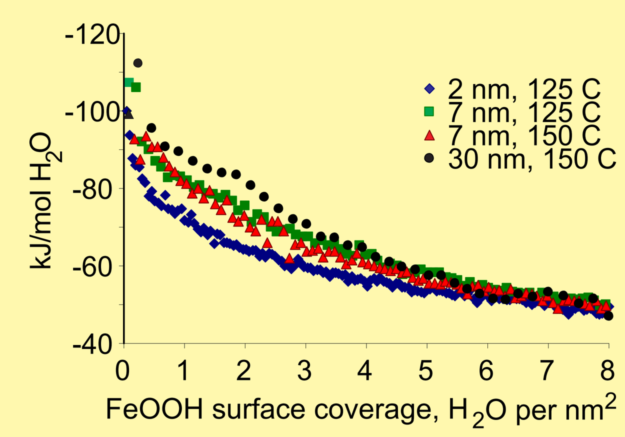
Synthesis route dependence



Differential enthalpies of water adsorption on monoclinic hafnia. Commercial Alfa Aesar samples compared with synthesized by precipitation (pr) and condensation from gas phase (gp) samples after degassing at 800 °C.

S.V. Ushakov and A. Navrotsky, Applied Physics Letters 87, 164103 (2005)

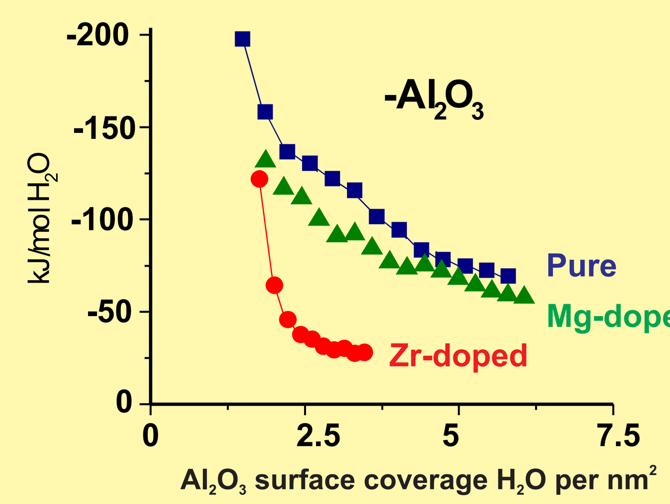
Particle size dependence



Differential enthalpies of water adsorption on goethite particles of different size.

L. Mazeina and A. Navrotsky, Clays and Clay Minerals, 53 (2), 113 (2005)

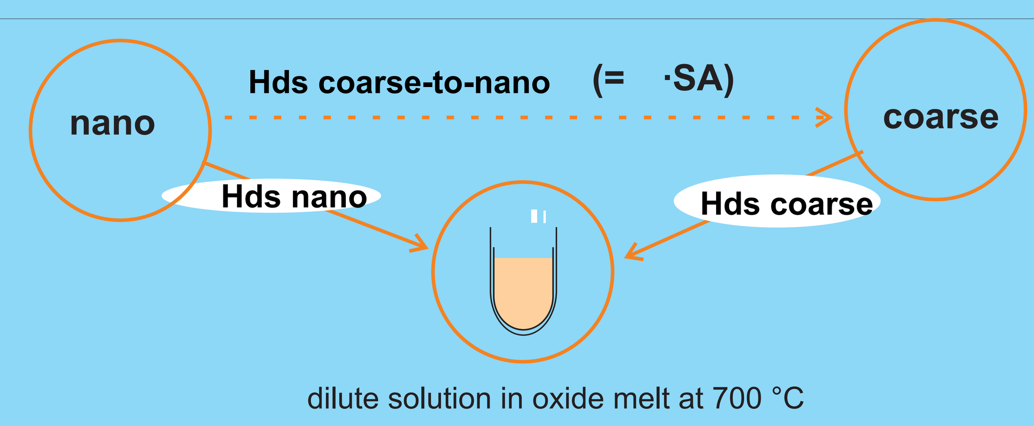
Dopant dependence



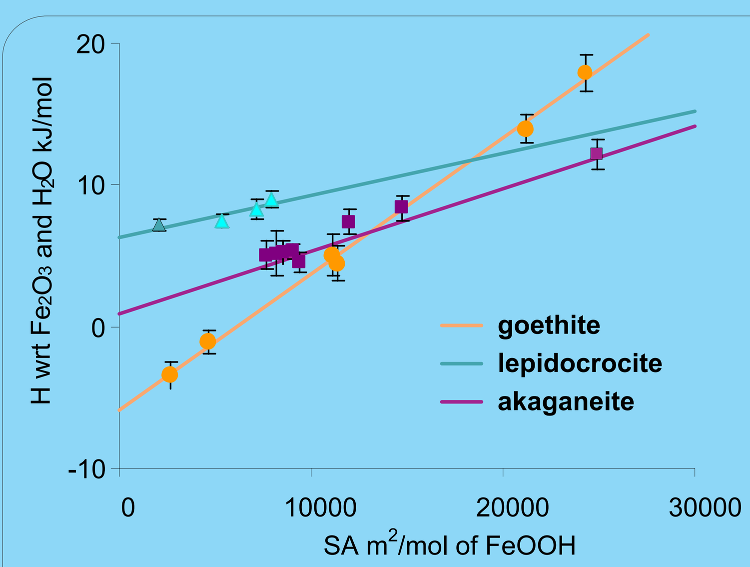
Differential enthalpies of water adsorption on pure gamma alumina compare 1 % Zr and 3 % Mg doping.

R.H.R. Castro, S.V. Ushakov, L. Gengembre, D. Gouvêa and A. Navrotsky, Chem. Mater., In press

Determination of energies of anhydrous surfaces from solution calorimetry on hydrated phases

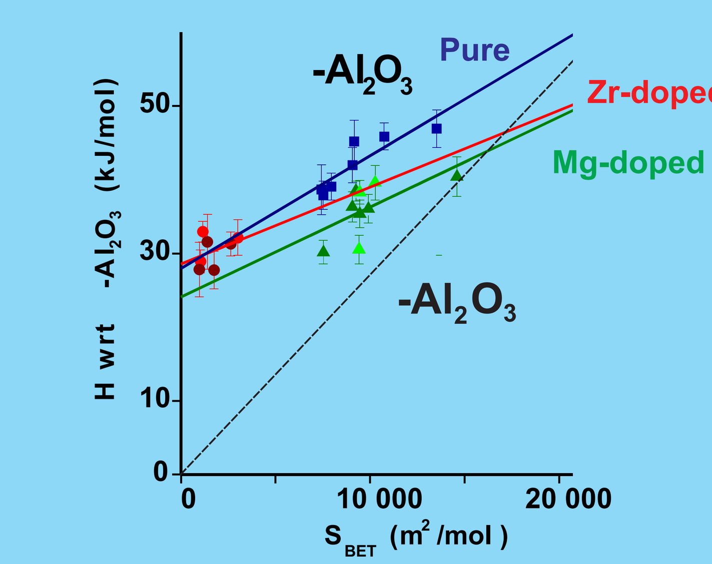


If adsorbed water present, one needs to account for H_{des} to estimate energies of anhydrous surfaces



Enthalpies of FeOOH phases relative to bulk hematite and liquid water vs. surface area. Values are corrected for adsorbed water assuming H_{des}= - H_{ads} Slope of the lines corresponds to average surface enthalpy for each phase.

L. Mazeina, S.W. Deore, A. Navrotsky, Chemistry of Materials, in press
L. Mazeina, A. Navrotsky et al., In preparation



Enthalpies of pure and doped -Al_2O_3 wrt to bulk -Al2O3 vs. surface area. Values are corrected for adsorbed water assuming H_{des}= - H_{ads} Slope of the lines corresponds to average surface enthalpy for each phase.

R.H.R. Castro, S.V. Ushakov, L. Gengembre, D. Gouvêa and A. Navrotsky, Chem. Mater., In press