Surface Area and Porous Material Characterization

Notes from Martin Thomas' Short Course

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Contents

Lec 3: Special Topics, Water   **14**

Lec I: Physisorption and Basic Measurements

Dr. Martin A. Thomas is the speaker for the day.

- Surface Area
- Catalysis

Essential Techniques

- Surface area
- Pore size distribution
- Catalyst active area/dispersion
- TPR and other flow materials

Surface Area

For the purposes of this scale, the geometric extent of the interface between two materials in any phase would be the surface area. Surface area measurement is useful for a variety of situations:

- Reveals an excess of fines that PSA cannot
- Can distinguish between different morphologies of similar size
- Can follow the generation of particle-particle bonds Typically van-der-waals but under certain temperature and pressure can cause sintering which would be "true" bonds in

terms of ionic and covalent bonds.

- Temporal morphological stability
- Confirms brittle fracture under compression
- Tighter control on specifications of raw materials to avoid surprises during later processing
- Can explains unxepected dissolution behavior

Discussion

The PSA (particle size analysis) is not always of much use. Even the 90% median measures may miss out on certain complexities which broaden or alter the spread without changing the median measures. The surface area considerations are significant then. Of course the surface area is most important when one considers porous materials. The surface as defined here extends through the bulk of the material due to the porosity. "Stickiness" is simply when the gravitational pull on the particle cannot overcome the molecule's attraction to the surface. The surface free energy is the amount avaliable for work. At the surface when the surface free energy increases, there is an increase in the dissolution rate. When the surface area decreases, the commiserate reduction in the surface free energy reduces dissolution while increasing strength. Especially when there is a liquid, the surface area is a very good measure of the liquid lost to the porosity.

Dissolution rate

The Noyes-whitney or the nerst-brunner equation is used for the dissolution rate:

$$\frac{dW}{dt} = \frac{DA(C_S - C)}{L}$$

Pore Size

The pore size distribution is inversely proportion to the fluid adsorption.

Hierarchical Pore Stuctures

Inspired by the lungs, the idea is to have progressively larger surface area with increasing depth.

Catalyst Turnover

A general trend in the turnover, that is, the number of reactions which may occur at a reactive site is seen to be strongly correlated to the pore-size.

Gas Adsorption

This is the only technique which directly mesasures and quantifies the surface area accurately. Hg intrusion is important too since it covers a wider range but then it isn't a really direct measure. The only biase is the sieving effect.

IUPAC definitons:

- Micropore is less than 2nm

- Mesopore is between two to fifty nm

- Macropores are larger than 50nm

Calculation mMethods

A small pore version is a stronger absorber. The pore causes the adsorption force to "focus" in a sense. LJ potential energy analysis shows that the entering molecules "see" more than one surface during adsorption. The isotherm is used to directly measure the gas interacting with a surface and within the pore.

Gas adsorption goes upto 500nm. The BJH is a classical method based on the Kelvin equation. There are also DFT kernel methods. Smaller pore has lower pore filling pressure. The pore filling pressure is used to calculate the pore size and the extent of the surface. This also means we can get the pore volume. The pore size distribution is a volume distribution, not a spatial distribution.

1. Basics We need to remember to have the saturation pressure in mind for physisorption.

Total Physisorption

This analyzes extensive ranges of physical properties. The BET surface area is the Brunnet-Emmet-Teller method. Typically the BET surface area is one of the total area. The T plot method is used in the multi-layer portion and is used to get the micropore distribution. The mesopore size distribution shows a hysteris curve from which information about the pore structure can be **qualitatively** obtained

Flow Analysis

Cooling is important to get the information required. The desorption peak is used to measure BET areas due to quick heating of the sample and get a sharper peak.

Vacuum Volumetric Principle

This is a manometric principle. The point is still to obtain the isoterm. So the construction involves a sample cell, cooled with liquid nitrogen. There is a evacuation system to ensure that the full isotherm can be obtained. The temperature (measured), volume (calibrated), and the pressure (controlled) in the manifold, the ideal gas law can be used to figure out the amount absorbed.

Typically for surface area and pore size analysis:

- Nitrogen at 77K. For micropore size distribution for microporous carbons will take upto 2 hours. For zeolites, argon at 87K is about twice as fast.

- Argon at 87K. Is recommended by the IUPAC. This is very good for micropores because it is monoatomic, no orientation issues, is non-polar and inert (surface changes have no effect). Ar (87K) kinetics are faster than nitrogen at 77K (shorter equilibration times).

- CO_2 at 273K. The polarization makes it unsuitable for zeolites. It is typically used for narrow pores in microporous carbons. Can get a micropore carbon in a few hours (4 to 6). A lot of this is because of the increased temperature.

- Krypton 77K or 87K for very low temperatatures since it is really expensive. Used when Nitrogen cannot be used.

Practical Rules of Thumb

Sample Cell Selection

The cell which minimizes the void volume is the right one. Overfilling risks elutriation. Larger void volumes will cause a loss in precision. The smallest bulb which accomodates the optimal TSA but no more than two thirds full.

Minimize negative impact of cold volume

Coolant level controlled at the top creates a large cold zone. Coolant level controlled at the bottom causes a smaller cold zone.

Sample Preparation

Degassing is normally done by heating under flow, or by using a vacuum. The highest temperature which will not ruin the material is what should be used. Ensure that the substance does not degrade. Flow methods will not be very good in some cases, namely because there is a water molecule in the pore which has to come out slowly.

Degassing Time

The complete time is by experimentation. Typically its sixteen hours, which is considered to be overnight. Samples that require low temperatures generally require the longest outgas times.

P/Po Range Selection

The multi-point BET is lower than the single point BET.

Micropore challenges

Typically there are many extended range micropore stations each with a dedicated manifold and a complete set of transducers.

Data Reduction

Micropores are upto the leveling out of the isotherms. Multilayer use the Tplot. The mesopore region is beyond that. Right at the top end is where the gas absorbs into the interparticle space. This is essentially a feature of the undefined interparticle sizes.

IUPAC pores:

- Pores smaller than 2nm

- Supermicropores 0.7 to 2nm

- Ultramicropores are less than 0.7nm

The density of the absorbed gas is estimated to figure out geometric aspects of the pore being studied. Type four regions are essentially the macropore range. For micropores you need the data from ten to the power minus ten to see the micropore filling.

For different P/Po the same micropores may be observed. Nitrogen's strong quadrupole shifts the pore filling to much lower P/Po. DFT can correct somewhat, but argon is much more reliable. Micropores usually have a turbo pump and a diaphragm pump.

The take away is that pore filling pressure is directly proportional to the pore size diameter.

- Nitrogen is great for good for SA, Mesopore and total pore volume but not for

micropore sizes.

- Argon is recommended in all cases greater than 0.5nm because the gases listed are least affected by surface chemistry.
- Carbon dioxide cannot do anything other

DFT

Lowell, sheilds thomas and Thommes. Characterization of porous solids and powders. Neimark, Ravikovitch, Thammes, Carbon (2009) Thommes Cychosz, Neimark

NLDFT skernel of metastable isotherms take into accound delays which may occur.

M. Thommes. In Nanoporous Materials Science and engineering

When there is a network defect, then there are ink-bottle pores, M. Thommes, B. Smarsly, M. Grenewold, Ravikovitch, Neimark, Langmuir 2001.

> Rutgers University under Alex Neimark carries out much of the academic DFT calculations

> For these systems, though earlier studies have used MC, DFT is actually faster.

> The temperature effects (local heating due to the exothermic nature of adsorption) does cause a delay for accuracy, that is, the system is to be equilibrated and cannot be hastened.

Lec 2: Chemisorption

This is also known asn reactive gas adsorption. This is typically used to quantify the number of reactive sites. Silver catalysts are low dispersion.

Table 0.1: *Chemisorption*

Feature	Analysis
Active Metal Area	TPR
Dispersion	TPO
Crysallite size	TPD
Acid site concentration	Activation Energy
Heat of adsorption	

The crystallite size is typically not the true size, except in some special systems. Protonated zeolites have acidic sites, and that is the visual metric used expressed as the amount of gas. There is no real conversion as there is no real surface area calculation.

A wetting syste is such that the metal to the support affinity is higher than that of the metal-metal affinity. There may be steric hinderance, but essentially the wetting systems tend to-wards to spreading out over the surface. When there is less dispersion, the metal will tend to coagulate in lumps, which will cause some of the atoms to be not be accessible for reactions.

Physorption areas and chemisorption areas are different. The cross sectional area is used for the physisorption, that is some 16 angstrom. The metal area does not use the area of the adsorbed gas. It uses the size of the absorbing site. The internuclear distance for the metal can also be used. The projected area estimates can vary.

Forming a chemical bond does not require cryogenic conditions. Hydrogen is very popular since it chemisorbs to a lot of metals. Since it forms a hydride sometimes, there is some "solubility" in the metal, so the adsorbed gas may not actually be localized on the surface. Typically where hydride formation is an issue, CO is used. Twice as many CO moleculas are adsorbed compared to H_2 for Platinum. Multiple isotherms can be used to get the heat of adsorption and correlate them to the acid site strength.

Ni may also be volatile enough to form a Ni mirror somewhere cooler.

Table 0.2: *Metals and Reactive Gases for Chemisorption*

Metal	Reactive gas	Comment
Pt	hydrogen, CO	Twice as many Co as H_2
Pd	CO	Pd forms bulk hydrides, i.e. not limited to the surface
Ni	Hydrogen	Ni forms carbonyls, not limited
Fe	Hydrogen	Fe forms carbonyles, not limit to the surface
Ag	Oxygen	At elevated temperatures

Stochiometry

The number of metal atoms per gas molecule. The instrument can measure how much gas is adsorbed. Normally it is assumed that hydrogen dissociates on the surface, so one hydrogen molecule will dissociate over two metal atoms. In some cases in the literature they use the number of atoms reating per molecule, so that is half. When we consider CO, it may be one or bridged, and therefore two. At low pressures of Co, the bridged system is more likely, so as the pressure increases, it is reasonable to assume a steric geometry of one.

Setup and Quantification

The volumetric version of the equipment is usually the same as that used for physisorption. A flow of reactive gas is used to get rid of water as well.

We try to stay close to the critical temperature for chemisorption studies. In theory, after a layer is chemisorbed there is only pressure created over the surface with the addition of gas after saturation. The first isotherm is generated, then the system is evacuated, and another isotherm is plotted. Now since we have not changed the temperature, to remove the extra effects which may be in the system, the second isotherm is the weak, reverible isotherm. Thus we can not calculate the strong or irreversibly adsorbed isotherm. To get the amount we can do a simple least squares extrapolation to get the volume adsorbed. The strongly adsorbed isotherm is considered to be pressure independent. A cheisorption isotherm will typically have a much smaller number of points, since it's essentially a straight line generation. Ten is a reasonable default. It's much faster than physisorption of course. The exotherm in chemisorption is unlikely to cause any changes while for physisorption a the exothermic energy might cause the neighboring molecules to pop off. Close to the desorption temperature there might be some curvature for chemisorption as well.

Flow Methods

Pulse titration is also used. Typically, the gas is pulsed (fixed volumes are injected, typically 100 micro liters), in a carrier which is typically N_2 or He. Helium is common for carbon systems. Downstream, a TCD is used to analyze the rest of the stuff. The process is isothermal but an isotherm is not generated. Reversible adsorption esorbs after the puslse has passed. The weakly adsorbed gases are swept away, and so not reversible equilibruim with the rest of the surface. The TCD reacts to what was not taken up by the sample. Peak integration is done to figure out how much was adsorbed. The difference between the peak areas is used to figure out how much has been adsorbe. Sometimes the peaks overlap when there isn't enough of a delay between the pulses. Weaker pulses have more tailing. Upto six partial peaks are usually relevant. For some systems like Pd/Ni where H and CO might not be a good fit to either Pd or Ni, typically both are used. Flow techniques are also better for such systems too. In bimetallics it is very difficult to create situations where one is adsorbing and the other is not.

Sample Preparation

The system has to be activated. Not just dried. Most samples are oxidized metals so they need to be reduced with a suitable gas to the active state at elevated temperatures, and then it needs to be purged and cooled. This is usually in a u-shaped flow pattern cell. Unlike physisorption, preparation is done in-situ at the analysis port under flowing gas conditions. The setup is easier for chemisorption than physisorption in terms of protocols.

Flow Methods

Typically 300K might be a good start, but not always. Nickel luminate needs around 600K. Most plants which use steam reforming don't have temperatures that high, so any nickel-luminate created is lost. So with a TPR you can figure out what you can't from just a total nickel analysis.

- Oxide reducibility by TPR

- Carbon oxidaion

- Acid site concentration by TPD

- Activation Energy

You can determine the nature of an acide ste by swamping the system in ammonia, then heat it until it gets off.

TPR (Temperature Promgrammed Reduction)

Water is the main product of the reaction and can be removed from the gas flow using a cold trap prior to the detector for a clean TCD signal. The exact shape of the distribution depends on the amount of sample as well.

- Cerium IV oxide

- Nickel oxide

- Iron oxide

- Cobalt oxide

Aluminum oxide won't reduce even at maximum instrument temperature.

TPO (Temperature Programmed Oxidation)

Similar to TPR in that a gas mixture dilute in the reacting gas is passed over the sample as the temperature is increased in a liner fasion. The main products are CO and CO_2. These are not trapped and allowed to go through.

- Carbon Nanotubes

- Cerium III oxide

- Coke on catalysts

- Pre-reduced metals

Spikes in these curves may be due to the catalyst being left in the product.

TPD (Temperature Programmed Desorption)

Can also be decomposition. The only way to be really sure of all the products is a downstream mass spectrometer but this is typically overkill.

- Acid sites (NH_3)

- Basic sites (with CO_2)

- Methanol from reactive oxides

- Hydrogen form hydrides

It is assumed that they are Bronsted sites, but is not typically proven with pyridine methods.

Lec 3: Special Topics, Water

Water absorption is interesting due to the difficulty in classication in terms of the ambigous nature of the bond (H-bonding). Water at 25C in mesoporous carbon (micro mesoporous) then water is of Type V, while Nitrogen at 77.4K is Type IV. The nitrogen has large sections which are basically accessible via necks. For water, the isotherm creeps along the P/Po. Basically Nitrogen forms a wetting isotherm, and water on carbon is a non-wetting isotherm for a while. Water has **delayed** micropore filling. For nitrogen, micropore pressure takes place at very low pressures. Water is smaller than nitrogen, so it does enter pores which nitrogen will always ignore. Since it is non wetting on carbon, the micropore will fill **after** the mesopore. The hysteresis has been suspected to be through a cooperative mechanism, that is through the hydrogen bonds. The pore space fills with a dense phase of a vapor without any of it getting on the surface. Essentially these are confined systems.

Nitrogen

There is no characteristic microporous filling for nitrogen at 77K, this is because the pore sizes are approximate. There are crosses, even when considering DFT systems.

Water

So in the same microporous systems, we can see that the non wetting system behave differently. Essentially for these systems, the water isotherm is a better classifier.

Thommes, M; Morell, J.; Cychosz, K.A; Froeba, M. Languir 2013