surface 11-12 first cut

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(0:00 - 2:28)

On Tuesday we arrived to define the different molecules that we can use to evaluate the textural properties of materials and we saw as nitrogen at 70-70 usually is the best choice, then the first choice that we can do, but it cannot be the best one when we work with microporous material, for this reason in that case we prefer to use argon at 87 Kelvin, but if argon is not enough to see specific pores that can be very very small and not accessible both to nitrogen or argon, we have the possibility to use carbon dioxide at 273 Kelvin, this molecule is very small and being absorbed at this higher temperature, not at a cryogenic temperature, but a temperature that is closer to room temperature, we have the possibility to minimize the problem of diffusion in more small micropores and to exploit the very low kinetic diameter of this molecule. But what we obtain is an isotherm that is usually collected in a range of relative pressure that is very very small because the vapor pressure of CO2 at 273 Kelvin is very high and so we can cover just a small range of relative pressure, but it is enough to have information about the micropores that are below 1.5 nanometers, and so we use this problem just when we want to explore micropores that are very very small. I want to show you an example of the use of CO2 instead of nitrogen that can be useful, it is the case of a specific zeolite that is called LTA in type A, zeolite that is a microporous material in which the micropores are very very small, which are the feature of this zeolite.

(2:28 - 3:26)

This is the picture that represents the cavities of the zeolites, and so a feature of this zeolite is that, you will see with Professor Portiga, but the zeolites are alumino silicate, so they are made of silicon, aluminum and oxygen. Aluminum is substituted to the silicon in the framework, so considering that silicon is 4+, and aluminum is 3+, you generate a negative charge that must be balanced, and to balance this negative charge to allow the material to exist, you need to have counter ions inside the micro cavities that are cations that compensate this negative charge. The cations are located inside the micropores of the zeolite.

(3:26 - 4:23)

These zeolites can be synthesized using different silicon to aluminum ratio, different content of aluminum, it depends on the type of the framework. For example this framework, this specific framework that is called LTA, is a zeolite that can be synthesized only if the silicon to aluminum ratio is equal to 1, so it means that we have a silicon aluminum atom for each silicon atom. So it means that the amount of aluminum is very very high, and so it means that the amount of counter ions that are present inside the micro cavities to compensate this negative charge induced by the presence of aluminum is very very high, and so it means that our micropores

are in some way indirect by the presence of these cations.

(4:23 - 5:01)

And so if we have a lot of cations inside, the problem is that when we try to absorb nitrogen at 77 K, in our first probe to study the textural properties of the material, what we obtain is this. This is the isotherm, the blue one. You see that basically if you should say me what type of isotherm is it, you should answer me that the blue one is type 1, 2, 3, 4, 2 of a non-porous material.

(5:02 - 5:47)

But we know that the zeolite is a microporous material. The problem is that nitrogen is not able to enter the micro cavities because they are too indirect to allow nitrogen that is large and that we are larger than CO2 and that we absorb at 77 K, which is a very low temperature, and so in this case the diffusion can be very problematic, is not the right probe to detect the textural properties of this material. And so what happens when we try to absorb carbon dioxide instead? What you see is that we obtain the orange isotherm.

(5:47 - 6:41)

Pay attention that the isotherm are reported in relative pressure from 0 to 1, so with nitrogen at 77 Kelvin, the p0 is 0.95 atmosphere, so it means that you basically reach 1 of relative pressure. You are able to reach a relative pressure of 1, and so this is what we arrive at. Instead for the CO2, you see that the isotherm is reported just in a small range of relative pressure that is no more than 0.02. Why? Because the relative vapor pressure of CO2 at 273 Kelvin is larger, and so the range that we can cover is smaller.

(6:42 - 7:26)

We cannot reach 1 of relative pressure, because we should reach 34.26 atmosphere, and it is not possible. But what is interesting is that, look at the first point, here you see a magnification of this region of relative pressure, you see that CO2 is able to enter inside the material, because you see a very large amount of CO2 absorbed, indeed the orange isotherm is a sort of type 1 isotherm. We reach a plateau very soon.

(7:27 - 8:42)

And so if we use the orange isotherm or the blue isotherm to calculate the specific surface area, so to calculate the monolayer capacity, and then the specific surface area, you can imagine that already by just seeing the position at which the monolayer, so in this case the monolayer capacity should be more or less here, the blue one, and the other one should occur in some place here, so here we are reaching the plateau. And so you can imagine that the surface area calculated with this monolayer capacity should be very very high compared to this, and this is what we obtain, 25 m2 per g with nitrogen, 300 m2 per g with CO2. Why? Because CO2 is able

to enter where nitrogen cannot enter, and so in this case you understand what are the limits of nitrogen and what are instead the advantages in using CO2 as a probe to evaluate the textural properties of this material.

(8:50 - 9:42)

Ok, so with this slide we should have finalized the part concerning the choice of the different probes, and the evaluation of the different isotherms that we can obtain, and the information that we can derive from an isotherm when we want to use the isotherm to evaluate the textural properties of a material. But I want to explain to you that we don't use volumetric absorption just to obtain information about the textural properties of a material. This is a technique that can be used with different probes, argon, nitrogen, CO2, krypton, and so on, to evaluate the textural properties of polished materials, to evaluate the specific surface area for volume, for size, for distribution.

(9:42 - 10:13)

We will see later on how to derive this information. But sometimes we need just to collect an isotherm to understand if a material is able or not to absorb a specific gas. Imagine for example to work with, as I do in my research activity, to work with materials that can be used for the capture of carbon dioxide.

(10:15 - 10:55)

In that case, after the synthesis of the material, and after the characterization of the material, if I have a porous material, I can study the material with the different probes to evaluate the surface area, the pore volume, the pore size. But then imagine that I can do it with argon at 87 Kelvin and I obtain that my material has a surface area of 500 square meters per gram, and so on. After that I know that this material is a material that I want to use to exploit to capture CO2.

(10:55 - 11:24)

And so what I do is to measure isotherms of CO2 just to understand if the material is able to capture and to absorb CO2. So sometimes the evaluation of the absorption is done not to characterize the material, but just to have information about its capacity or not to be exploited in the application that you design. The example of carbon dioxide capture.

(11:25 - 12:13)

And so we also have the possibility to collect with the same polymicron instrument isotherms of CO2, not only at 273 Kelvin, but at different temperatures. Because when we capture CO2, for example from a post-combustion gas, the temperature that the flue gas that contains usually nitrogen and CO2 mainly is at a temperature that is between 40 and 90 degrees. And so what I desire is to understand the amount of CO2 that is captured by the material and the condition in which I will use the material itself.

(12:15 - 12:47)

And so I will just show you some examples in which the volumetric measurement can be exploited just to evaluate the absorption performance of a material. This is something that we did in our lab. We developed some peculiar composites made of a metamorphic framework that is called UTSA-16.

(12:47 - 13:26)

This is the name of this metamorphic framework. And we mixed the metamorphic framework with a crystalline polymer to obtain a composite, which is this one. Because often the problem that you have when you use material in the capture of carbon dioxide is that when you use the powder, so use the powder is not so easy because when you have a reactor in which you need to capture on site the CO2, to have a powder can be a problem.

(13:26 - 13:51)

A problem because you can have pressure drops in the reactor. And so what you prefer and you desire is to have something with a specific shape. And we developed this special composite to be able to absorb CO2 not with a powder but with something with a specific shape.

(13:52 - 14:15)

And the active phase for CO2 in this composite is the MOF. The UTSA-16 is a MOF that is often used in the literature and you will find that it has a high affinity towards CO2. And so we can collect isotopes of CO2.

(14:15 - 14:36)

For example, I took 298 candy to evaluate the capture capacity of the material for CO2. And you see that in case of CO2 we have a type 1 isotope. So it means that it is capturing a lot of CO2.

(14:37 - 14:59)

And we can also evaluate the materials that we use to capture CO2 in a mixture of gases. As for example, usually CO2 is separated from nitrogen or from methane. As for example in the case of the biogas application.

(15:00 - 15:28)

In which you need to purify the biogas from CO2 to remove the fraction of CO2. In this case you see that the capacity of the material to capture the star symbols are related to experimental points that we obtained by absorbing methane on the material at the same temperature of CO2. And you see that the amount of methane that is captured is very low compared to CO2.

(15:28 - 15:55)

So we can say that probably the selectivity of the gas towards CO2 is higher compared to methane. And so sometimes we use this experimental technique, the volumetric, to just evaluate the capture performances of the absorption capacity of a material towards a specific gas, CO2 or methane and so on. We collect isotopes.

(15:58 - 16:26)

These are just examples that I showed you to explain what we do in lab with the volumetric. If you want more information you can find everywhere in the paper that we published. Another possibility for example is to use the same ATA zeolites that we saw before as material to capture CO2.

(16:26 - 16:51)

Because we already saw that compared to nitrogen it has a very high selectivity towards CO2. It absorbs basically just CO2 and not nitrogen because nitrogen cannot enter inside the pores of these zeolites. And so in this case I'm showing you some isotopes that we collected at different temperatures on these zeolites.

(16:51 - 17:29)

Here you see the different isotopes collected at room temperature. And we changed the cation that is present inside the zeolite to see if you have a different affinity towards CO2. And so we saw for example that if you put calcium as counter ion inside the frame of the state of sodium what you obtain is a higher capture capacity of the material, the orange cube instead of the red one.

(17:29 - 17:54)

And we for example compared this zeolite with another zeolite that is a natural. The LTA zeolite is a synthetic zeolite. Instead for example this one, clinopyrite is a natural zeolite that contains inside the frame of the different cations because the natural zeolites are not as the synthetic ones.

(17:54 - 18:18)

So in the synthetic one you can select the cation that you have inside. In the natural one often you have a mixture of cations inside the frame. And so we compared the natural zeolite with the synthetic one and we evaluated the absorption capacities.

(18:18 - 18:52)

Here in the histogram you see the amount adsorbed that we derived at 100 millibars from the isotope. So these values are here at 100 millibars and you take the pressure, the amount of gas adsorbed, you can build this histogram and this one instead is obtained at 1000 millibars. To observe if there is a trend among the materials and so on.

(18:53 - 19:43)

So in this specific case we can evaluate the adsorption capacity of different materials by volumetric adsorption and we can compare the adsorption capacity of different materials synthesized in different conditions or with different nature as in this case a natural zeolite with a synthetic one. These are just two examples of what we do in lab when we use exploit volumetry just to obtain information about the capture capacity. Here I have something to tell you because it is very interesting.

(19:43 - 20:05)

It is a new in some way research topic that is developing nowadays. It is related in the last 15 years more or less. It is related to a new class of adsorbent that are able to give rise to very strange isotopes that are not present in the IUPAC classification from the moment.

(20:05 - 20:55)

Maybe in the future they will be added. These isotopes are very peculiar because you have here you have the standard isotopes that we saw, the type I isotopes. You see that for example in that case you have a standard microporous material in which you have here the pressure, the amount of gas absorbed and a microporous material that gives rise to an isotope that is type I with a gas.

(20:57 - 21:34)

For example let's consider CO2 as a problem. The different cures, blue, purple and red are collected at different temperatures. So if we increase the temperature which is T1, T2, T3 and you have that T1 is lower than T2 and T3 what you see is that you observe a decrease of the amount of gas absorbed.

(21:35 - 22:07)

It is normal. So when you increase the temperature usually the amount of gas that is absorbed by the material decreases because it decreases the interaction between the gas that is absorbed and the material. And this is what happens usually with a standard microporous material that gives rise to a type I isotope.

(22:10 - 29:56)

When I absorb the material and I want to use for example my material to capture CO2 at the end what I want also is to release the CO2 that is captured because in my idea and our idea is to use the material to capture then release the CO2 but not in the atmosphere but to store the CO2 in some place then use again the material to capture CO2 then release CO2 and so on. And so to release the CO2 what we can do for example if we have the material that is here at this pressure and the maximum amount of CO2 that can absorb is the same what we can do is for

example or decrease the pressure and come back but to decrease the pressure we need to apply vacuum and so you need to spend a lot of energy to release the CO2 or what you can do is to increase the temperature if you increase the temperature you see that the amount of gas absorbed here is this one but if you increase the temperature you can decrease at the same pressure or if you increase more the temperature you decrease the amount of gas absorbed but also by increasing the temperature to release the gas that is absorbed you in some way are using a lot of energy to release the CO2 and this is the paradox of the material that are used for the capture of CO2 because they capture CO2 then to release the CO2 you need in some way to spend energy and the energy that you are using is produced by producing, emitting a lot of tons of CO2 and so you are not sure that what you are capturing and what you are using to capture the CO2 is in some way compensating the amount of CO2 that you are emitting so you have also to evaluate the amount of CO2 that is released in the atmosphere by all the cycle of your material so what we did, what the scientists do is to perform what is called the life cycle assessment of a process to see if at the end what you are doing is good or not and so to have a material with this feature is a problem because the release of the CO2 for example can be energetically demanding too much and what the scientists are studying nowadays are materials with this peculiar shape of the eyes sometimes it is called S shape what is the main difference? you have basically a material that at the beginning is not able to capture the molecule that you are or absorbing the molecule that you are absorbing for example CO2 then when you reach a specific pressure you absorb all the CO2, all the gas that you can absorb and then you reach the plateau this type of isotope is called S shape isotope not CO2 absorbed at the beginning, all the CO2 absorbed all together and then you reach the plateau this for example at temperature 1 if you are at temperature 2 what you obtain is usually something like this so you have that the pressure at which you capture the CO2 all together and the S is shifted at higher pressure this is Q1, this is Q2 and it is collected at temperature 2 if you increase the temperature again what you obtain is this so by increasing the temperature I move the step of the isotope to a higher value of pressure but if we observe a single isotope of this for example this one at the temperature 1 it is very interesting because if I decide to be exactly at this pressure I can capture all the CO2 all together and then if I decrease the pressure I can release all the CO2 all together it is different from here in which I increase the pressure and slowly I increase the amount of gas and so on and you see the difference nothing absorbed, all together you reach the plateau when you have a material like this you have basically something to say ok if I arrive here and I turn on the light I push the button and I say ok light on and you can say to the material if you are at this threshold pressure ok absorbed all, all together then when you want to release you can release all together ok this is a very peculiar behavior and what for example imagine that you are at temperature 1 at this pressure and you absorb everything you are at this pressure at this pressure with this material at the temperature 1 you are reaching the plateau of the material the material is absorbing all the CO2 that you have how can you release the CO2? if you simply increase the temperature a bit what happens? if you increase the temperature and you pass from here to here what you have is that at this temperature the material here if you increase the temperature is not able to absorb nothing and so if you are at this pressure at this temperature you absorb all you increase a little bit the

temperature and you release all all together but you need to increase the temperature just a bit to release the CO2 in this case to release the CO2 all the CO2 you need to increase a lot the temperature in this case not because at the beginning you are here at the pressure between the side at the pressure of the step you increase the pressure you are at this pressure at this temperature you absorb everything to release what is absorbed

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