

surface 11-12 second cut

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(0:00 - 0:29)

The pressure, you have this pressure, at this temperature, you absorb everything. To release what is absorbing, I increase the temperature, but if I increase the temperature, the new isotherm is this one, and not this one. And so, at the new temperature, it can be T , T_x , in which T_x is between T_1 and T_2 , the amount of CO_2 absorbed by the material is zero, and no more this one.

(0:30 - 0:53)

And so you release, absorb and release CO_2 in a very small, with a very small variation of temperature or of pressure. It's totally different from here. What is changing in this case, is what is reported there, is the working capacity of the material.

(0:53 - 1:11)

The working capacity is the capacity of the material to capture and release the molecule. You see that the working capacity of a microporous material is very, very small. A microporous, a standard one.

(1:12 - 2:05)

Instead, for a microporous material like this, the working capacity is given by this arrow, because it can absorb and release all the gas together. So, this new class of material is very interesting, and these are new absorbers with new features, because they are able to capture the molecule that you want, that you desire, in the condition that you prefer, without requiring a lot of energy to release the molecule. So, this is the new frontier of the absorbent, especially in the world of this material for us, this will be captured.

(2:10 - 2:39)

This type of isotherm are not listed by Utah still, but maybe they will be in the future. It's something that is totally new, and we work a lot on this type of material. The temperature is low, but how low? Low, just low, medium, high means that the three isotherms are collected as T_1 , T_2 .

(2:40 - 3:18)

Low means that the blue one can be 298, the purple one can be 300, the red one can be 320. So, low means simply that this is lower than this, but depending on what you are absorbing, the trend is usually this. If you increase the temperature, the step moves at higher pressure, and so

it is very useful to absorb and release the molecule that you desire.

(3:18 - 4:16)

And so there are material absorbent that are used for CO₂ absorption or for COO absorption and that they have this particular shape, and they are very, very interesting for the scientific community. Usually, these S-shaped isotherms are generated by a rearrangement of the material when the material absorbs the molecule, the adsorption. A rearrangement of the material that can be generated by different situations, and I can just give you some example of the materials that are able to give rise to these very strange S-shaped isotherms.

(4:17 - 4:48)

This is, for example, a moth that contains magnesium as metal and a very peculiar link and inside the moth, the moth is functionalized with this DMI inside. You see? These are DMIs that are connected to the moth. This is the pore, the micro-pore of the moth.

(4:48 - 5:33)

The moth is made of magnesium and of an organic link, and here you have this DMI. This material is very interesting because when it absorbs CO₂, it is able to give rise to these S-shaped isotherms, as you can see from here, because if you see the isotherms here, they seem very similar as type 1, but if you make a zoom here, you see very well that they have the same shape, like this, and the different colors represent different temperatures, so you see that you are moving the step by increasing the temperature. This is collected at room temperature, more or less.

(5:33 - 6:06)

By increasing the temperature, you move the step at higher values, 25 degrees for this and for the right, 25, 40, 50, and 75 degrees Celsius. This, if you are interested to know how, why we have this specific behavior, you can read this paper from Nature. It is a paper that is very interesting.

(6:08 - 7:38)

This material was studied also by me, by Professor Bordiga in this lab, in collaboration with some colleagues in California that synthesized the material, and they asked help to us to understand why you observe these isotherms when you use CO₂ as adsorptive, to understand why they were able to observe this strange shape. This was one of the first materials with these very strange isotherms, and so we understood with the use of different techniques that there was a sort of cooperative mechanism of absorption, in which when the first molecule of CO₂ interacts with the amine present graphically, on the MOSFET, we have that there is a modification of the material that gives rise to a sort of cooperative absorption. So all the CO₂ is adsorbed all together in the same way.

(7:39 - 8:44)

This type of mechanism is called cooperative adsorption and gives rise to this type of isotherm. But if you want more information, you can read the paper. What is interesting is that this material was synthesized in this way because it is very similar to a natural enzyme, it is the rubisco, it is responsible for the biological fixation of carbon dioxide, and if you see the size for absorption of the enzyme and of the MOF that we studied, you see that the magnesium is more or less surrounded by the steps and functional groups, and so the material was developed by considering this enzyme and trying to mine the active sites for absorption that were present on the enzyme.

(8:49 - 9:46)

And this is very interesting also because this material is one of the first absorbents that is exploited now in real application for the capture of this CO₂. ExxonMobil bought the material, so the patent for the synthesis of the material by this company, it was a small company that synthesized the material first after the first trial in the lab and they are exploiting from 2019 the material to try to capture CO₂ on real plants and so on. Maybe it is one of the first solid absorbents that now is used for the capture of CO₂ from post-combustion gases.

(9:48 - 11:05)

Another example of a material that can give rise to this S-shaped isotope is again a MOF, a metal-organic framework that contains instead of magnesium or cerium as metal, and this is a MOF that contains specific linkers that are perfluorinated, that contains four fluorine atoms on the aquatic ring. Here you see the linker. This material is able to absorb CO₂ and give rise to this S-shaped isotope, these are collected at different temperatures, and while we were able to understand that these S-shaped isotopes are generated by the rotation of this linker, so when CO₂ is absorbed at a specific pressure the linker can rotate and so they can move in a position to allow CO₂ to enter inside the micropores of the MOF and interact with the cerium site and so this is the reason why we have this very peculiar shape of the isotope.

(11:07 - 12:26)

This is generated by the rotation, the rearrangement of the linker that can rotate when CO₂ is absorbed and they rotate all together at a specific pressure giving rise to the S-shaped isotope. There is another material that we are studying a lot, another MOF, that in this case gives rise to S-shaped isotopes, as you see here, because this MOF is able to have a specific when it absorbs CO₂, is able to give what we call the pore breathing, so the pore can change, so the cell volume of the material changes, so you have an enlargement of the pore when CO₂ is absorbed. This mechanism is called breathing, because you increase the size of the pore when you absorb CO₂ and also this gives rise to these S-shaped isotopes when you absorb CO₂ at different temperature.

(12:32 - 13:52)

Another possibility is given by instead a zeolite that is able to give rise to an S-shaped isotope in presence of nitrogen, when you absorb nitrogen at 77 Kelvin. If you remember, I told you that when we absorb nitrogen at 77 Kelvin and when we observe a step in the isotope above 0.3 of relative pressure, usually that step is generated by the capillary condensation, so the formation of the liquid inside the gas, inside the pore, of the mesopores, but the zeolite that we are measuring here, that is this one, is a micropores material without mesopores and we observe a step at around 0.2 of relative pressure. This step is located in a position that cannot be credible for the formation of the liquid because we know that in micropores we cannot form liquid, and so I told you that if you see a step below 0.3, 0.25, 0.3 means that it is generated by something else.

(13:53 - 14:29)

In this case, the step indicates the occurrence of a phase transition of the zeolite framework between its monoclinic and orthorhombic form that is induced by the absorption of nitrogen. So the absorption of nitrogen triggers the phase change of the material. When the material passes from the monoclinic to the orthorhombic phase, in the orthorhombic phase it is able to absorb more nitrogen and so you observe a step in the isotope.

(14:31 - 15:41)

This phenomenon in this specific material depends on the aluminum content of the zeolite that the zeolite contains silicon and aluminum. It was discovered that by decreasing the silicon to aluminum ratio, if you decrease the silicon to aluminum ratio it means that you are increasing the content of aluminum in the framework, the magnitude of the phase transition can be reduced or can be totally removed and so what you observe is a step by increasing the amount of aluminum in the zeolite framework you see that the step decreases and at a specific value of content of aluminum it disappears because it can undergo just when the aluminum content is low in the zeolite. But this is another possibility that we can observe in the presence of another material that is a zeolite.

(15:41 - 16:17)

In this case the step in the isotope is generated by a phase transition. So these are just different examples of materials that can give rise to these very strange S-shaped isotopes. It is just for you to know that this material exists and they are in some way the new frontier in the world of the absorption of, for example, small molecules like CO₂, CO.

(16:18 - 16:29)

Ok, so we can have a breath and then we do this.

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