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Influence of the size of coal ash FAU zeolites used as dopants on the sensing properties of Nb_2O_5 thin films.

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1. Coal ash - pollutants and possibilities for their utilization

Coal is the largest source of energy from fossil fuels used for generating electricity in the world.

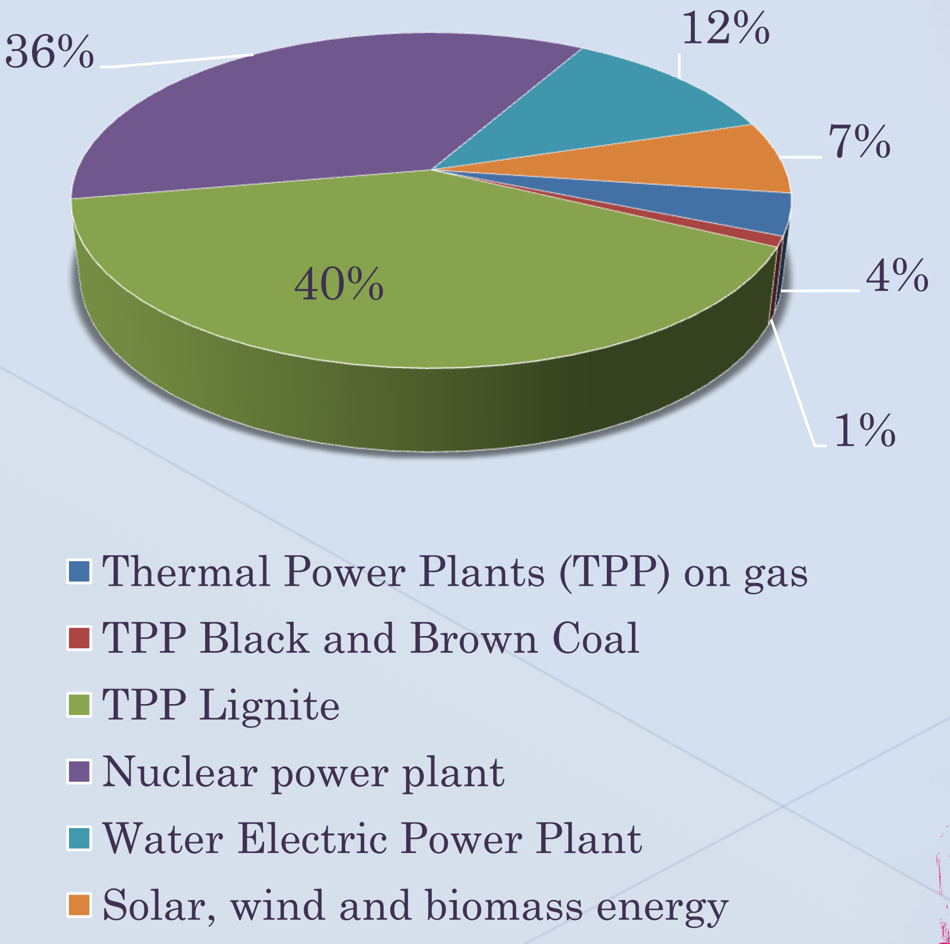
1. Releases of gaseous emissions - sulfur, nitrogen and carbon oxides

2. Generation of solid waste - ash

- Ash macro-component composition is considered as an alumosilicate material.

- Different opportunities for utilization have been explored, including for the synthesis of zeolites.

The electricity produced in Bulgaria in 2018, allocated according to the primary energy resource and used production technology.



1. Coal ash - pollutants and possibilities for their utilization

Released gas emissions → Carbon dioxide CO_2 → Greenhouse effect

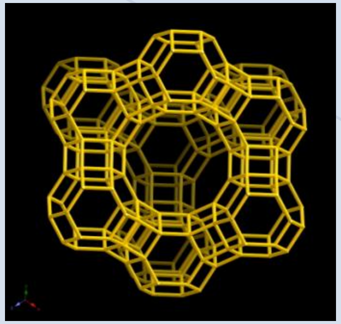
Volatile Organic Compounds (VOCs) → Greenhouse effect

! For the purposes of developing CO_2 capture technologies in the search for new solid phase sorbents, **zeolites** have also been studied.

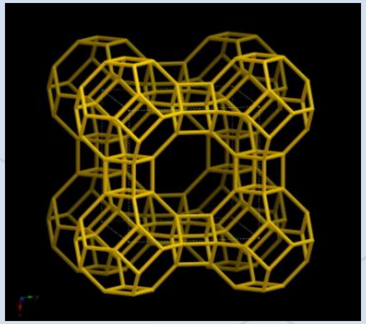
They have valuable features such as :

- adsorbents
- catalysts
- ion exchangers
- separators

Zeolites are materials with a unique porous structure, with active centers and mobile cations of alkaline and alkaline-earth metals. !



FAU



LTA

2. Na-X Faujasite (FAU) zeolites - synthesis from coal ashes

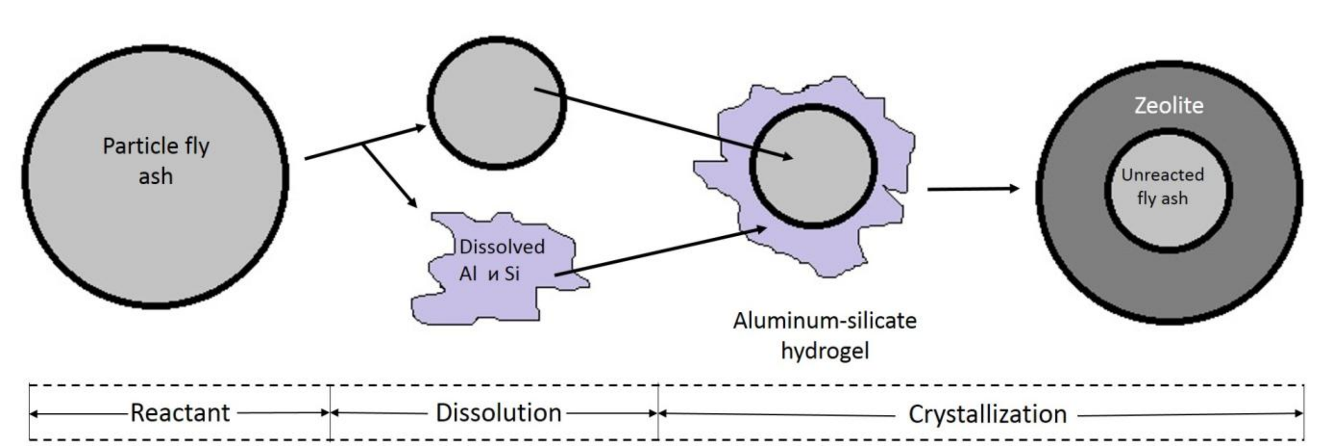
highly developed specific surface

LTA and FAU zeolites have the highest carbon capture potential →

	FAU	LTA
Pore size	7.35 Å	4.21 Å
Free volume	27.42 %	21.43 %

→ Allowing the physical adsorption of molecules of CO_2 from size 3.2 Å

Zeolites synthesized from pure starting materials ! ≠ Zeolite from coal ash - they → High content of iron oxides (γ-Fe_2O_3, α-Fe_2O_3, γ-Fe_3O_4) + In combination with microcomponents such as Cu, Co, Mn, V, W = Determine their good catalytic activity



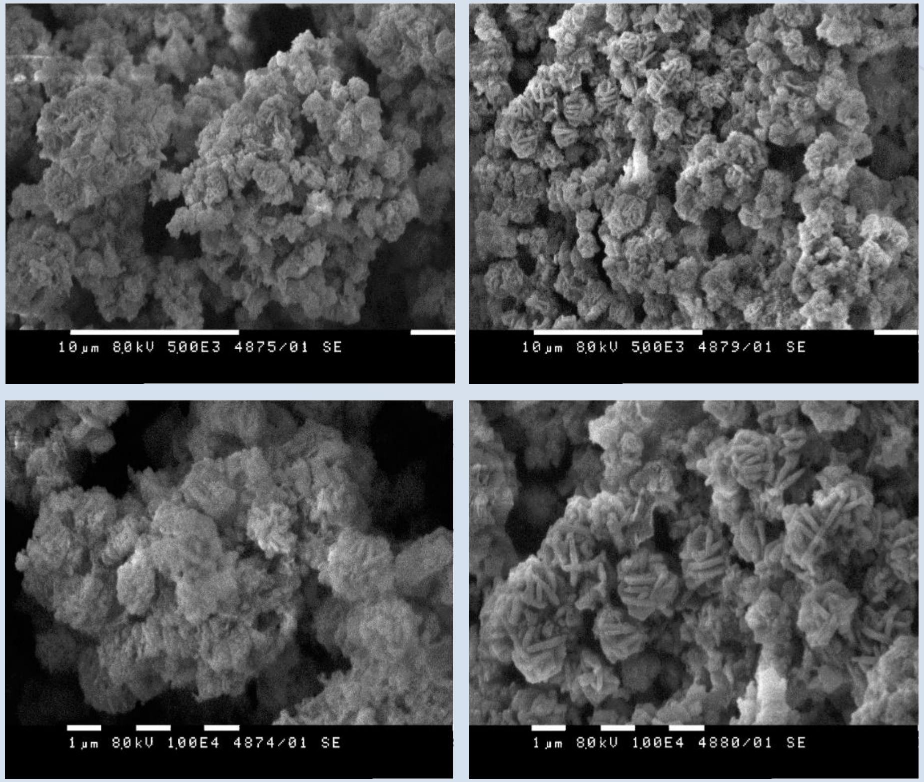
The process of synthesis is carried out in three stages:

1) Dissolving aluminosilicates of the ash in the alkaline solution;
2) Precipitation of an alumosilicate hydrogel;
3) Crystallization of zeolite from the alumosilicate gel on undissolved solid particles.

3. Wet-milling of synthesized zeolites

FAU type zeolites synthesized from coal fly ash → Part of the zeolites are subjected to subsequent wet milling in a ball mill for 60 s to reduce their size to submicron values.

Not milled zeolites | Milled zeolites



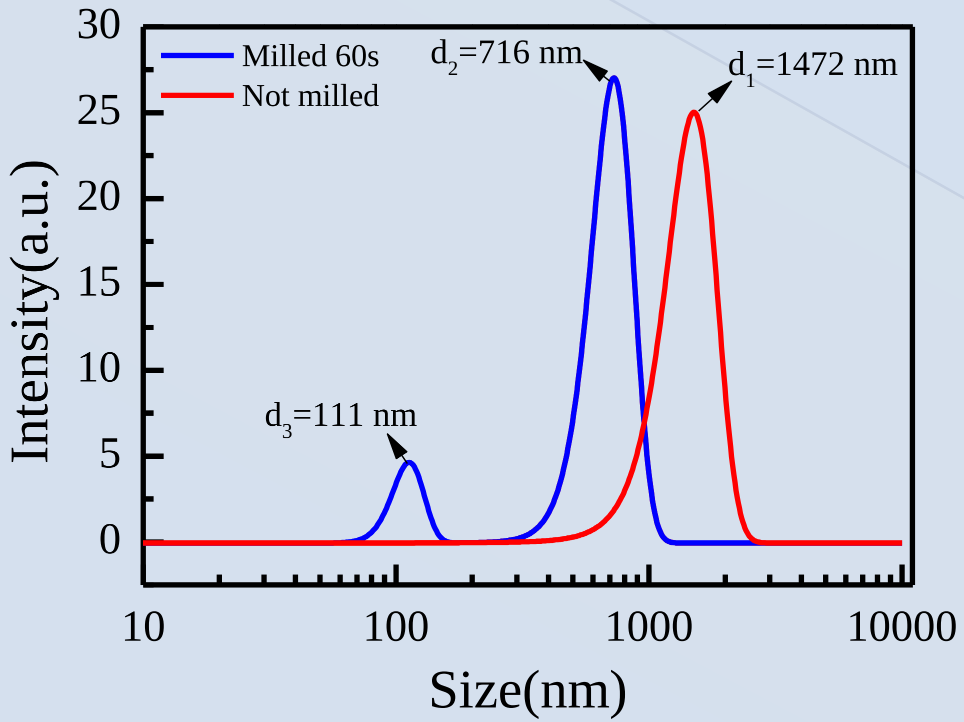
5 000x

10 000x

- Agglomerations of indistinguishable particles are observed before milling and octahedral shape crystallites typical of the FAU phase.
- Inclusions of particles from other zeolite phases are also found, which often accompany the crystallization of FAU from coal fly ash.
- After the mechanical processing, a clear separation of the individual particles of about 1-1.5 μm size is observed.

3. Wet-milling of synthesized zeolites

FAU type zeolites synthesized from coal fly ash → Part of the zeolites are subjected to subsequent wet milling in a ball mill for 60 s to reduce their size to submicron values.



Size distribution changes from monomodal (d_1) in the case of non-milled zeolites to bimodal (d_2 and d_3) for milled samples:

d_1 = 1470 nm

d_2 = 716 nm and d_3 = 111 nm

4. Thin films from Nb_2O_5 doped with milled and not-milled zeolites

Sol-gel method → Spin-coating → Thin films from Nb_2O_5 doped with milled and not-milled zeolites → Deposited on a silicon substrate, Speed - 4000 rpm, Heated for 30 min at 320°C

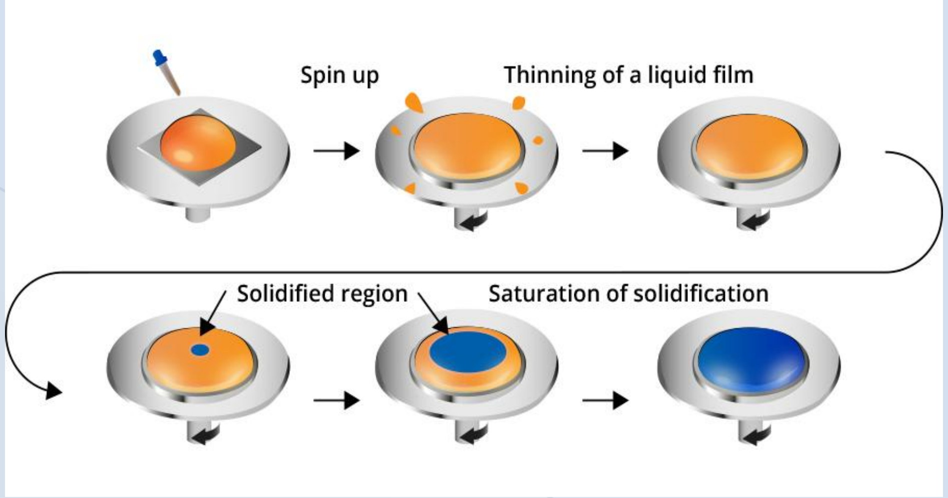
Milled and not-milled FAU zeolites

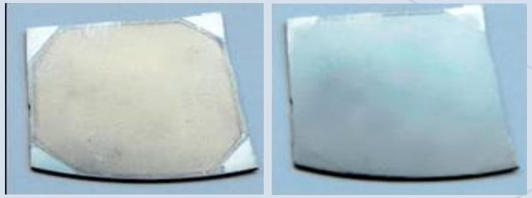
Deposited thin films

Nb_2O_5 + not-milled FAU and Nb_2O_5 + milled FAU

in three volume concentrations

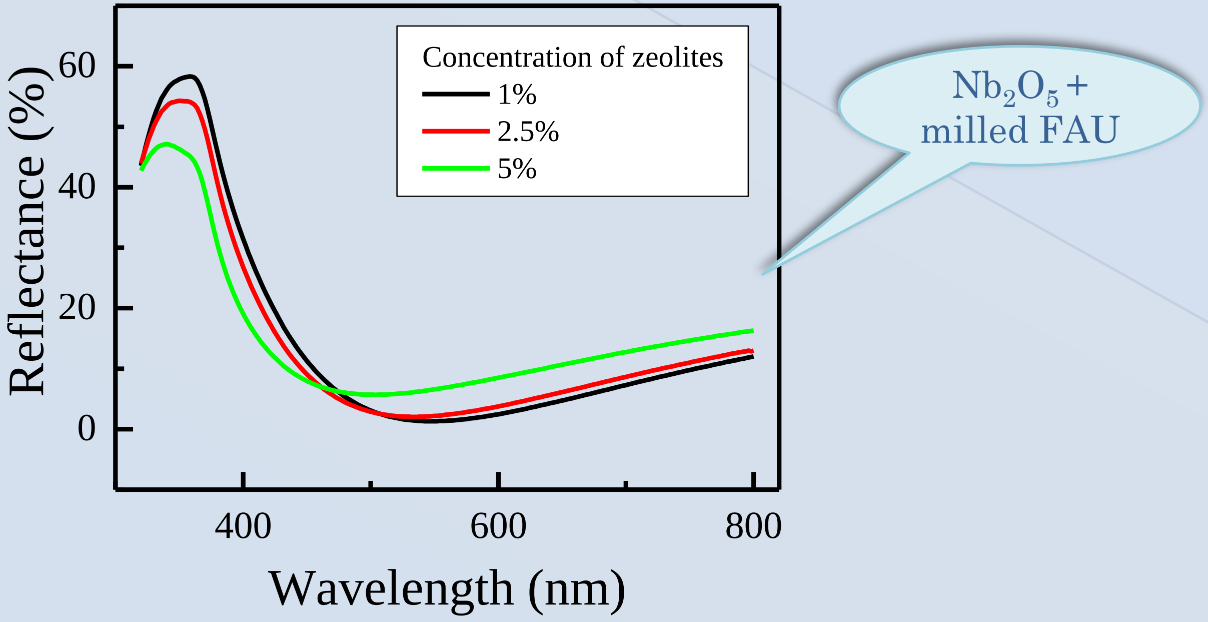
1% 2.5% 5%





5. Characterization of thin films - optical and sensing properties

Reflectance spectra of the films are measured in order to study their optical properties and to calculate the thickness.

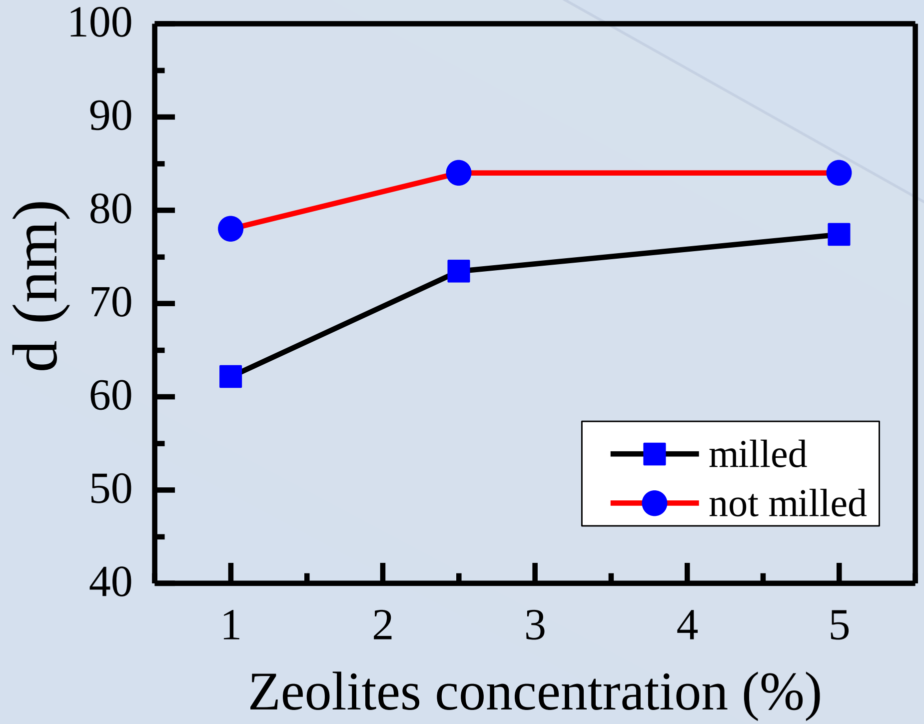


Reflectance spectra of Nb_2O_5 films with milled zeolites

n, *k* и *d* - calculated by nonlinear algorithm for minimizing the difference between measured and calculated values of the reflectance R.

Thickness (*d*)
Refractive index (*n*)
Extinction coefficient (*k*)

5. Characterization of thin films - optical and sensing properties

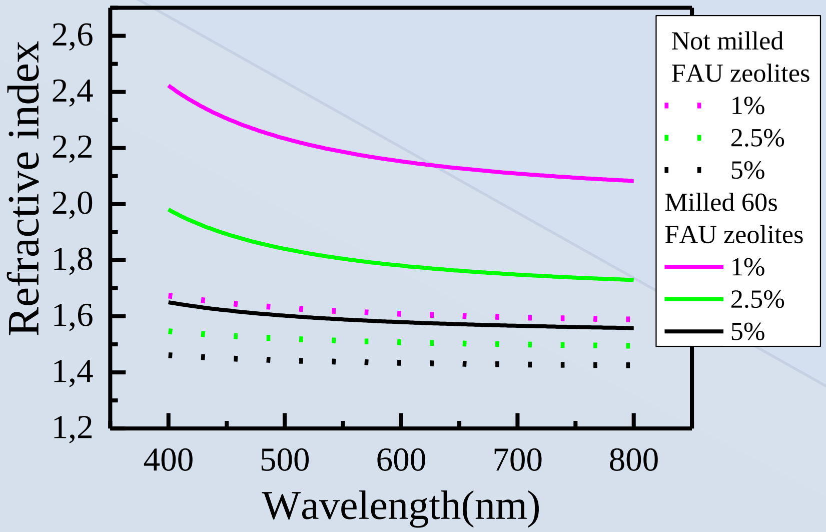


Dependence of thickness *d* on zeolite concentration (**b**) of thin Nb_2O_5 films embedded with not-milled and milled fly ash FAU zeolites.

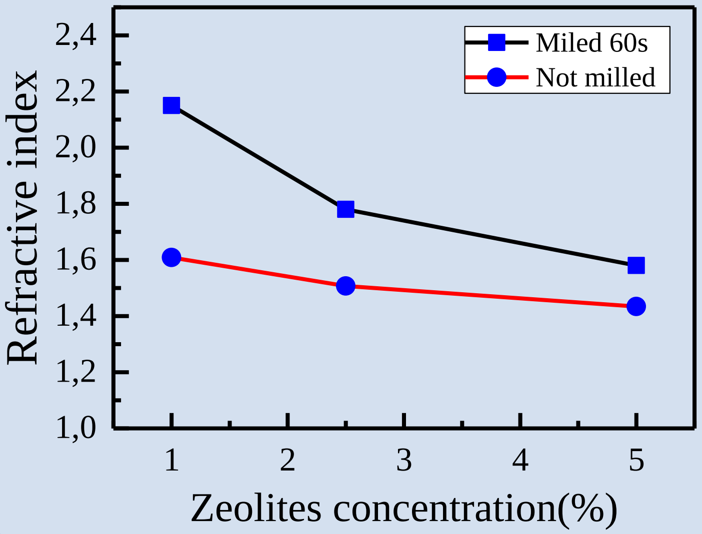
- Films doped with **not-milled** zeolites have thickness around 78 nm - 80 nm for 1% concentration and there is a slight increase in d to 84 nm at concentration of 2.5 %. There is no further increase of d with concentration.

- Films doped with **milled** zeolites have clear tendency of increasing thickness with concentration of zeolites – from 62, 73 and 77 nm for 1, 2.5 and 5 % respectively.

5. Characterization of thin films - optical and sensing properties



Dispersion curves of refractive index of thin Nb_2O_5 films embedded with not-milled and milled fly ash FAU zeolites.



Dependence of refractive index n at wavelength of 600 nm on zeolite concentration of thin Nb_2O_5 films embedded with not-milled and milled fly ash FAU zeolites.

Films of Nb_2O_5 + milled FAU

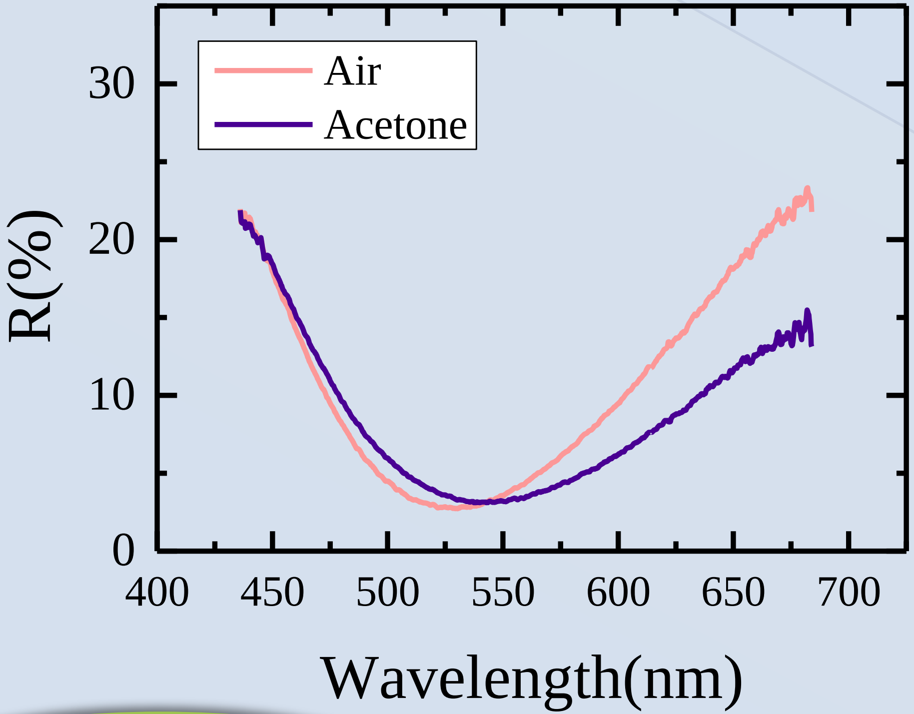
- normal dispersion curves
- lower thickness, higher density and refractive index as compared to samples doped with not - milled zeolites.
- more pronounced decrease in n with increasing the zeolite concentration.

Using smaller zeolites

1. Precise control and deposition of thin films with a specific thickness.
2. Control of the refractive index of the films.

5. Characterization of thin films - optical and sensing properties

Sensing properties toward liquid acetone



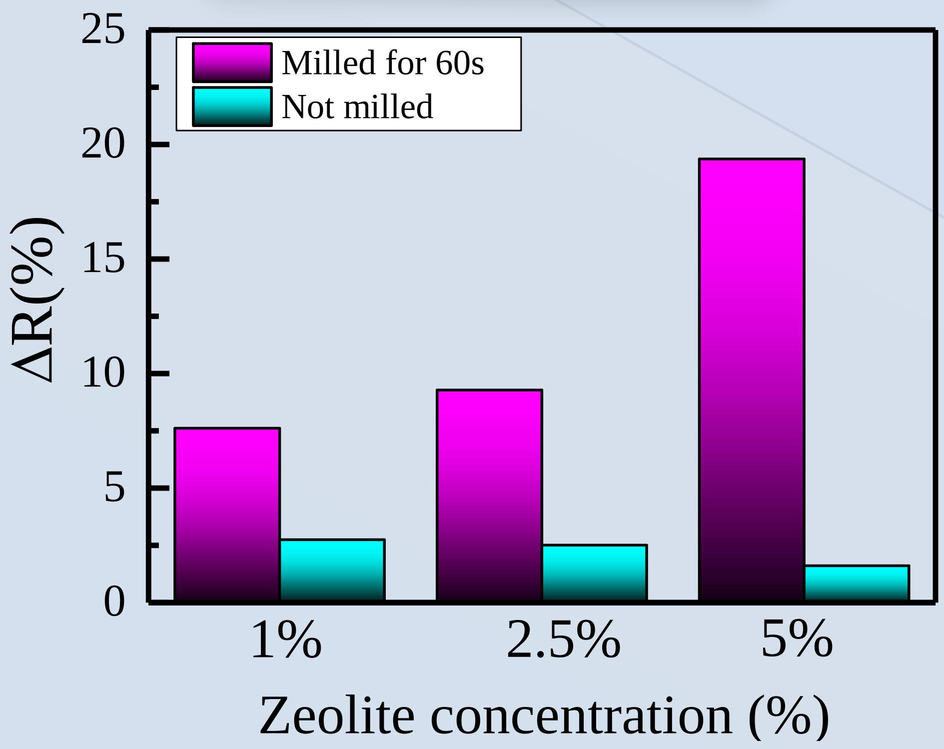
2.5 % milled zeolites film

Sensing properties determination method

1. Measuring of the reflection spectra of thin films before and after exposure to liquid acetone.
2. Calculation of the acetone induced change in the reflection ΔR.

5. Characterization of thin films - optical and sensing properties

Sensing properties toward liquid acetone



Zeolite concentration dependence of reflectance change induced by exposure to liquid acetone of FAU not-milled (blue bars) and milled (magenta bars) embedded in thin Nb_2O_5 films. Measurements are conducted at room temperature.

1

✓ The addition of not-milled zeolites results in a 1.6 - 2.5 % change in ΔR as increase of concentration leads to decrease of reflectance change.

Not - milled zeolites samples: 2.5 % max change

2

✓ In the case of films with milled zeolites - as the amount of zeolites increases, the change in the reflection coefficient ΔR increases from 7.6 to 19.4.

!

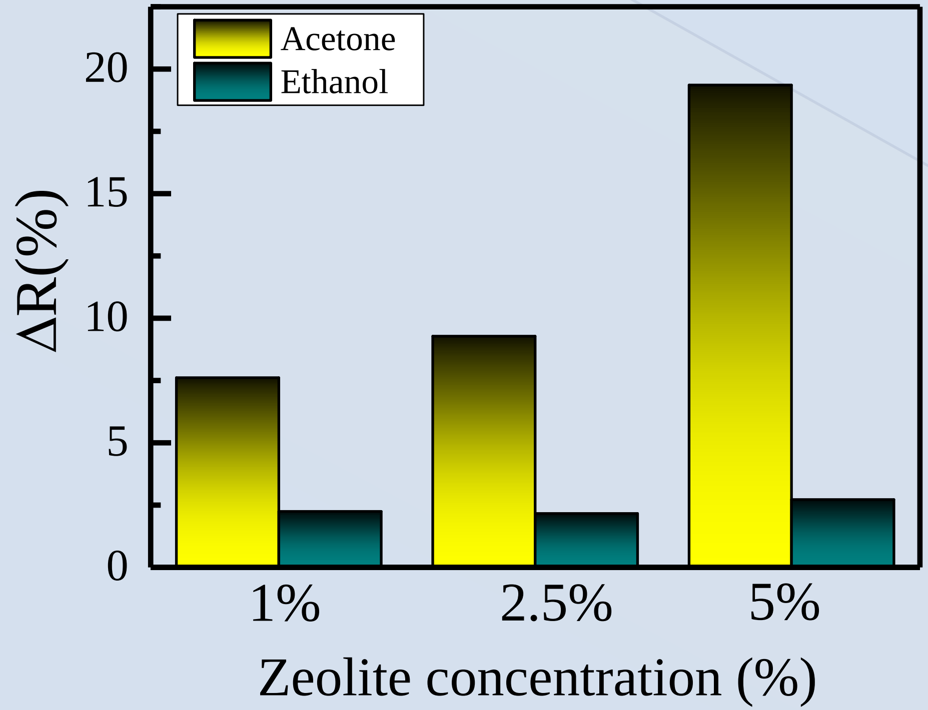
Milled zeolites samples: ≈20 % max change

5. Characterization of thin films - optical and sensing properties

Selectivity

for films of Nb_2O_5 + milled FAU

- Similar measurements made with liquid ethanol for films with milled zeolites .
- Ethanol selected as probing liquid due to its similar to acetone refractive index: 1.361(eth) and 1.359(ac).



Zeolite concentration dependence of reflectance change induced by exposure to liquid acetone (yellow) and ethanol (green) of milled zeolites embedded in thin Nb_2O_5 films. Measurements are conducted at room temperature.

1 ✓ The optical response toward ethanol is almost 8 times weaker as compared to acetone.

Ethanol:
av. 2.5 % max change
for all concentrations

2 ✓ Increase of concentration of milled zeolites leads to increase of the change in the reflection coefficient ΔR.

! **Acetone**:
≈20 % max change for
highest concentration

Summary

- ✓ FAU zeolites of coal ash with a particle size of 1470 nm have been synthesized by alkaline atmospheric conversion.
- ✓ The possibility of reducing zeolites particle size in half and simultaneously obtaining particles of about 100 nm in size by wet milling has been demonstrated.
- ✓ Successfully have been deposited composite thin films comprising Nb_2O_5 matrix and fly ash FAU zeolites in concentrations from 1 to 5 % with good optical quality and reflectance coefficient in range 47 – 58 %.
- ✓ The possibility of controlling the refractive index and sensing properties of the films through variation of concentration and size of particles has been shown. The value of n varies in a wide range from 1.6 to 2.2.
- ✓ The liquid-induced changes for samples with milled zeolites are eight times higher than changes in films doped with not-milled zeolites.
- ✓ The sensitivity is higher toward acetone compared to ethanol.

#stayhome

Thank you for your kind attention!

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