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Coal fly ash zeolites – from synthesis to application in acetone optical detection

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Table of content

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

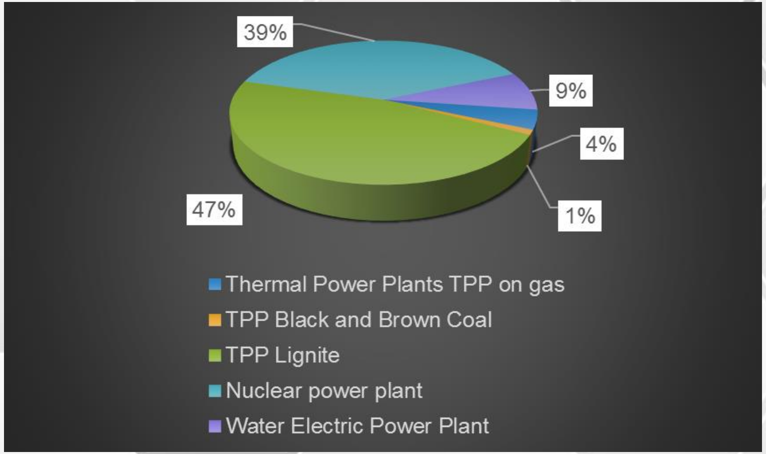
releases of gaseous emissions - sulfur, nitrogen and carbon oxides

generation of solid waste - ash

- Its 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 2017, allocated according to the primary energy resource and the used production technology.



Coal ash - pollutants and possibilities for their utilization

Carbon dioxide CO_2

Volatile Organic Compounds (VOCs)

→ Greenhouse effect

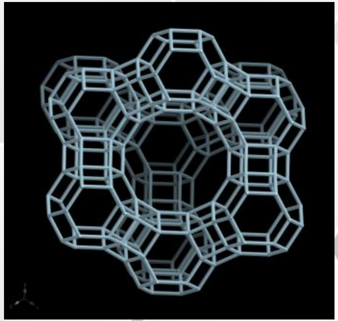
For the purposes of developing CO_2 capture technologies in the search for new solid phase sorbents, **zeolites** have also been studied.

They have valuable features such as :

- **adsorbents**
- **catalysts**
- **ion exchangers**
- **separators**

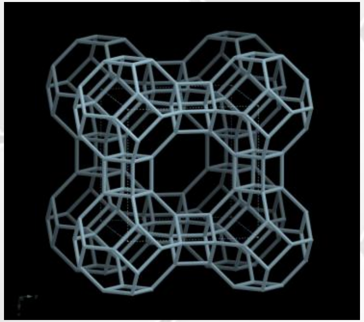
! **Zeolites** are materials with a unique porous structure with active centers and mobile cations of alkaline and alkaline-earth metals.

Faujasite (FAU)



FAU

Linde Type A Zeolite (LTA)

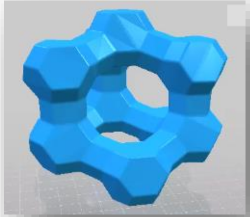


LTA

Na-X(FAU) zeolites

HIGH SILICA ZEOLITE

Faujasite (*FAU*) is a rare natural zeolite which has a synthetic counterpart, zeolite X. The sodium form of the synthetic zeolite X – *Na-X* is widely used because of its structural supercage, with a large pore size and high specific surface area.



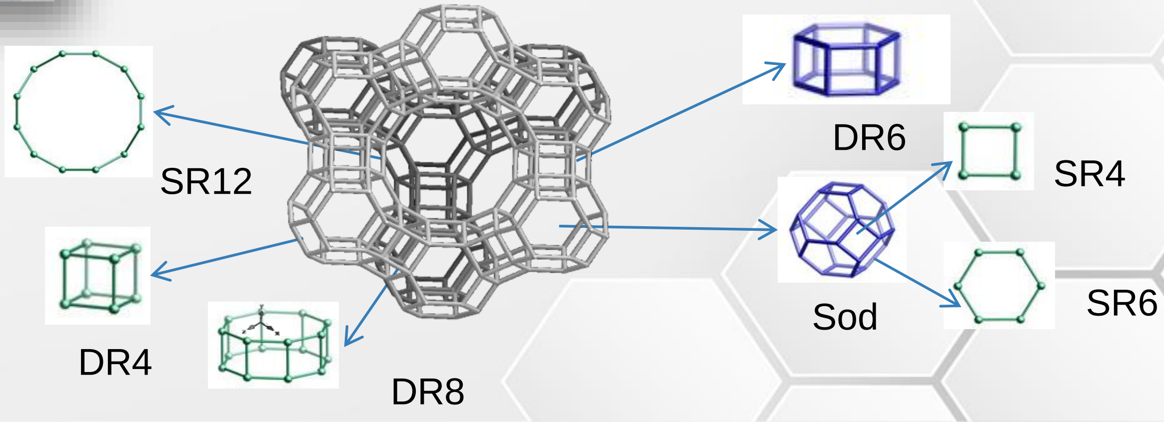
$|(Ca^{2+},Mg^{2+}Na^{+}{}_{2})_{29}\ (H_2O)_{240}|\ [Al_{58}Si_{134}\ O_{384}]$

Maximal diameter of sphere:

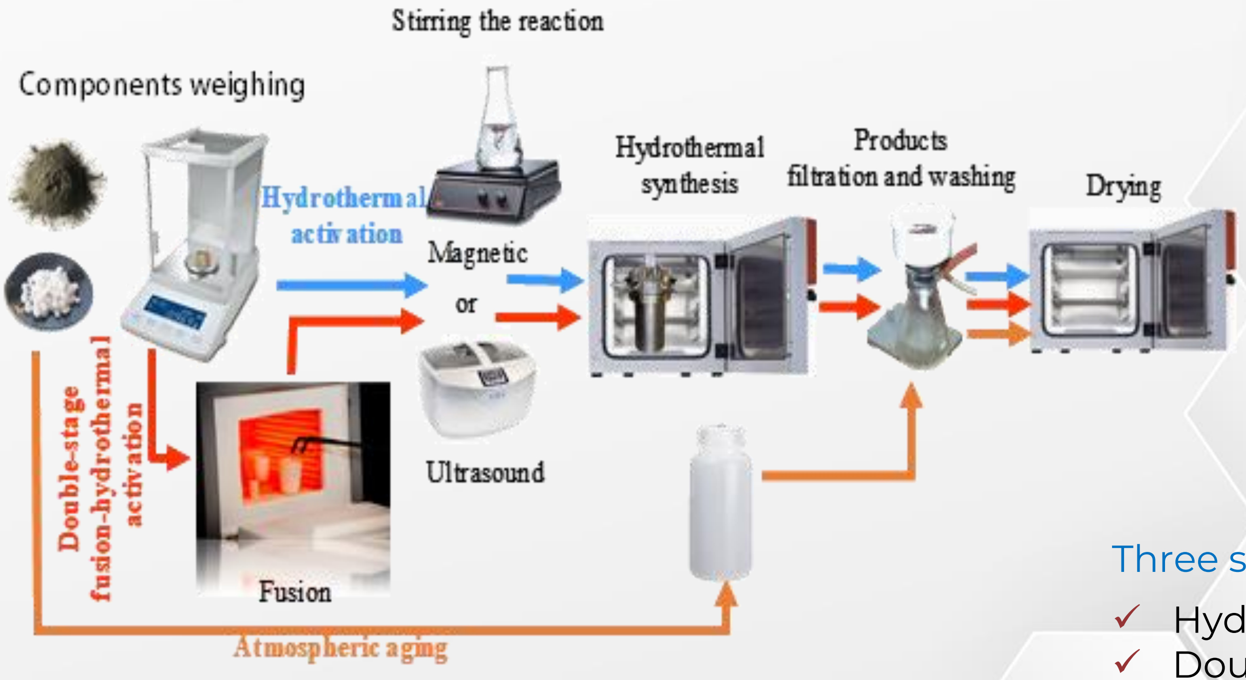
- ✓ To be included in the structure - **11.24 Å**
- ✓ To diffuse around the structure - **7.35 Å**

Free volume: 27 %

FAU



Na-X(FAU) zeolites



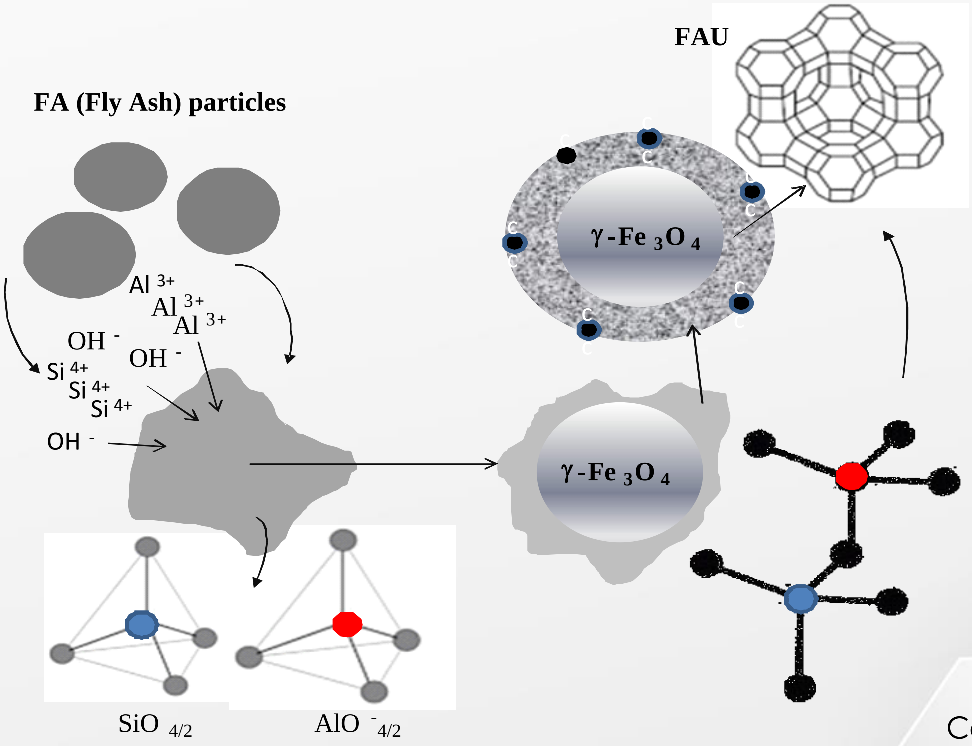
Coal ash alkaline conversion to zeolites

Integrated scheme of the synthesis approaches

Three synthesis approaches:

- ✓ Hydrothermal activation
- ✓ Double stage fusion-hydrothermal activation
- ✓ Atmospheric crystallization – Quasi-natural crystallization process

Na-X(FAU) zeolites



Coal ash alkaline conversion to FAU zeolites

Coal fly ash zeolites of the FAU type are easily synthesized by the alkaline conversion of coal fly ash, saving raw materials by utilizing solid waste.

Na-X(FAU) zeolites

LTA and FAU zeolites have the highest carbon capture potential

highly developed specific surface

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

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

Zeolite from coal ash ≠ They are distinguished from zeolites synthesized from pure starting materials

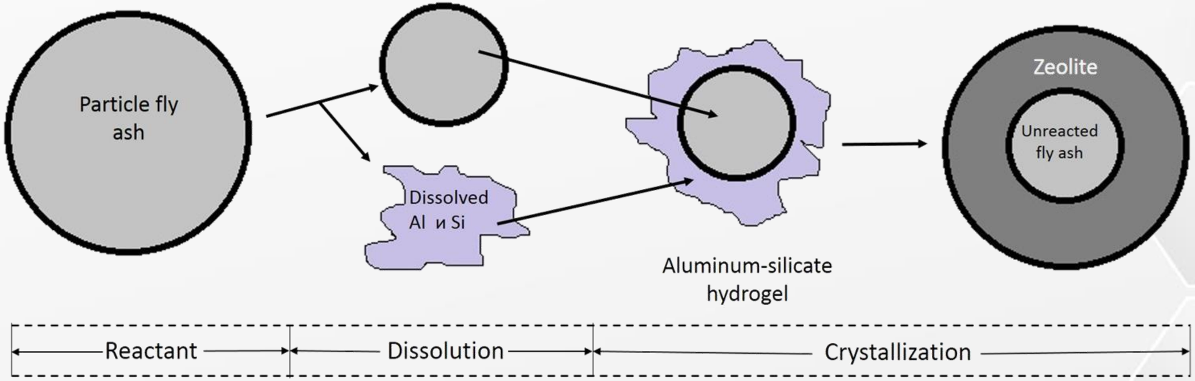
High content of iron oxides (γ-Fe_2O_3, α-Fe_2O_3, γ-Fe_3O_4)

\+

In combination with microcomponents such as Cu, Co, Mn, V, W

= Determine their good catalytic activity

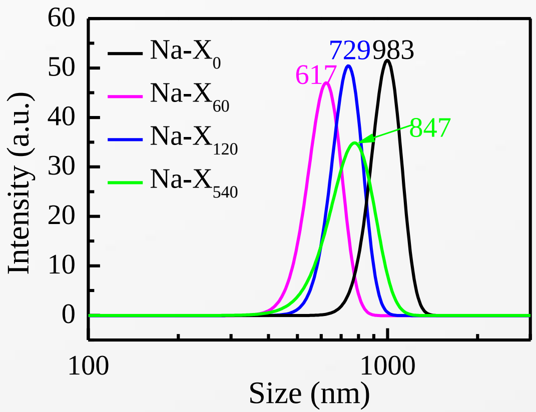
Na-X(FAU) zeolites



The process 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 germinator.

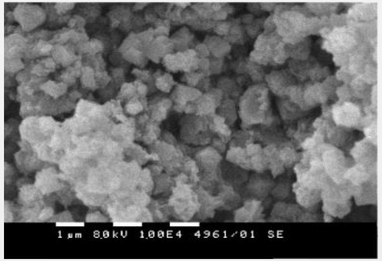
Na-X(FAU) zeolites



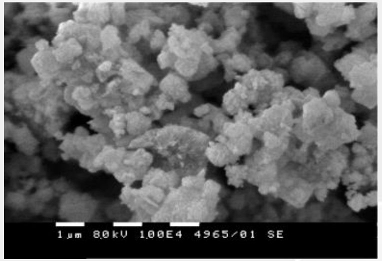
DLS curves for colloidal aqueous solutions of initial Na-X_0 zeolites and zeolites after milling for 60, 120, and 540 s.

Na-X type zeolites obtained

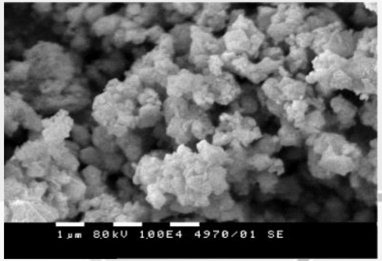
Zeolites are subjected to subsequent wet milling in a ball mill to reduce their size to sub-micron values.



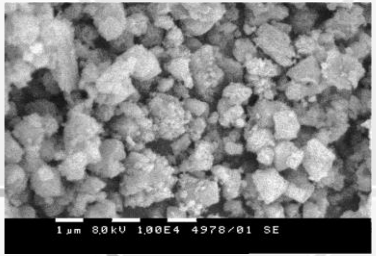
Not milled zeolites Na-X



Milled 60 seconds

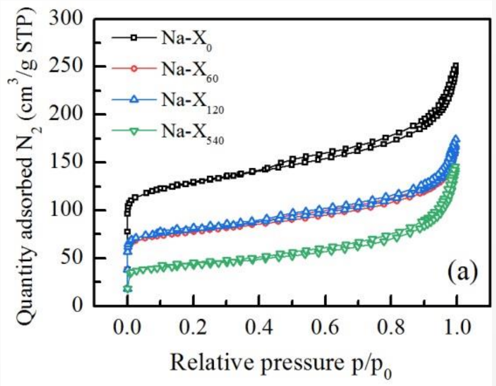


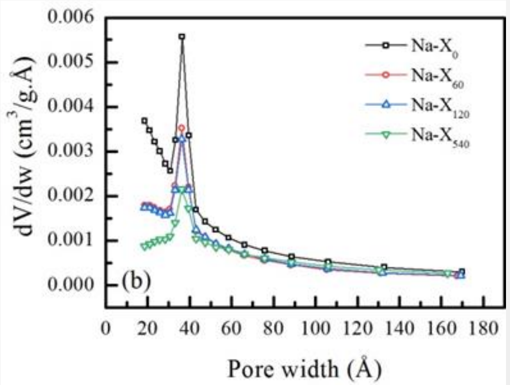
Milled 120 seconds



Milled 540 seconds

Na-X(FAU) zeolites





Experimental N_2 adsorption/desorption isotherms (a) and BJH plot of pore size distribution (b) of parent Na-X zeolites and zeolites after milling for 60, 120, and 540 s.

- ✓ Non-milled Na-X zeolite possesses the highest free volume indicated by an intensive peak at a pore width range of 35–45 Å, and a trend of increasing the pore volume in the direction of the micropore sizes.

- ✓ The main part of the free volume at all samples is pro-vided by pores with a width of 38 Å, as the BJH plots of Na-X_{60} and Na-X_{120} almost overlap but the intensity of the peaks determining the pore volume is reduced as compared with Na-X_0.

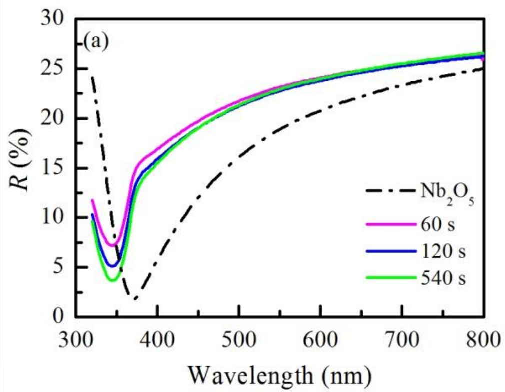
- ✓ The sample Na-X_{540} possesses drastically reduced free pore volume, which shows that the excessively prolonged milling time leads to destruction of the zeolite framework.

Thin films from Nb_2O_5 doped with milled zeolites

Nb sol
+
zeolites
dispersion

→ Spin-coating → Thin layers from Nb_2O_5 doped with zeolites → Deposited on a silicon substrate, Speed - 4000 rpm, Heated for 30 min at 320°C

Nb_2O_5 composite thin films with two different levels of doping with Na-X zeolites were deposited on silicon substrates - 1% and 5%



Reflectance spectra of thin Nb_2O_5 film and composite films of Nb_2O_5 doped with 5% Na-X zeolites milled for 60 s, 120 s, and 540 s.

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

Characterization of thin composite films - optical and sensing properties

Sample/ Variable	Pure Nb_2O_5	Na-X (1%)/Nb_2O_5			Na-X (5%)/Nb_2O_5		
		60 s	120 s	540 s	60 s	120 s	540 s
n *	2.06	2.00	1.93	1.98	1.73	1.83	1.87
k *	0.017	0.018	0.018	0.018	0.017	0.017	0.017
d (nm)	37	33	34	34	39	37	36
S_q (nm)	4.5 ± 1.2	5 ± 0.3	5.8 ± 1.4	4.3 ± 1	8 ± 2.4	6.2 ± 1.4	6.6 ± 0.9
Δn	-	0.42×10^{-2}	1.08×10^{-2}	$<1 \times 10^{-3}$	1.16×10^{-2}	4.44×10^{-2}	1×10^{-3}

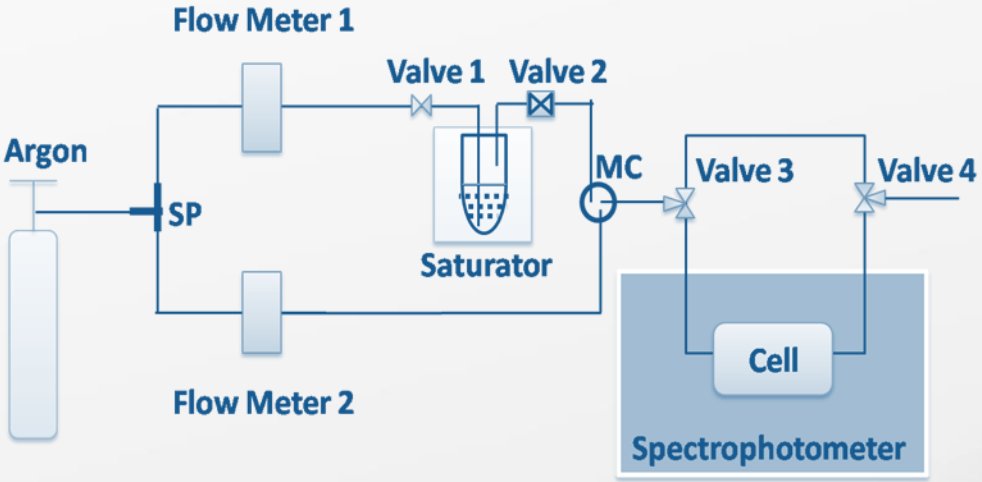
* Values of n and k are taken at a wavelength of 600 nm.

Refractive index n, extinction coefficient k, thickness d, surface rms roughness Sq, and refractive index change Δn upon exposure to acetone vapors of thin films from pure Nb_2O_5 and Nb_2O_5 doped with Na-X zeolites wet milled for 60, 120, and 540 s. [1]

- ✓ Refractive index of composite films is lower as compared with the oxide matrix. The reduction in the refractive index depends on the concentration of zeolites and is stronger for highly doped samples.
- ✓ For the composite with 5% Na-X zeolites, the refractive index increases with the duration of milling, while a minimum is observed for the 1% doped composite when Na-X zeolites milled for 120 s are used as dopants.
- ✓ The milling duration does not influence the film roughness.

(1) Lazarova, K.; Boycheva, S.; Vasileva, M.; Zgureva-Filipova, D.; Georgieva, B.; Babeva, T. Acetone-Sensitive Thin Films Comprising Coal Fly Ash Na-X Zeolites and Sol–Gel Nb_2O_5 Matrix. Nanomaterials 2021, 11, 2399. https://doi.org/10.3390/nano11092399

Characterization of thin composite films - optical and sensing properties



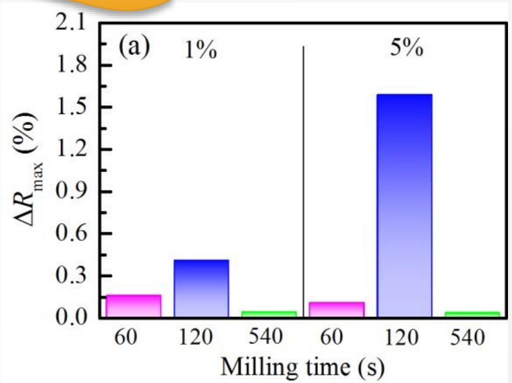
Schematic process of testing the sensing properties of the films toward acetone or ethanol vapors.

Changes in reflectance induced as a result of exposure to acetone and ethanol vapors:

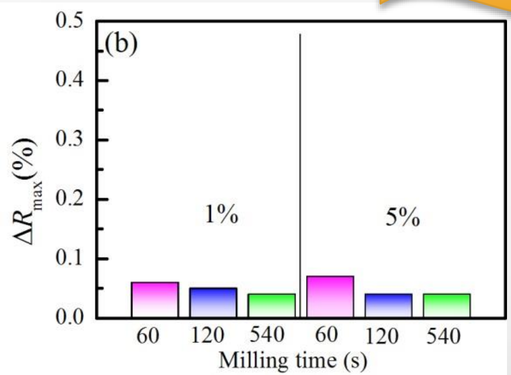
$$\Delta R_{max} = |R_{ac/et} - R_{argon}|$$

Characterization of thin composite films - optical and sensing properties

Acetone



Ethanol



- ✓ For acetone vapors, the same dependence of the reflectance change ΔR_{max} on the milling time is clearly observed for both zeolite concentrations.
- ✓ The greatest change is obtained for films doped with zeolites milled for 120 s, and the smallest for 540 s.
- ✓ Significant decrease in films response to ethanol vapors as compared to acetone.
- ✓ The maximum value for ΔR_{max} achieved is 0.07 % (more than 20 times smaller as compared to the response towards acetone vapors). [1]

This result clearly indicates the selectivity of Nb_2O_5/Na-X composite thin films toward acetone.

(1) Lazarova, K.; Boycheva, S.; Vasileva, M.; Zgureva-Filipova, D.; Georgieva, B.; Babeva, T. Acetone-Sensitive Thin Films Comprising Coal Fly Ash Na-X Zeolites and Sol–Gel Nb_2O_5 Matrix. Nanomaterials 2021, 11, 2399. https://doi.org/10.3390/nano11092399

Summary

1. Zeolite Na-X synthesized by ultrasonic-assisted double stage fusion-hydrothermal alkaline conversion of coal fly ash are successfully incorporated in Nb_2O_5 thin matrix and the composite films thus obtained are applied as sensitive elements for optical sensing of vapors.

2. Increasing the concentration of zeolites leads to a decrease in the refractive index. The reduction is stronger for highly doped samples. For the composite with 5 % Na-X zeolites refractive index increases with the duration of milling, while a minimum is observed for the 1 % doped composite when Na-X zeolites milled for 120 s are used as dopants.

3. After 60 s wet milling the initial size of the zeolites decreases from 983 nm to 617 nm. Additional 60 seconds of milling leads to slight increase of zeolites size from 617 nm to 729 nm. The longest milling with duration of 540 s does not influence substantially the particles size, but changes significantly their size distribution. Prolonged milling of zeolite for 540 s leads to destruction of crystallites and probable recrystallization of the zeolite phase.

4. Enhancement of the sensitivity toward acetone along with achieving good optical quality of the composite films are realized via wet-milling of the zeolites powder for 60, 120 and 540 seconds prior to film deposition. It is demonstrated that the milling time influences particle size, films’ morphology, optical and sensing properties of the composite thin films.

5. The greatest reflectance change of 1.6% after exposure to acetone is obtained for films doped with zeolites milled for 120 s, and the smallest for 540 s.

THANK YOU!

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