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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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Abstract: In this study, solid waste from coal combustion in thermal power plants (TPPs) was used for the synthesis of zeolite Na-X samples. They were prepared by the long-term alkaline atmospheric conversion of coal ash collected from the electrostatic precipitators in the TPP "AES Galabovo". When used in the form of thin films/layers, the optical detection of volatile organic compounds (VOCs) is possible due to a change in their reflectance spectra and color. In order to improve the sensing properties of synthesized zeolites, they were wet milled for 60 s and both milled and unmilled zeolites were used as dopants for the niobium oxide matrix in the form of thin films deposited by the spin-coating method on a silicon substrate. The surface morphology and structure of both zeolite powders were studied by scanning electron microscopy, while their size was determined by dynamic light scattering (DLS) spectra. Optical constants (refractive index, n, and extinction coefficient, k) and the thickness of the films were calculated from reflectance measurements. The change in the reflection coefficient ΔR of the films was determined from measured reflectance spectra prior to and after exposure to probe acetone molecules. An increase in the reaction of the films with milled zeolites to acetone, compared to the samples with unmilled zeolites, is demonstrated.

Keywords: thin films; Nb_2O_5; zeolites; optical constants; sensing of acetone

1. Introduction

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 [1]. The specific surface area is a dominant parameter for zeolites and it is well known that mechanical processing in ball mills can change the structure, morphology, and specific surface area of zeolite-containing materials and occasionally improve their properties [2,3]. Gas adsorption, separation, ion-exchange, etc., are the usual applications for zeolites (also known as molecular sieves) due to their crystalline nature with a framework-type structure made up of pores with molecular dimensions [4]. Coal fly ash zeolites of the FAU type (CFAZ-FAU) are easily synthesized by the alkaline conversion of coal fly ash, saving raw materials by utilizing solid waste [5]. In particular, CFAZ-FAU has potential and can be used for traditional applications in

waste water and gas purification by adsorption or separation [5–7]. Recently, novel advanced applications of zeolite materials have been extensively explored [1,8]. Zeolites are integrated as active media in various sensor devices [9,10], zeolite films with low dielectric constants are used as isolators for computer chips [11,12], one-layer zeolite antireflective coatings have been developed [13], etc. If the optical and sensing properties of thin zeolite films or zeolite-doped films can be optimized or controlled [14], then practical applications will be numerous. For the fabrication of zeolite-based films, the spin-coating method is widely used among various techniques due to its advantages, such as rapidity, simplicity, and the high uniformity of the surface of the films [10,11,15]. In most cases, the synthesized zeolites used are in form of powder, and according to our knowledge, thin films of fly ash zeolites are a novelty and are made here for the first time. As we have already shown in our paper [16], one of the ways to obtain good optical quality films from powdered CFAZ-FAU is to incorporate them into a metal oxide matrix.

In this paper, the optical and sensing properties toward acetone of Nb_2O_5 thin films doped with CFAZ-FAU, obtained by the spin-coating method, are studied. Aqueous zeolite dispersions of CFAZ-FAU, both wet milled for 60 s and unmilled, are used for doping the Nb sol prior to the deposition of the films. Three different concentrations of dopants are prepared—1, 2.5, and 5% for both types (milled and unmilled). The influence of the size of CFAZ-FAU on the sensing properties of metal oxide thin films is studied and demonstrated. Besides, the possibility of controlling the thickness (d) and refractive index (n) of the films through the variation of the concentration or size of the zeolites is investigated.

2. Materials and Methods

For the synthesis of CFAZ-FAU, as a starting material, fly ash is used. Solid waste ash is collected from coal combustion in the "AES Galabovo" thermal power plant (TPP), one of the biggest in Bulgaria, which is supplied by domestic lignite coal from the "Maritza East" basin. Synthesized Na-X phase zeolite powder samples are prepared by long-term alkaline atmospheric conversion. In this conversion approach, slurries of coal fly ash in 1.5 mol/L NaOH are incubated continuously at room conditions. A detailed method of the synthesis and characterization of zeolites is described in [17].

Zeolites, obtained after the synthesis in the form of powder, are subjected to wet milling with a PULVERISETTE 23 Mini-Ball Mill (FRITSCH) for 60 s and 50 osc/min, with 0.08 g CFAZ-FAU powder and 3 mL distilled water. The size of the zeolites is determined by dynamic light scattering (DLS) spectra measured by a Zetasizer Nano ZS (Malvern Panalytical, UK), while their morphology is studied with a Philips 515 electron microscope.

For the deposition of metal oxide thin films, Nb sol is used, prepared by the sonocatalytic method according to the recipe described in [18]: 0.400g $NbCl_5$ (99%, Aldrich, St. Louis, MO, USA) precursor mixed with 8.3 mL ethanol (98%, Sigma-Aldrich) and 0.17 mL distilled water. The obtained solution is subjected to sonication for 30 min and aged for 24 hat ambient conditions prior to spin coating. Three different concentrations of Nb sol doped with milled and unmilled zeolites (Nb_2O_5-CFAZ-FAU) are prepared—1, 2.5, and 5%. Initially, the selected amounts of zeolites from the aqueous solution and small amounts of ethanol are mixed, and then added to the corresponding amount of Nb sol in order to keep the mixture clear.

Thin Nb_2O_5-CFAZ-FAU films are deposited by the spin-coating method at a rate of 4000 rpm for 60 s by dropping of 0.3 mL of the sol/zeolite solution on pre-cleaned Si substrates. After deposition, the films are annealed in air at 320 °C for 30 min. A CARY 05E UV-VIS-NIR spectrophotometer, with an accuracy of 0.3%, is used for the measurements of the reflectance spectra of the films in order to study their optical properties. The thickness (d) and optical constants—refractive index (n) and extinction coefficient (k)—are determined from the measured reflectance spectra of the films at a normal light incidence using a non-linear curve-fitting method [19] with experimental errors for n, k, and d of 0.005, 0.003, and 2 nm, respectively. All n and k values are taken at a wavelength of 600 nm. In order to study the sensing properties of the Nb_2O_5-CFAZ-FAU films, reflectance spectra are measured in the same spot prior to and after exposure to liquid acetone by using a Zeta-20 (Zeta Instruments, Bengaluru, India) optical profiler with a built-in spectrometer.

3. Results and Discussion

Zeolite Size

The DLS analysis is performed to determine the hydrodynamic diameter and particle size distribution of the zeolite particles before and after wet milling along with an SEM (scanning electron microscope) examination of the powder samples. The selected wet milling time of 60 s is based on unreported previous preliminary experiments with Na-X zeolites subjected to mechanical processing in ball mills for a period of 30 min. The experiment shows the deterioration of the optical quality of metal oxide films after doping with milled zeolites and a change in the reflectance spectra ΔR when exposed to liquid acetone at about 1.4%. According to the theoretical curve of the developed specific surface as a function of grinding time [20,21], three well-shaped areas can be observed: (1) Rittinger zone: the increase in the specific surface is proportional to the grinding time; (2) aggregation zone: the intensity of the specific surface growth decreases with grinding time; (3) agglomeration zone: the specific surface decreases with comminution time. Depending on the type of zeolite, the time corresponding to the different stages is different [21]. In light of this, and our results, we choose a short milling period of 60 s.

Figure 1 shows the results of the DLS measurement and indicates a relatively narrow distribution of particle size, with an average crystal size of 1470 nm (d_1) prior to the milling of the zeolites obtained directly after synthesis.

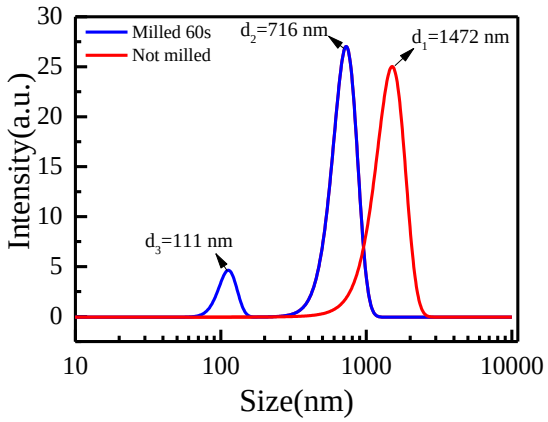


Figure 1. Distribution of particle size of CFAZ-FAU (Na-X coal fly ash zeolites of the FAU type) before (red curve) and after (blue curve) wet milling for 60 s.

This result is consistent with the results obtained by Tao Hu et al. in [22], according to which the average crystal size of Na-X zeolites synthesized from coal fly ash, estimated using the cumulative distribution method, ranges from 1 to 2 μm. From our previous studies with unmilled zeolites [16], we found that zeolites with this size impair the optical quality of the films. After wet milling for 60 s, the size decreases and the particle size distribution changes from monomodal in the case of unmilled zeolites to bimodal for milled samples. The two peaks are centered at $d_2 = 716$ nm and $d_3 = 111$ nm. A smaller particle size implies a reduction in the scattering and an improvement in the optical quality compared to Nb_2O_5 doped with unmilled zeolites. Besides, an enhancement of the sensing properties due to an increase in the specific surface area could be expected. M. Fathizadeha et al. synthesized, by the hydrothermal method, Na-X-type zeolites, with a size of 112 nm [23], proven by the DLS method, which is in accordance with our results.

Figure 2 shows SEM pictures of unmilled (a,c) and milled for 60 s (b,d) powder fly ash zeolites at two different magnifications—5000× (a,b) and 10,000× (c,d), respectively. Agglomerations of indistinguishable particles are observed before milling with octahedral-shaped 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 [17]. After the mechanical processing, a clear separation of the individual particles of about 1–1.5 μm in size is observed.

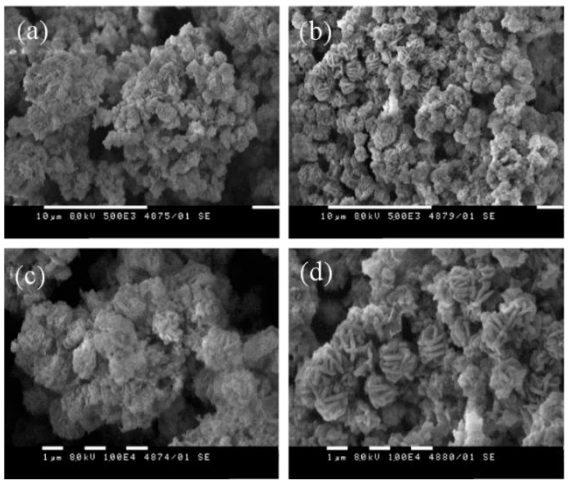
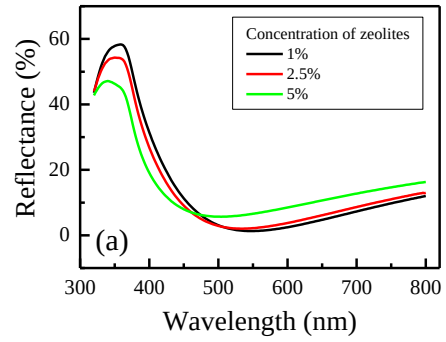
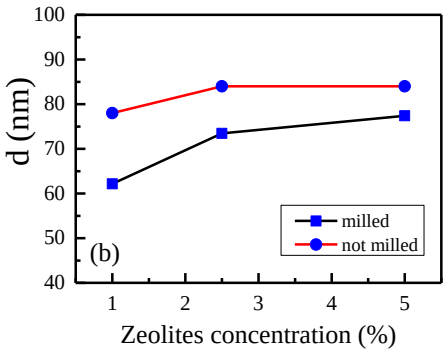


Figure 2. SEM pictures of unmilled (**a**,**c**) and milled for 60 s (**b**,**d**) fly ash zeolites powders at magnifications of 5000× (**a**,**b**) and 10,000× (**c**,**d**).

The two sizes of powdered zeolites are used for doping the thin niobium oxide films in three different concentrations—1, 2.5, and 5%. Reflectance spectra of the films are measured in order to study their optical properties and to calculate the thickness. Figure 3 presents measured reflectance spectra of Nb_2O_5 films doped with milled zeolites (a) and the dependence of thickness d on zeolite concentration (b) of thin Nb_2O_5 films embedded with unmilled (red line) and milled (black line) fly ash FAU zeolites.



(**a**)

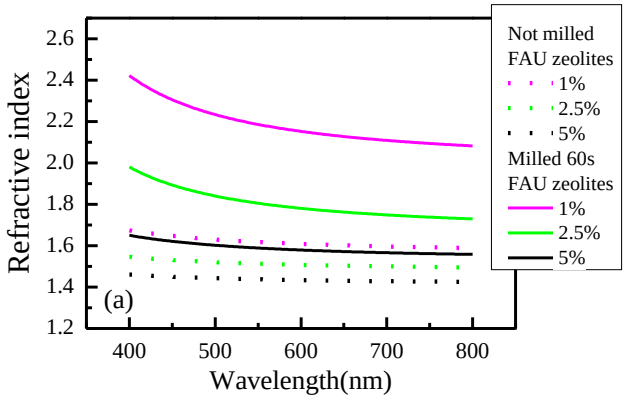


(**b**)

Figure 3. Reflectance spectra of Nb_2O_5 films with milled zeolites (**a**) and the dependence of thickness *d* on zeolite concentration (**b**) of thin Nb_2O_5 films embedded with unmilled and milled fly ash FAU zeolites.

It is seen from Figure 3a that the spectra shift towards shorter wavelengths, which is most pronounced for the film doped with 5 wt %. Considering that the reflectance is a periodic function of optical thickness (the product of refractive index and film thickness), a decrease in optical thickness could be expected with doping. In order to verify this assumption, the thickness d and refractive index *n* are calculated from the measured reflectance spectra of the films. In Figure 3b, it is seen that the two d vs. concentration curves are very similar and both have a slight change in thickness with increasing zeolite concentration, which is more pronounced and even in the films with milled particles. As is shown, films doped with unmilled zeolites have a thickness around 78 nm–80 nm with a 1% concentration and there is a slight increase in d at concentrations of 2.5 and 5%, which is the same in both cases—84 nm. The films with milled zeolites have a clear tendency to increase in thickness with the concentration of zeolites—from 62, 73, and 77 nm for 1, 2.5, and 5%, respectively. Bearing in mind that the films are deposited from the same amount of Nb sol and zeolites for each concentration, the difference observed in d is only due to the different particle sizes for milled and unmilled zeolites. Thus, by using smaller zeolites, we can more precisely control and obtain thin films with a specific thickness, as needed. Additionally, this applies to the control of the refractive index of the films, which is very important in terms of depositing 1D photon crystals, for example, where layers with exact d and *n* are needed in order to obtain optical contrast and achieve a reflectance band gap [24].

Dispersion curves of the refractive index of thin Nb_2O_5 films doped with unmilled and milled fly ash FAU zeolites and the dependence of the refractive index *n* on zeolite concentration are shown in Figure 4. Generally, films with milled zeolites have a higher refractive index as compared to films doped with unmilled zeolites. Considering that *n* is directly proportional to the density of films, we could conclude that films doped with milled zeolites have a higher density. Because the smaller size of the milled zeolites, their packing density in the niobia matrix is higher, resulting in a lower thickness (Figure 3b) and a higher density and refractive index as compared to samples doped with unmilled zeolites. Furthermore, for samples with milled zeolites, a clearer and more pronounced decrease in *n* is observed with increasing zeolite concentration. This is expected since the zeolites themselves are a material with a low refractive index ($n = 1.466–1.480$) and their addition to a material with high *n* (such as Nb_2O_5, $n \approx 2.20$) [19] results in a decrease in the value of *n* of the composite thin film. The value of *n* for a 1% concentration of milled zeolites is 2.15, which is very close to the *n* of a pure film of Nb_2O_5 and, at 2.5 and 5% concentrations, *n* is, respectively, 1.8 and 1.6. From Figure 4, it is also seen that films with unmilled zeolites have a lower *n*, with a range of 1.43–1.6. All samples have normal dispersion curves. It can be seen that, by doping with different zeolite concentrations and sizes, we can obtain a composite material with a refractive index varying in a wide range—from 2.15 to 1.43.



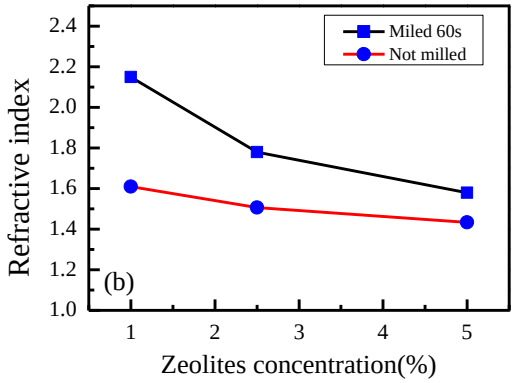


Figure 4. Dispersion curves of the refractive index (**a**) and the dependence of the refractive index *n* at a wavelength of 600 nm on the zeolite concentration (**b**) of thin Nb_2O_5 films embedded with unmilled and milled fly ash FAU zeolites.

By adding zeolites to a metal oxide matrix, we could assume that the overall porosity of the Nb_2O_5 matrix increases and this is confirmed by the observed reduction in the effective refractive index. In addition to the microporosity of the zeolites, it is also possible for additional free volume (air) to be introduced into the samples, whose volume fractions are different depending on the concentration and size of the FAU particles. Both zeolites and air (n = 1.0003) contribute to the decrease in the effective refractive index of doped films. A higher porosity/free volume is a prerequisite for stronger absorption into the micropores and mesopores of the films when exposed to liquid analyte, thus controlling the sensing properties.

To verify this, we measure the reflectance spectra of composite thin films before and after immersion in liquid acetone for 5 min and calculate the induced change in reflectance ΔR for films with both milled and unmilled zeolites (Figure 5). The addition of unmilled zeolites results in a 1.6–2.5% change in ΔR, as the increase in concentration leads to a decrease in reflectance change. The opposite is true in the case of films with smaller zeolite particles: as the amounts of zeolites increase, the change in the reflection coefficient increases from 7.6 (for 1% concentration) and 9.3 (for 2.5% concentration) to 19.4 for 5% sample. In addition, a maximum change of nearly 20% was achieved, compared to 2.5% for the unmilled samples.

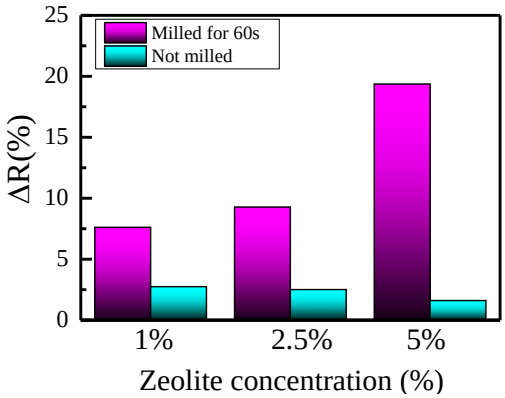


Figure 5. Zeolite concentration dependence of reflectance change induced by exposure to liquid acetone on CFAZ-FAU unmilled (blue bars) and milled (magenta bars) embedded in thin Nb_2O_5 films. Measurements are conducted at room temperature.

In order to check the selectivity of the films, similar measurements are made with liquid ethanol for films with milled zeolites. Ethanol is selected as a probing liquid because its refractive index is similar to that of acetone: 1.361 and 1.359 are the respective refractive indices of ethanol and acetone at a wavelength of 600 nm [25]. As can be seen from Figure 6, the change in the reflection coefficient ΔR due to ethanol exposure is on average about 2.5%, without pronounced concentration

dependence. This means that the optical response toward ethanol is almost eight times weaker as compared to acetone. Considering the similarity of the refractive index, we may conclude that a significantly smaller amount of ethanol is absorbed by the films as compared to acetone. The possible reason is the different impacts of polarity, surface energy, hydrophilicity/hydrophobicity, etc., on the analyte absorption.

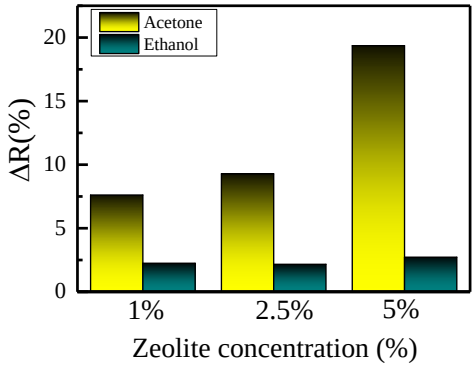


Figure 6. Zeolite concentration dependence of reflectance change induced by exposure to liquid acetone (yellow) and ethanol (green) on milled CFAZ-FAU embedded in thin Nb_2O_5 films. Measurements are conducted at room temperature.

4. Conclusions

FAU zeolites of coal ash with a particle size of 1470 nm have been synthesized by alkaline atmospheric conversion. The possibility of reducing their size in half and of also obtaining particles of about 100 nm in size by wet milling has been demonstrated. Composite thin films comprising an Nb_2O_5 matrix and fly ash FAU zeolites in concentrations from 1 to 5% with good optical quality and reflectance coefficients in the range of 47–58% have successfully been deposited. The possibility of controlling the refractive index and sensing properties of the films with milled zeolites through the variation of the concentration and size of particles has been shown. The value of n varied in a wide range, from 2.2 to 1.8 and 1.6. The presence of porosity has been verified and confirmed by the reflectance coefficient change of the films before and after exposure to liquid acetone and ethanol, thus also confirming selectivity toward acetone. The maximum liquid-induced changes for samples with milled zeolites are eight times higher the change in films doped with unmilled zeolites and the dependence of the reflectance change on concentration has been proved for films with small FAU particles. Thin films with milled zeolites show a change in reflectance induced by acetone of 20% compared to a 2.7% change after exposure to liquid ethanol at the same concentration (5%).

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