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Preparation and characterization of Ag doped TiO_2 incorporated in natural zeolite

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The hybrid materials based on natural zeolite and undoped and Ag-doped TiO_2, i.e., Z-TiO_2, Z-TiO_2-Ag2 and Z-TiO_2-Ag3, were successfully synthesized by solid state reaction in ethanol solution. Undoped TiO_2 and Ag-doped TiO_2 nanocrystals were previously synthesized by sol-gel method. The surface characterization of undoped TiO_2 / Ag-doped TiO_2 and natural zeolite hybrid materials has been investigated by X-ray diffraction, FT-IR spectroscopy, SEM microscopy and EDX analysis. The results indicated that anatase TiO_2 is the dominant crystalline type as spherical form onto zeolitic matrix. The presence of Ag into hybrid materials was confirmed by EDX analysis. Also the XRD results revealed that the natural zeolite used is mostly clinoptilolite.

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1. Introduction

Zeolites are hydrated aluminosilicates build from an infinitely extending three dimensional network of AlO_4 and SiO_4 tetrahedral linked to each other by the sharing of oxygen atoms [1, 2]. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by a cation, normally from the group IA or IIA. The framework contains channels and interconnected voids which occupied by the cation and water molecules.

Nanomaterials have attracted much attention over the past decade due to their unique properties which include quantum confinement and a heightened reactivity associated with changes in their molecular electronic structure and/or an increase in surface-to-volume ration. Nanostructured titanium dioxides (TiO_2) have been widely used as photovoltaics, electrochromics, photochromics, and sensors [3]. Titanium dioxide (TiO_2) is an interesting and promising photocatalyst to purify wastewater by the organic compounds decomposition and to produce hydrogen by water splitting [4, 5], due to its low cost, photostability, chemical inertness, nontoxicity, and high efficiency [6]. TiO_2 occurs mainly in three crystalline phases namely anatase, rutile and brookite; and rutile is the thermodynamically most stable phase. While TiO_2 in anatase phase has high photocatalytic activity, the rutile TiO_2 shows no appreciable activity. On the other hand, the modification of TiO_2 by means of metal doping can also affect the crystallization process, influencing the photocatalytic efficiency of TiO_2 [7].TiO_2 has been doped with silver ion in order to improve its photocatalytic efficiency and settleability [8].

TiO_2 has a bandgap of 3.0 eV for the rutile phase and 3.2 eV for the anatase phase. These values require ultraviolet (UV) radiation to activate. Recently, many attempts have been made to make TiO_2 highly reactive under visible light excitation to allow utilization of the solar spectrum [9].

The sol–gel process, offering unique advantages for the preparation of homogeneous metal oxides, would be a method suitable to obtain TiO_2 in powder, bulk, and thin film forms [10,11]. It is also the most effective way to obtain homogeneous hybrid materials showing molecular scale mixtures of organic and inorganic components using a soft chemistry.

Zeolites have been chosen as support since they can delocalize band gap excited electrons of TiO_2 and thereby minimize electron-hole recombination [12]. In addition, the ability of zeolites favoring photoinduced electron-transfer reactions and retarding undesired back electron transfer has been reported [12]. Supporting of TiO_2 in zeolite matrix depends on several factors, such as location and migration of cations, strength of the interactions between cations, and guest molecules dimensions of cavities and channels. The combination of the two properties will lead to distinct and different properties as compared to those with semiconductor alone. The functionalization of zeolite with TiO_2 can be carried out through three ways, namely solid-solid, solid-liquid and solid-gas reactions. Solid-state reactions between inorganic species have been studied [13, 14], however solid-state reaction in hydrothermal conditions between TiO_2 powders with natural zeolite has not been studied so far.

In the present study, hybrid materials based on natural zeolite modified with TiO_2 / Ag-doped TiO_2 were synthesized through solid-state reaction in reaction in ethanol solution and characterized by X-ray diffraction, FT-IR spectroscopy and SEM/ EDX analysis.

2. Experimental

2.1. Chemicals

Romanian zeolitic mineral from Mirsid, used as support for doped TiO_2 loading, was supplied by Cemacon Company, Romania. The mineral was powdered and sieved with a Multilab sieve shaker. The diameter of grains size selected to carry out the experiments was between 0.8-1.2 mm with the mass composition 62.20% SiO_2, 11.65% Al_2O_3, 1.30% Fe_2O_3, 3.74% CaO, 0.67% MgO, 3.30% K_2O, 0.72% Na_2O, 0.28% TiO_2.

Titanium (IV) isopropoxide (TTIP, 98%), silver nitrate ($AgNO_3$), hydrochloric acid (HCl), ethanol, natrium nitrate ($NaNO_3$) and nitric acid (HNO_3) were purchased from ALDRICH Company.

2.2. Photocatalyst preparation

The hybrid materials based on natural zeolite modified with undoped TiO_2 and Ag-doped TiO_2 nanocrystals were prepared by solid-state reaction in ethanol solution. The hybrid materials synthesis are performed in two steps, in the first one the undoped and doped TiO_2 nanocrystals were synthesized by sol-gel method (a) and the second step supposed the hybrid material synthesis by solid-state reaction (b).

(a) The undoped and silver doped TiO_2 (TiO_2-Ag) nanocrystals were synthesized by sol-gel method [15]. An amount of ethanol was stirred with 5 mL TTIP and after 10 minutes, 30 mL of distilled water was added in dropwise. The pH of the initial solution was 5.5 and before adding the doping precursor ($AgNO_3$) the pH was adjusted with HNO_3. Two different quantities were used for TiO_2 doping, such as 2 wt% (TiO_2-Ag2) and 3 wt% (TiO_2-Ag3) The solutions were filtered, washed and dried to 60ºC for 5 hours. For crystallization the materials were annealed into an oven at the temperature range between 300 - 600ºC for 2 hours.

(b) The hybrid materials based on natural zeolite functionalized with undoped and doped TiO_2 presumes the preparation of the chemically modified zeolite in two stages. To reach acid form (H form) it was used 2M HCl solution and for sodium form (Na form) 2M $NaNO_3$ solution for a more efficient ion exchange. This is the reason that Na forms are the most frequently prepared for research in clinoptilolite literature [16]. The hybrid materials based on natural zeolite and undoped and doped TiO_2 were synthesized by solid-state reaction in ethanol solution. 5g of natural zeolite as Na form was mixed with 30 mL ethanol and undoped TiO_2 (Z-TiO_2), TiO_2-Ag2 (Z-TiO_2-Ag2), respectively TiO_2-Ag3 (Z-TiO_2-Ag3) nanocrystals under continuous stirring for 1 hour [17]. The solution was filtered, washed and dried to 60ºC. The thermal treatment was performed for 1 hour in an oven to 150 ºC.

2.3. The materials characterization

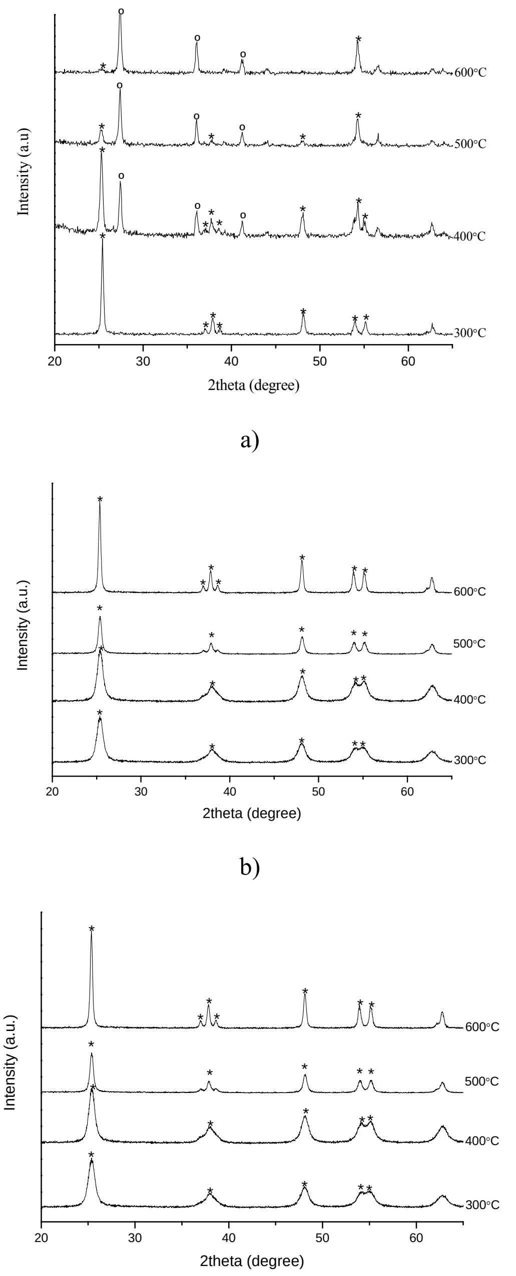
The crystallinity of the prepared samples was measured by X-Ray diffraction (XRD) using PANalytical X'PertPRO MPD Difractometer with Cu tube. A scanning electron microscopy (SEM) using Inspect S PANalytical model coupled with the energy dispersive X-ray analysis detector (EDX) was used to characterize the external surfaces of the hybrid materials, using catalyst powder supported on carbon tape. The bond vibration of modified materials was analyzed by Fourier transform infrared spectrometry (FT-IR) using a JASCO FT/IR-430 spectrometer.

3. Results and discussion

3.1. Photocatalyst characterization

3.1.1. XRD results

In Figs. 1a, b and c are presented the XRD patterns of undoped TiO_2 (a), TiO_2-Ag2 (b) and respectively TiO_2-Ag3 (c). It is known that annealing improved the crystallization of TiO_2 powders and accelerated the transformation from amorphous phase to anatase or rutile phase. It can be seen that for a temperature of 300°C the crystalline phase of undoped TiO_2 nanocrystals reveals anatase form and by temperature increasing at 400°C the phase transition from anatase to rutile occurred (Fig.1a). At 600°C the anatase phase of undoped TiO_2 is almost disappeared and the rutile form is predominantly (Fig. 1a). In according with the literature [18,19], this behavior is expected and can be explained by the effect of the annealing temperature on the anatase phase, which become metastable at higher temperature and it is converted into stable rutile phase. The Ag-doped TiO_2 nanocrystals exhibited a different behavior under the same annealing temperature rang. The pure anatase form was noticed until to 600°C temperature, without the appearance of the rutile form (Fig. 1b and c). It can be seen that the doping degree did not influence the phase transition. Based on the literature data [20] this behavior is own to the fact that the presence of Ag ions decreased the oxygen vacancy concentration, which inhibited the phase transition under the studied temperatures range. Thus, the diffraction peaks of anatase TiO_2 corresponding to 2 theta: 25.3º, 37º, 37.8º, 38.6º, 48º, 54º, 55° [21] and of rutile phase to 2 theta: 27.3º, 35.9º, 41.1º, 54.1º were noticed [22].



a)

b)

c)

Fig. 1. XRD patterns of a) undoped TiO_2, b) TiO_2-Ag2 and c) TiO_2 - Ag3 at different calcinations temperatures (-anatase, ○ – rutile).*

For further experiments it were selected only the nanocrystals crystallized in anatase form, for obtaining the hybrid materials based on natural zeolite and TiO_2. Therefore the nanocrystals selected from the XRD results are undoped TiO_2 annealed 300°C and TiO_2-Ag2, respectively TiO_2-Ag3 annealed 600°C. Anatase TiO_2 exhibits higher photocatalytic activity than rutile TiO_2 due to its conduction band position which demonstrates stronger reducing power [23].

Fig. 2 described XRD patterns of hybrid materials based on natural zeolite and undoped/ Ag-doped TiO_2 nanocrystals, *i.e.*, Z-TiO_2, Z-TiO_2-Ag2 and Z-TiO_2-Ag3. For comparison, the XRD pattern of the natural zeolite in Na form is also shown in Fig. 2 (spectra a). The presented results revealed that the natural zeolite used is mostly clinoptilolite (2 theta: 10º; 22.5º; 30º) [24].

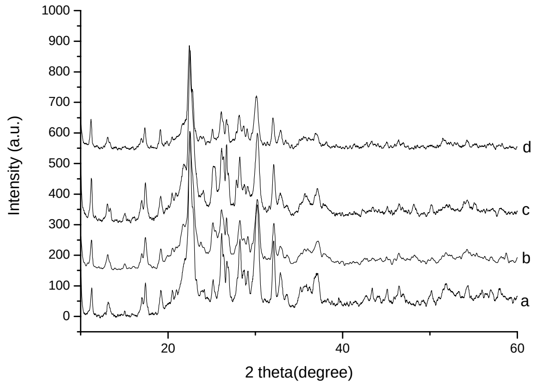
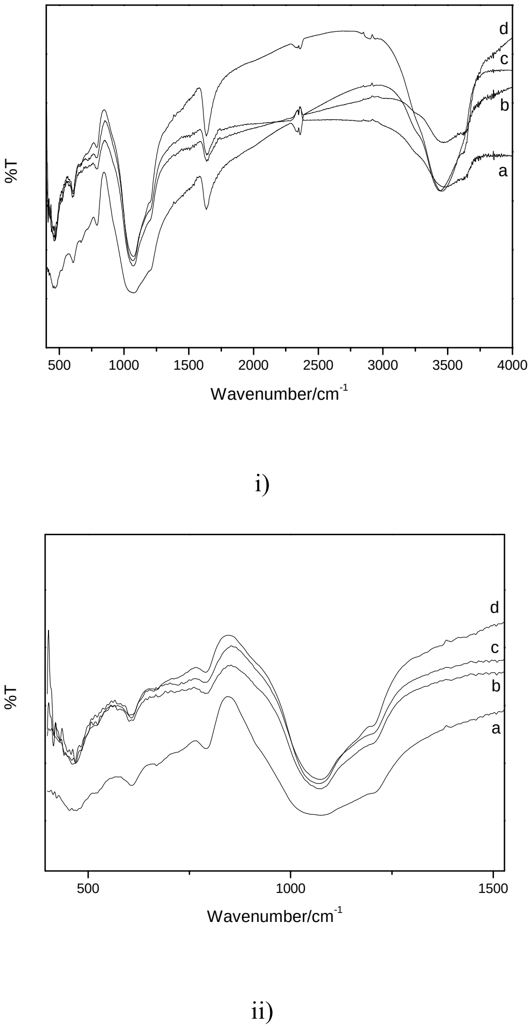


Fig. 2. XRD patterns of a) Z-Na; b) Z-TiO_2; c) Z-TiO_2-Ag2; d) Z-TiO_2-Ag3.

X-ray diffraction studies reveal that the structural damage of zeolite is negligible during the modification process [25, 26].

3.2.2. FT-IR results

Figs. 3i and ii represent the FT-IR spectra of hybrid materials functionalized with TiO_2-Ag2 and TiO_2-Ag3 in comparison with Na form of the zeolite. The bands at 3540 and 3360 cm^{-1} have been attributed to the symmetric and anti-symmetric stretching modes of molecular water coordinated to the magnesium at the edges of the channels. The presence of doped TiO_2 into hybrid materials seems to affect the symmetric stretching modes of water coordinated to the magnesium at the edges of channels (Fig. 3i). The band at 1630-1640 cm^{-1} (Lewis sites) region is assigned to the zeolite water in channels of the samples [23, 18]. The shoulders at 1350 cm^{-1} noticed for the hybrid materials (Z-TiO_2, Z-TiO_2-Ag2 and Z-TiO_2-Ag3) can be attributed to stretching and vibration of the Ti-O-Ti group, indicating the formation of the inorganic matrix [28]. For the hybrid materials synthesized by solid state reaction in ethanol solution the corresponding tetrahedral loadings bands from 450-900 cm^{-1} are not modified, so the zeolite network is not affected



i)

ii)

Fig. 3. i) FT-IR spectra of a) Z-Na; b) Z-TiO_2-Ag3; c) Z-TiO_2; d) Z-TiO_2-Ag2 for the wavenumber range 4000-400cm^{-1}; ii) FT-IR spectra of a) Z-Na; b) Z-TiO_2-Ag3; c) Z-TiO_2; d) Z-TiO_2-Ag2 for the wavenumber range 1300-400 cm^{-1}.

FT-IR results clearly showed for hybrid materials in comparison with Z-Na some modifications specific to presence of TiO_2 bounded at zeolite within absorption band range between 945 and 860 cm^{-1}. Thus, according to Liu et al. [29] the absorption bands at 920 and 860 cm^{-1} are originated from the Ti-O stretching vibration and Ti-O-Ti linkage vibration, respectively [29, 30]. Also, the absorption band range from 945 to 905 cm^{-1} corresponds to the stretching vibration of Ti-O-Si and Ti-O-Al [31].

3.2.3. SEM and EDX results

Figs. 4 and 5 shows the SEM and EDX results of Z-TiO_2-Ag2 and Z-TiO_2-Ag3.

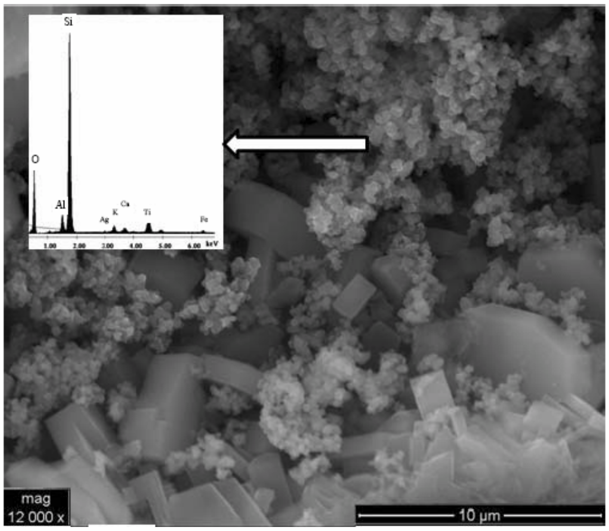


Fig. 4. SEM morphology for Z-TiO_2-Ag2; Inset: EDX spectra for elemental analysis.

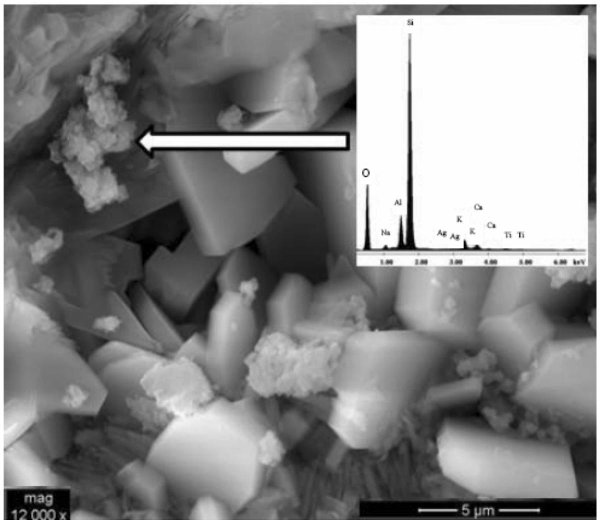


Fig. 5. SEM morphology for Z-TiO_2-Ag3; Inset: EDX spectra for elemental analysis.

From the SEM images it can be observed the lamellar texture of clinoptilolite, which is in line with the literature [32]. The particles of TiO_2 only adhered to the surface and in the cavities of zeolite and were not inside the pores (Figs. 4 and 5). TiO_2 particles have crystallized like spherical agglomerates with a non-uniformly distribution on the zeolite surface and in the zeolite cavities whose size allows the placement of the TiO_2 conglomerate.

EDX analysis provided a semiquantitative elemental analysis of the surface indicating that Ti and Ag were present on the zeolite surface. Also, this natural zeolite contain the major elements such as Na, Si, Al, Ca, K, Mg as can be seen from the EDX spectra (Inset Figs. 4 and 5).

4. Conclusions

The hybrid materials based on natural zeolite and undoped and Ag-doped TiO_2 were successfully synthesized by solid state reaction in ethanol solution. The optimum annealing temperature was set up at 300 °C for undoped TiO_2 and 600°C for TiO_2-Ag2 and TiO_2-Ag3 to obtain pure anatase TiO_2 form. For hybrid materials synthesis it was chosen only the samples crystallized in anatase form. Silver presence was confirmed by EDX analysis. XRD analysis demonstrated that natural zeolite is commonly clinoptilolite and the TiO_2 nanocrystals are present in the zeolite network. The FT-IR spectra evidenced the presence on TiO_2 bounded at the zeolite network by Ti-O-Al and Ti-O-Si, which indicated the load of TiO_2 into zeolite more durable than simple physical combination. SEM morphology showed that undoped and doped TiO_2 nanocrystals (spherical particles) are distributed in the cavities and on the surface of the natural zeolite.

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