

# Synthesis of hybrid zeolitic materials with TiO<sub>2</sub> nanocrystals using solid-solid method

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The aim of this paper was the synthesis and characterization of hybrid zeolite materials functionalized with Fe-doped and N-doped TiO<sub>2</sub> nanocrystals. The hybrid zeolite materials synthesis based on titanium dioxide was achieved using the solid-solid method, in two different synthesis conditions. TiO<sub>2</sub> doped with metallic (Fe) and non-metallic (N) ions was obtained directly from precursors by sol-gel method. The titanium dioxide nanocrystals and the hybrid zeolite materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) and IR spectrometry (IR).

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## 1. Introduction

Zeolite based photocatalysis is a new method and the work reported so far involved the use of high TiO<sub>2</sub> loadings [1-14]. Zeolite seems to be a promising support for TiO<sub>2</sub> photocatalyst because of its regular pores and channel sizes and good adsorption ability [15]. TiO<sub>2</sub> supported on zeolite integrates the photocatalytic activity of TiO<sub>2</sub> with the adsorption properties of zeolite, which induce a synergistic effect, resulting in the enhancement of photocatalytic efficiency [1]. Further reports revealed that supported TiO<sub>2</sub> shows high photocatalytic activity. TiO<sub>2</sub> supported on materials such as glass and alumina beads [24], MCM-41 and zeolites [25] have been reported as highly active photocatalysts for degradation of different water-borne pollutants.

Also, titanium atoms incorporated into the zeolite framework serve as catalytic sites, and thus the content of framework titanium in a zeolite has presented higher activity in performing some catalytic reactions [16-18]. Titania in anatase phase is the best photocatalyst reported so far, but the poor adsorption and low surface area properties lead to great limitations in the practical applications. On the other hand, support TiO<sub>2</sub> is commonly reported to be less photoactively due to the interaction of TiO<sub>2</sub> with support during the thermal treatments [19]. However, several attempts have been made to improve the photoefficiency of titania by adding adsorbents like silica, alumina, *zeolites*, clays, and active carbon [1, 20].

Zeolites synthesis has been extensively reviewed in several books and literature [21-26].

Zeolites can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework. Zeolites can also be used to separate harmful organics from water, and in removing heavy metal ions,

including those produced by nuclear fission from water [27-28, 34]. They also serve as ion-exchangers and molecular sieves. Potential applications are expected in a number of technological fields, such as photochemistry, biology [31-33], optoelectronics, semiconducting devices and chemical sensors. However, the high cost of the support limited the extensive application of such hosts of photocatalysts in usual industry. Comparing with the synthetic zeolites, the natural zeolites are much cheaper, more abundant and more easily available [29].

It is well-known that TiO<sub>2</sub> can be obtained by a number of methods, including mechanochemical, hydrothermal, sol-gel, microemulsion, electrochemical synthesis, gas phase methods [35]. The synthesis method is chosen to reach the nanoparticles with well-defined morphology and size distribution.

Our previous work also demonstrated the synthesis of supported TiO<sub>2</sub> on the natural zeolite through sol-gel method directly from precursors [15, 36]. The results revealed that supports possess good pollutant adsorption, diffusion properties and absence of light absorption, which exhibited the best photocatalytic activity. In this study, the preparation and characterization of TiO<sub>2</sub> photocatalyst impregnated on zeolite support using solid-solid method is presented.

## 2. Experimental

### 2.1. Materials

The starting materials used for the synthesis were: titanium isopropoxide (TTIP, Fluka), ethanol, distilled water, urea ((NH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>, Merk) and ferric nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>, Merk).

The Romanian zeolitic mineral from Mirsid, used as support for doped TiO<sub>2</sub> 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 315-500 μm with the mass composition 62.20% SiO<sub>2</sub>; 11.65% Al<sub>2</sub>O<sub>3</sub>; 1.30% Fe<sub>2</sub>O<sub>3</sub>; 3.74% CaO; 0.67% MgO; 3.30% K<sub>2</sub>O; 0.72% Na<sub>2</sub>O; 0.28% TiO<sub>2</sub>.

## 2.2. Methods

Two types of hybrid materials were synthesized, i.e., sodium natural zeolite modified with TiO<sub>2</sub>-Fe (Z-Na-TiO<sub>2</sub>-Fe) and sodium natural zeolite modified with TiO<sub>2</sub>-N (Z-Na-TiO<sub>2</sub>-N).

### 2.2.1. Photocatalyst synthesis

Titanium dioxide doped with metallic (Fe) and non-metallic (N) ions was obtained directly from precursors by sol-gel method.

Sol-gel (SG) method presumes the mixing of 30 mL of ethanol with 5 mL of TTIP (the precursor for Ti) added by dropwise. After a few minutes of stirring, distilled water was added also in drops. The doping precursors, Fe(NO<sub>3</sub>)<sub>3</sub> for TiO<sub>2</sub>-Fe synthesis and (NH<sub>2</sub>)<sub>2</sub>CO for TiO<sub>2</sub>-N synthesis, were added after the pH adjustment. The solution was continuously stirred for one hour and the obtained materials were filtered, washed and dried at 60°C.

The thermal treatment for both materials was achieved for 2 hours at 500°C temperature.

### 2.2.2. Solid-solid method for hybrid materials synthesis

For a more efficient ion exchange, the natural zeolite (315-500 μm) was modified as sodium form (Z-Na); the preparation of the chemically modified zeolite presumes two stages, an acid form using HCl (2M) and a sodium form using NaNO<sub>3</sub> (2M).

Solid-solid method for hybrid zeolite materials synthesis was performed in two different conditions:

*I.* 5g of natural zeolite as sodium form was mixed with 30 mL ethanol and TiO<sub>2</sub>-Fe, respectively TiO<sub>2</sub>-N under stirring for 1 hour. The solution was filtered, washed and dried to 60°C. The hybrid zeolite materials (Z-Na-TiO<sub>2</sub>-Fe(I) and Z-Na-TiO<sub>2</sub>-N(I)) were thermally treated for 1 hour in an oven to 150°C.

*II.* The mixture of natural zeolite as sodium form and TiO<sub>2</sub>-Fe, respectively TiO<sub>2</sub>-N nanocrystals, were stirred continuously for one hour in aqueous solution; the solutions were introduced in a Teflon-lined stainless steel autoclave with an 80 % degree of fullness. The autoclave was introduced in an oven, with the heating temperature of 150°C for 2 hours. After autoclaving, the hybrid zeolite materials (Z-Na-TiO<sub>2</sub>-Fe(II) and Z-Na-TiO<sub>2</sub>-N(II)) were washed with distilled water and dried at 60°C for 5 h.

Fig. 1 represents the schematic diagram of hybrid materials synthesis in conditions *I* and *II* previously discussed.

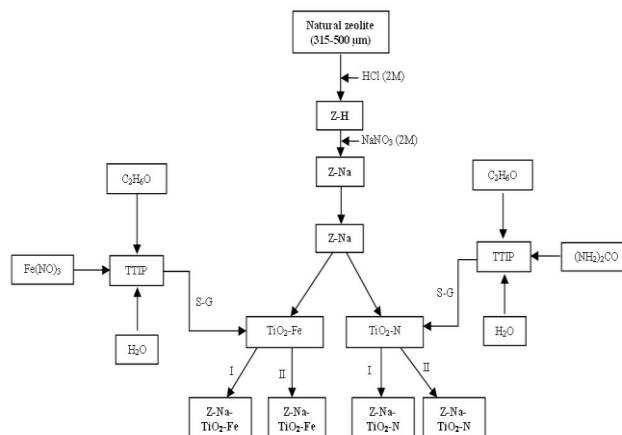


Fig.1. Schematic diagram of hybrid materials synthesized by solid-solid method

The solid-solid synthesis of hybrid zeolite materials under different conditions were achieved in order to provide a comparison of the crystalline structure and morphology for doped TiO<sub>2</sub> nanocrystals on the surface of the zeolite as the obtained hybrid materials.

## 2.3. Structural characterization

Phase characterization of the doped photocatalysts and hybrid zeolitic materials was carried out by X-ray diffraction (XRD) using a PANalytical X'PertPRO MPD Diffractometer, Cu tube. The particles size and morphology of the hybrid zeolitic materials were determined by Scanning Electron Microscopy (SEM) using an Inspect S PANalytical model and the energy dispersive X-ray analysis detector (EDX). The bond vibration was analyzed by IR spectrometry (IR) using a Jasco FT/IR-430 spectrometer.

## 3. Results and discussion

### 3.1. Photocatalyst characterization

#### 3.1.1. X-ray results

In Fig. 2 are presented the XRD spectra of TiO<sub>2</sub> doped with Fe and N. The peaks of anatase TiO<sub>2</sub> corresponding to 2θ ~ 25.2°, 37.87°, 48.01°, 53.81°, 62.67°, 75.07 [37, 38] appear for both doped TiO<sub>2</sub>.

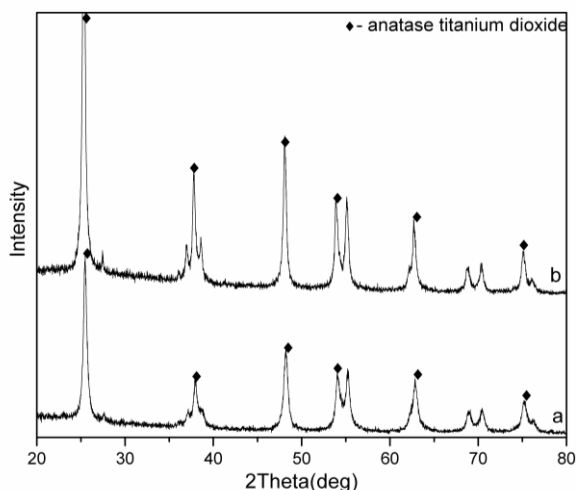


Fig.2. XRD spectra for a)  $TiO_2-Fe$  and b)  $TiO_2-N$

It can be seen that no peaks corresponding to Fe and N presence are found, probably because of small amount of the ions uniformly distributed in the crystalline lattice of the titanium dioxide.

### 3.1.2. EDX results

Figs. 3 and 4 present the results of elemental analysis, which confirm the presence of doping ions within titanium dioxide structure.

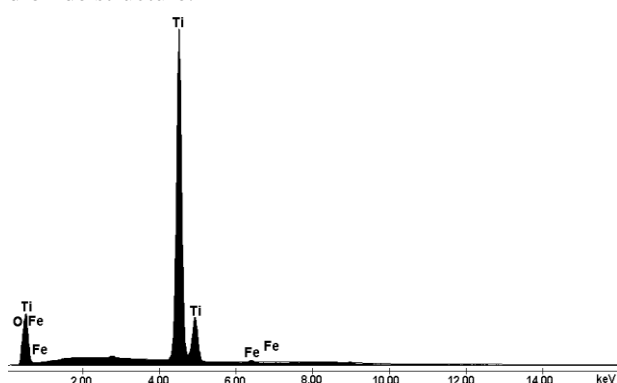


Fig.3. EDX analysis for  $TiO_2-Fe$

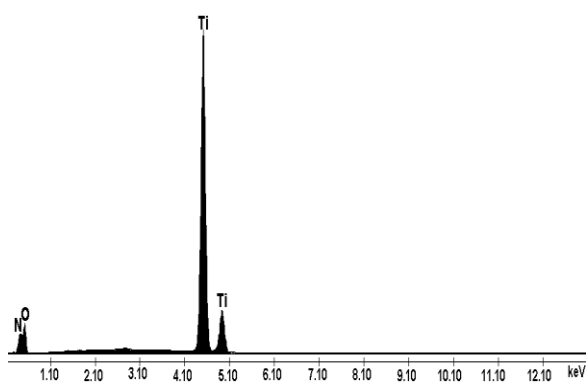


Fig.4. EDX analysis for  $TiO_2-N$

## 3.2. Hybrid zeolitic material characterization

### 3.2.1. X-ray results

Figs. 5 and 6 show the comparative XRD spectra of Z-Na- $TiO_2-Fe$  (I), Z-Na- $TiO_2-N$  (I) and Z-Na- $TiO_2-Fe$  (II), Z-Na- $TiO_2-N$  (II). The X-ray patterns reveal that the natural zeolite used in the experiment is mostly clinoptilolite ( $2\theta \sim 10^\circ; 22.5^\circ; 30^\circ$ ) [30]. Also, the specific anatase titanium dioxide peaks appeared in the XRD patterns.

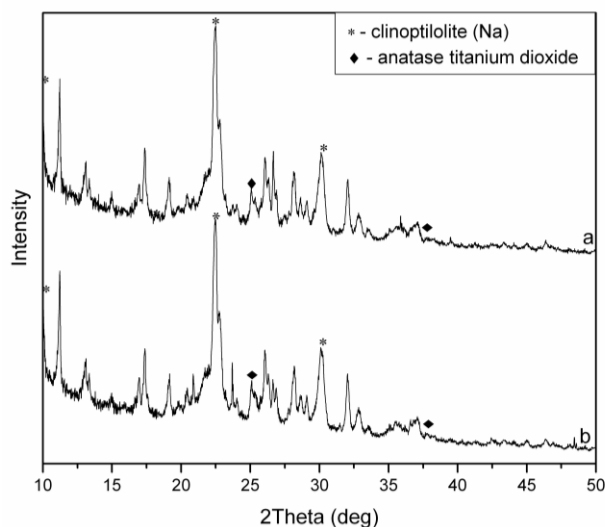


Fig. 5. XRD patterns for a) Z-Na- $TiO_2-Fe$ (I) and b) Z-Na- $TiO_2-N$ (I).

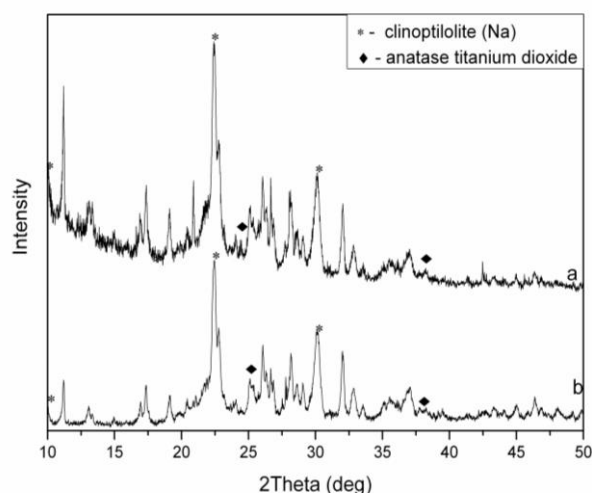


Fig.6. XRD patterns for a) Z-Na- $TiO_2-Fe$ (II) and b) Z-Na- $TiO_2-N$ (II)

X-ray diffraction studies reveal that the structural damage of zeolite is negligible during the modification process [39, 40].

### 3.2.2. IR results

Figures 7 and 8 represent the IR spectra of hybrid materials functionalized with TiO<sub>2</sub>-Fe and TiO<sub>2</sub>-N, synthesized by solid-solid method under both above presented conditions.

The bands at 3540 and 3360 cm<sup>-1</sup> have been attributed to the symmetric and anti-symmetric stretching modes of molecular water coordinated to the magnesium at the edges of the channels, which seems to be affected by the presence of doped TiO<sub>2</sub> (Figures 7, 8). The band at 1630-1640 cm<sup>-1</sup> (Lewis sites) region is assigned to the zeolite water in channels of the samples [29, 41]. The bands at 1350 cm<sup>-1</sup> observed for the hybrid zeolite material functionalized with TiO<sub>2</sub>-Fe and TiO<sub>2</sub>-N were attributed to stretching and vibration of the Ti-O-Ti group, indicating the formation of the inorganic matrix [36]. The bands at 2300 cm<sup>-1</sup> and 2400 cm<sup>-1</sup> could be attributed to the presence of TiO<sub>2</sub> on the zeolite surface or in the zeolite cavities [29].

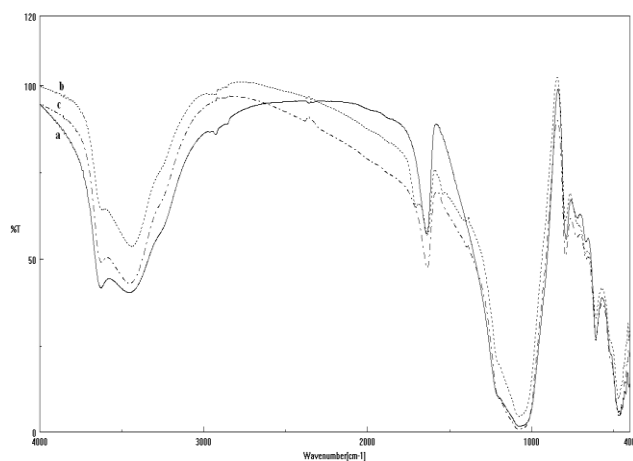


Fig.7. IR spectra of: a) Z-Na; b) Z-Na-TiO<sub>2</sub>-Fe(I); c) Z-Na-TiO<sub>2</sub>-N(I)

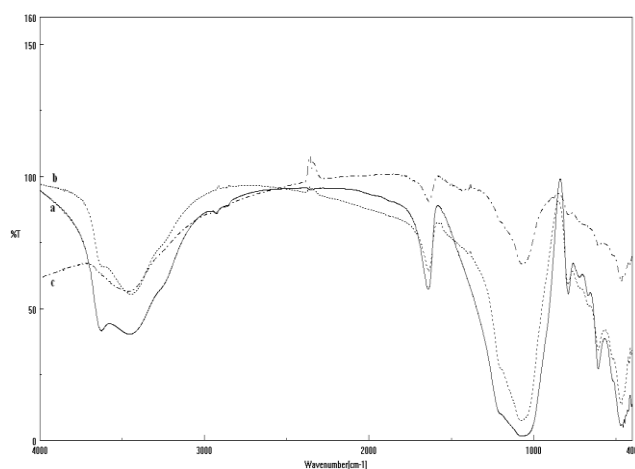


Fig.8. IR spectra of: a) Z-Na; b) Z-Na-TiO<sub>2</sub>-Fe(II); c) Z-Na-TiO<sub>2</sub>-N(II)

For the hybrid zeolitic materials synthesized under conditions I, the corresponding tetrahedral loadings bands from 450-900 cm<sup>-1</sup> are not influenced by the presence of TiO<sub>2</sub> which informed that the zeolite lattice is not affected. For the hybrid zeolite materials synthesized in conditions II the specific zeolite lattice bands present some modifications, probably because of hydrothermal synthesis conditions.

### 3.2.3. Scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX) results

Figs. 9-12 represent the SEM and EDX results of the Z-Na-TiO<sub>2</sub>-N (I), Z-Na-TiO<sub>2</sub>-N (II), Z-Na-TiO<sub>2</sub>-Fe (I), Z-Na-TiO<sub>2</sub>-Fe (II).

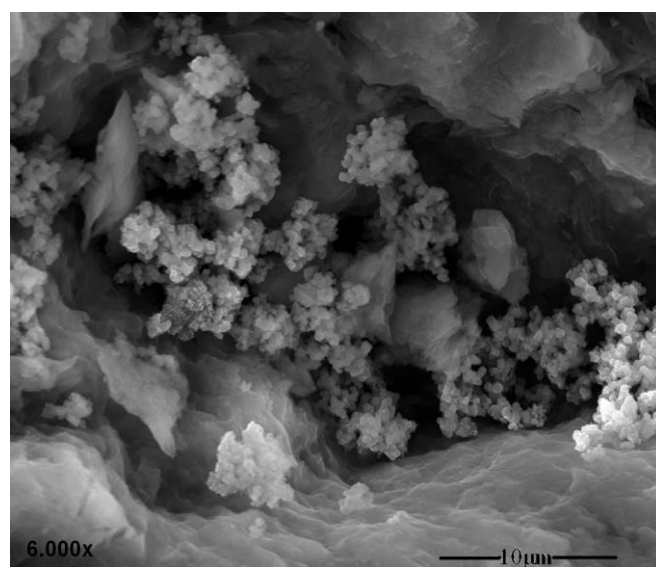


Fig.9. a) SEM morphology and b) EDX analysis for Z-Na-TiO<sub>2</sub>-N (I)

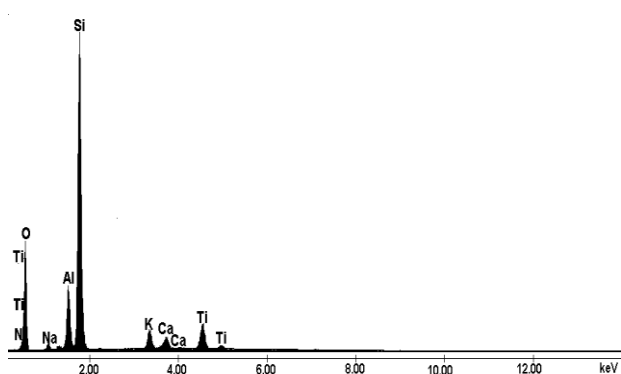
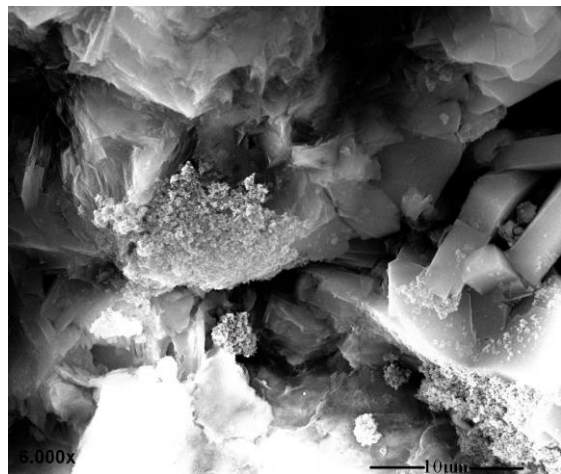


Fig.10. a) SEM morphology and b) EDX analysis for Z-Na-TiO<sub>2</sub>-N (II)

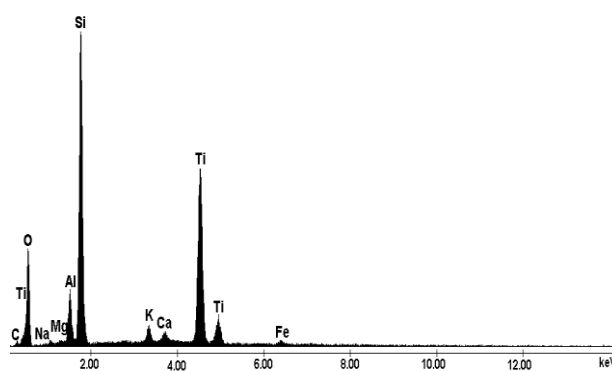
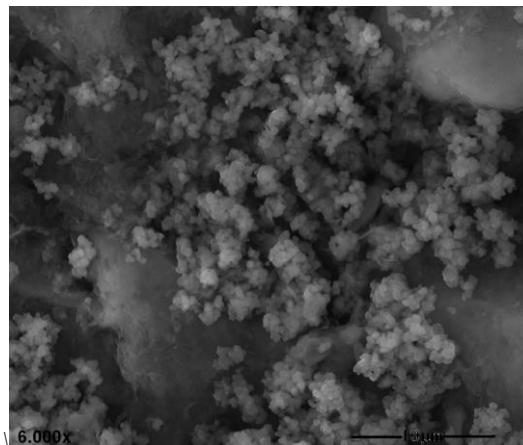


Fig.12. a) SEM morphology and b) EDX analysis for Z-Na-TiO<sub>2</sub>-Fe (II)

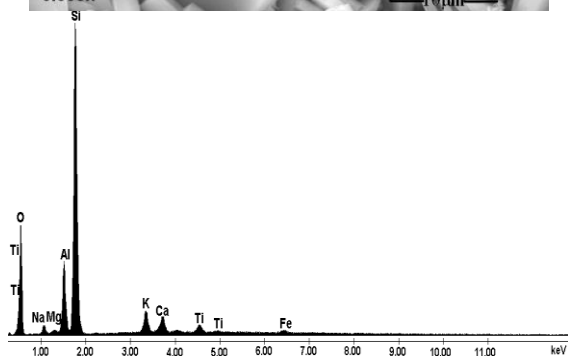
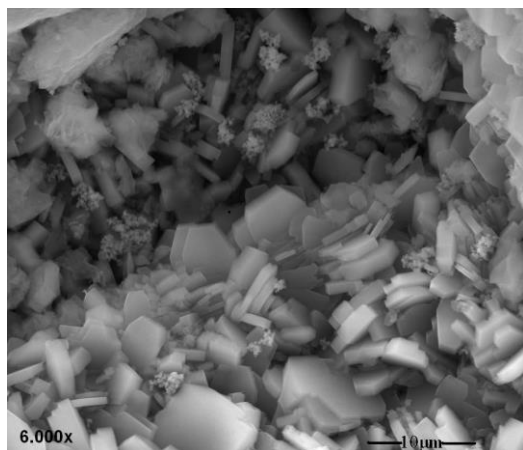


Fig.11. a) SEM morphology and b) EDX analysis for Z-Na-TiO<sub>2</sub>-Fe (I).

From all SEM images (Figs. 9a-12a) it can be observed the lamellar texture of clinoptilolite, which is in line with the literature [28]. The particles of TiO<sub>2</sub> only adhered to the surface and in the cavities of zeolite and were not inside the pores.

TiO<sub>2</sub> 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<sub>2</sub> conglomerate.

The presence of doping ion in every synthesized hybrid zeolitic material is confirmed by EDX results (Figs.9b-12b).

#### 4. Conclusions

TiO<sub>2</sub> nanocrystals doped with Fe (metallic ion) and N (non-metallic ion) were synthesized from precursors by the sol-gel method. The hybrid zeolite materials functionalized with TiO<sub>2</sub>-Fe and TiO<sub>2</sub>-N were prepared by the solid-solid method in two different conditions.

The characterization of photocatalyst based on the doped TiO<sub>2</sub> using X-ray analysis showed that the crystalline form of titanium dioxide is anatase. The doping ions (Fe and N) presence in titanium dioxide lattice was confirmed by EDX analysis.

For the hybrid zeolitic materials, X-ray analysis demonstrated that natural zeolite is commonly clinoptilolite and the TiO<sub>2</sub> nanocrystals are present in the zeolite lattice. SEM morphology showed that titanium dioxide nanocrystals (spherical particles) doped with Fe and N are distributed in the cavities and on the surface of the zeolite.

EDX results confirmed the presence of doping ions. IR spectra approved the presence of TiO<sub>2</sub> within the zeolite lattice. The hybrid zeolite materials exhibited some differences according to synthesis conditions. Application of the condition II, which was similarly with hydrothermal conditions, affected the zeolite lattice more than those similar with sol-gel method (I).

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