SYNTHESIS AND CHARACTERIZATION OF ZEOLITE MATERIALS FUNCTIONALIZED WITH UNDOPED AND N-DOPED TiO_2 NANOCRYSTALS

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Abstract

The aim of this paper was the syntheses and characterizations of functionalized zeolite materials with undoped and nitrogen-doped TiO_2 nanocrystals. These materials were obtained by using alternative methods, namely sol-gel and hydrothermal, directly from precursors.

The synthesis of TiO_2 by sol-gel and hydrothermal methods was achieved in order to compare the crystalline structures and morphologies of TiO_2 on the surface of the zeolite within the obtained hybrid materials. The obtained materials were characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), and scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX).

The XRD results revealed that the natural zeolite used for the synthesis is mostly clinoptilolite and the anatase form of TiO_2 for both applied methods. As it was desired, no the rutile phase of TiO_2 was evidenced. The surface morphology observed by SEM analysis showed that TiO_2 (spherical form) nanocrystals were attached on the zeolite surface. Therefore, the IR spectra confirmed the presence of TiO_2 in to the zeolite lattice. The presence of the nitrogen ion in the materials obtained by both synthesis methods was also confirmed by EDAX spectra.

Introduction

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 ratio. Nanostructured titanium dioxides (TiO_2) have been widely used as photovoltaics, electrochromics, photochromics, and sensors [1]. Titanium dioxide (TiO_2) is an interesting and promising photocatalyst to purify wastewater by the decomposition of organic compounds and to produce hydrogen by water splitting [2, 3], due to its low cost, photostability, chemical inertness, nontoxicity, and high efficiency [4, 5]. Although TiO_2 with different shapes such as nanoparticles [6], thin films [7], nanorods [8], nanowires [9], and nanotubes [10] has been synthesized by different methods, the mechanisms for the formation of different shapes are still a challenge to the scientist in this scope. Many techniques, such as CVD and thermal pyrolysis, have been developed to make nanostructured materials, among which the wet chemical methods, such as hydrothermal method and sol-gel method, show many advantages, such as mild reaction condition, less energy consumption, simple equipment required, and large quantity of changeable factors to control the sample morphology.

An aluminosilicate-type zeolite is a microporous material with framework anions (AlO_2^-) and exchangeable cations in its structure, and the anion-cation pairs form strong electrostatic fields [11, 12], which strongly interact with polar adsorbents. Because of such interesting properties, zeolites are widely used as catalysts and adsorbents for organic synthesis and decomposition [13] as well as in waste-gas adsorption and waste-water treatment [14, 15].

The incorporation of titanium dioxide in zeolite cavity offers advantages due to size quantization resulting in different optical and electronic properties [16–18]. In order to improve the efficiency of the titanium dioxide doped zeolite catalyst to operate in the visible region, attempts are made to assemble the semiconductor and sensitizer in the internal and external zeolite surfaces. While initial attention was paid to TiO_2 doping by transition metal ions, more recent research points to the introduction of nonmetallic light elements like carbon, sulfur and, in particular, nitrogen into the oxide matrix. There is an increasing interest in the synthesis of N-doped TiO_2 photocatalysts and related areas as these narrow band gap semiconducting materials can be used for visible light photocatalysts. This work aimed to the preparation and characterization of the hybrid materials based on zeolite materials functionalized with undoped and N-doped TiO_2 crystals by using two synthesis methods, i.e., sol-gel and hydrothermal ones, envisaging their application for the degradation of organic pollutants.

Experimental

Two synthesis methods were used in order to obtain TiO_2, TiO_2-zeolite, and N-doped TiO_2-zeolite, i.e., sol-gel and hydrothermal methods. As precursors for the synthesis, natural zeolites from the Mirsid-Romania area were used, of composition (wt %): 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 isopropoxide (Fluka) and urea have been used as TiO_2 and N precursors. For a more efficient ion exchange, the zeolite in the natural form (315-500 μm) must be converted in the sodium form (Z-Na); the preparation of the chemically modified zeolite presumes two stages: acid (HCl) and alkaline ($NaNO_3$) treatment. Using the sol-gel method, three samples were prepared: titanium dioxide (TiO_2-S-G), natural zeolite in sodium form with undoped TiO_2 (Z-Na-TiO_2-S-G), and natural zeolite with TiO_2 doped with N ions (1 wt % of the Ti amount) (Z-Na- TiO_2-N-S-G). Also, using the hydrothermal method, three samples were prepared: titanium dioxide (TiO_2-H), zeolite with undoped TiO_2 (Z-Na-TiO_2-H), and natural zeolite doped with N ions (1 wt % of the amount of Ti) (Z-Na-TiO_2-N-H). For the sol-gel method, 5 g of natural zeolite in sodium form (Z-Na) were mixed by the magnetic stirrer with 30 mL of ethylic alcohol and 2 ml urea; afterwards, 5 mL of titanium isopropoxide was added dropwise. After a few minutes of stirring, 30 mL of distilled water were added also in drops. The pH was adjusted with ammonia solution, reaching a value of 8.5. After one hour of continuous stirring the obtained material was filtered, washed, and dried at 60ºC for 1 hour. The thermal treatment was realized at 300ºC for 2 hours. The hydrothermal method was applied in the same way as the sol-gel one, with the exception of the thermal treatment. After stirring, the material was introduced in a Teflon-line stainless steel autoclave and heated at 150ºC for 6 hours. After autoclaving, the material was washed and dried at 60ºC for 5 h.

The morphology and composition of the unmodified/modified zeolite were characterized by X-ray Diffraction (XRD), infrared spectroscopy (IR), and scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDAX). XRD spectra were recorded at room temperature with a BRUKER D8 ADVANCE X-ray diffractometer using Cu Kα radiation in θ: 2θ configuration. The IR spectra were recorded in KBr pellets for solid compounds on a Jasco FT/IR-430 instrument. The SEM images were made on an Inspect S scanning electron microscope coupled with EDAX device.

Results and discussion

The syntheses were achieved at a temperature of 300ºC for the sol-gel method and 150ºC for the hydrothermal method, in order to avoid the transition of the anatase phase of TiO_2 into rutile phase. The comparative XRD spectra of Z-Na, Z-TiO_2, TiO_2, Z-Na-TiO_2-N-H, and Z-Na-TiO_2-N-SG are presented in Figs. 1a and 1b. The X-ray spectra reveal that the natural zeolite used in the experiment is mostly clinoptilolite (2 θ ~ 10º; 22.5º; 30º). The peaks of anatase TiO_2 corresponding to 2θ ~ 25.2º, 37.87, 48.01 appear for both sol-gel and hydrothermal methods and the crystalline rutile phase was not present in any spectra.

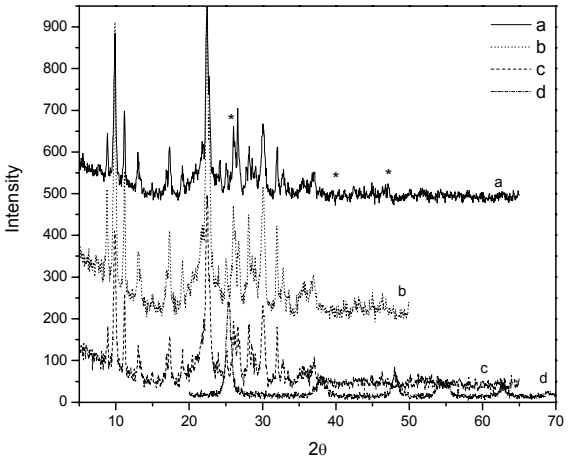


Fig. 1a. X-Ray pattern of: a) Z-TiO_2-N-SG; b) Z-Na; c) Z-TiO_2; d) TiO_2; *-TiO_2.

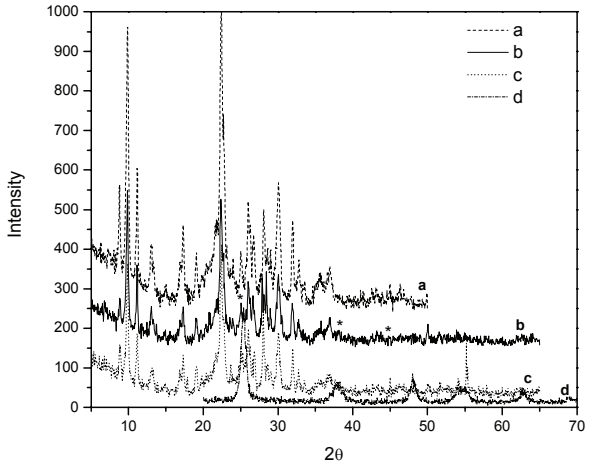


Fig. 1b. X-Ray pattern of: a) Z-Na; b) Z-TiO_2-N-H; c) Z-TiO_2; d) TiO_2; *-TiO_2.

In Figs. 1a and 1b corresponding to Z-Na-TiO_2-N-H and Z-Na-TiO_2-N-S-G, the peak of nitrogen is not found, that indicates that nitrogen amount in samples is very small. It can be observed that the nitrogen presence does not affect the crystalline lattice of the hybrid material.

The IR spectra of zeolite functionalized with TiO_2 doped with N by hydrothermal and sol-gel method are presented in Figs. 2a and 2b.

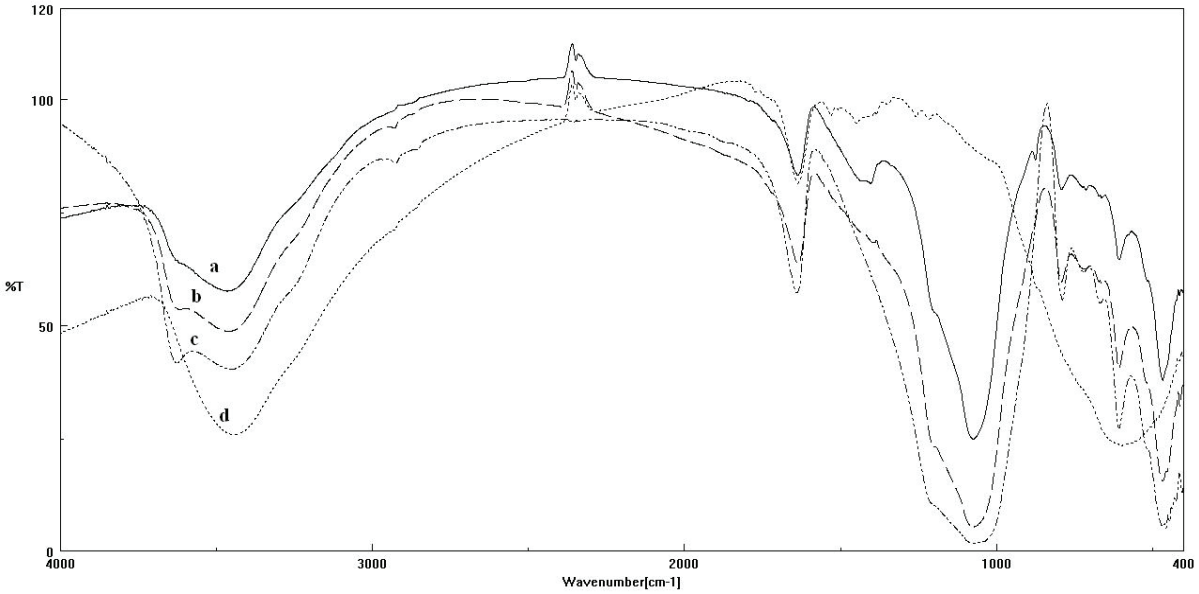


Fig. 2a. IR pattern of a) Z-TiO_2-N-SG, b) Z-TiO_2; c) Z-Na; d) TiO_2.

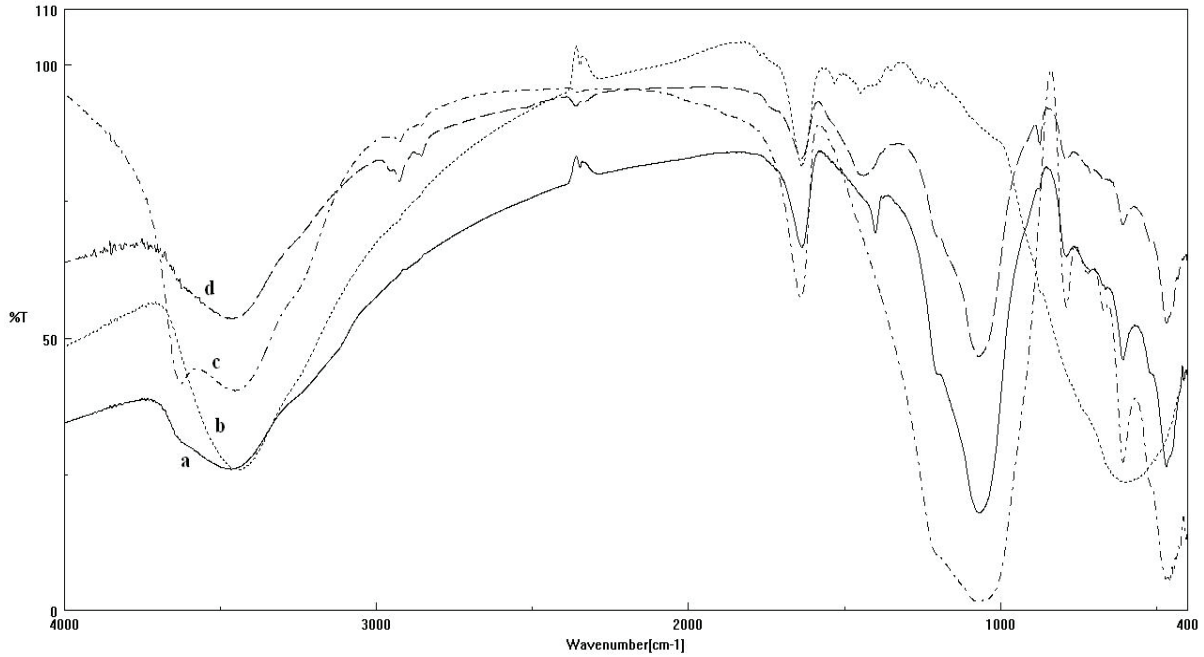
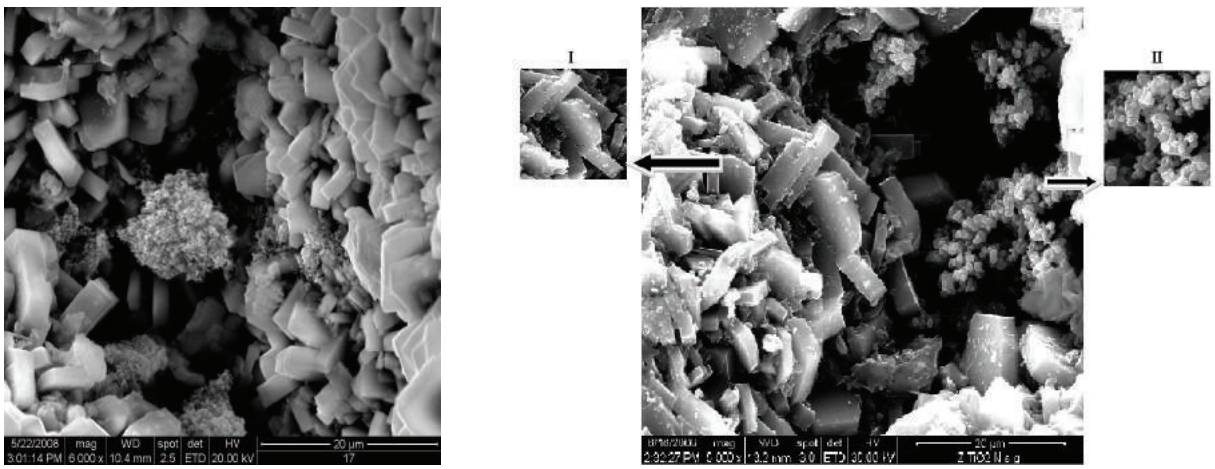


Fig. 2b. IR pattern of a) Z-TiO_2-N-H, b) TiO_2; c) Z-Na; d)Z-TiO_2.

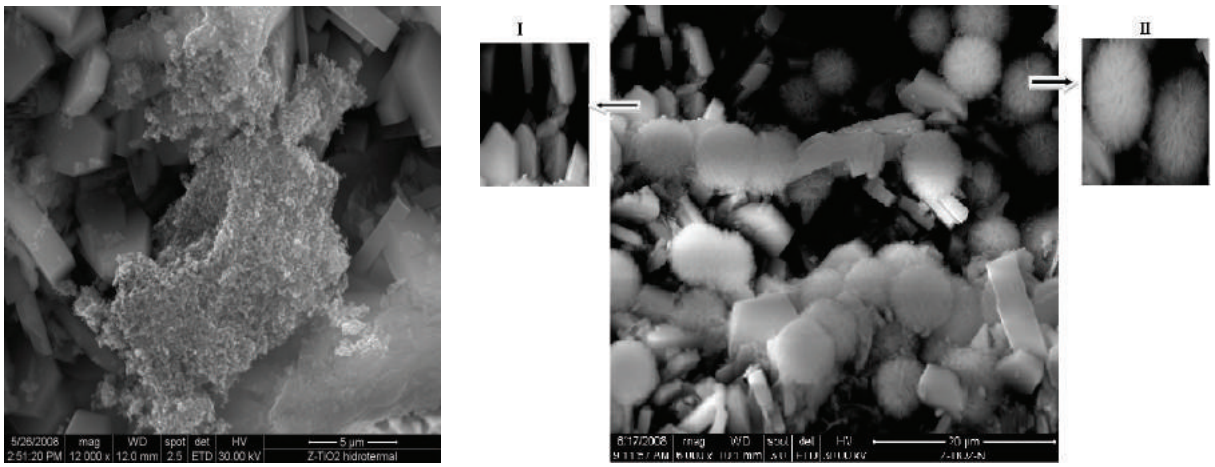
The IR spectra of the bands at 3540 and 3360 cm^{-1} have been attributed to the symmetric and antisymmetric stretching modes of molecular water coordinated to the magnesium at the edges of the channels. The band at 1630-1640 cm^{-1} (Lewis sites) region is assigned to the zeolitic water in channels of the samples [19]. The bands in the regions 1500-1350 cm^{-1} observed for zeolitic material functionalized with TiO_2 and for the zeolitic material functionalized with TiO_2 and doped with nitrogen were attributed to stretching and vibration of the Ti-O-Ti group, indicating the formation of the inorganic matrix [20]. Nitrogen doping of Z-TiO_2 by both materials favored the formation of inorganic matrix based on stretching and vibration of Ti-O-Ti group. The bands at 2300 cm^{-1} and 2400 cm^{-1} corresponding to TiO_2 may indicate the presence of TiO_2 in/on the zeolite surface. Additionally, the bands at 2927, 2856, and 1400 cm^{-1} were assigned to C-H vibrations. This could be attributed to the organic residues from TiO_2 precursors, which remained in sample.

Figures 3 and 4 show the surface morphology of the Z-TiO_2-N-SG and Z-TiO_2-N-H determined by using SEM.



a) b)

Fig. 3. SEM image of Z-TiO_2(a); Z-TiO_2-N-SG(b).

a) 

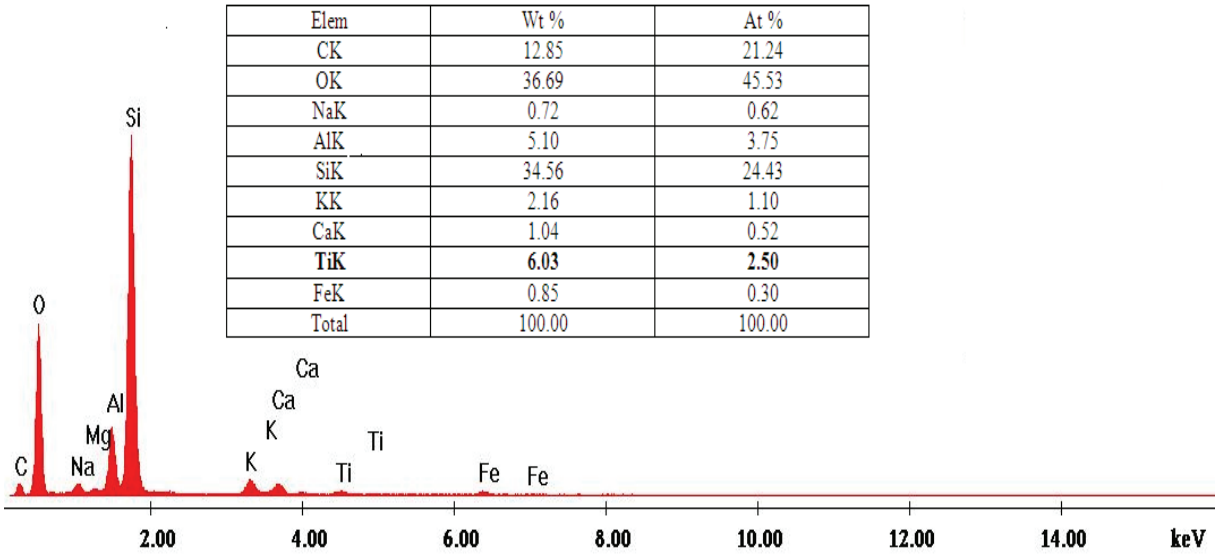
b)

Fig. 4. SEM image of Z-TiO_2(a) Z-TiO_2-N-H(b).

SEM images show the lamellar texture of clinoptilolite (Fig. 3, inset I), which is in line with literature [21, 22]. The TiO_2 particles (Fig. 3, inset II) are distributed randomized and form cluster agglomerate groups on the surface and in site of zeolite channels. The SEM images obtained for Z-Na show that the particles of TiO_2 only adhered to the surface of zeolite (Fig. 4, inset I) and were not inside the pores. TiO_2 particles (Fig. 4, inset II) have crystallize like nanorods and spherical agglomerates with a non-uniform distribution on the zeolite surface and in the zeolite cavities whose size allows the placement of the TiO_2 conglomerate.

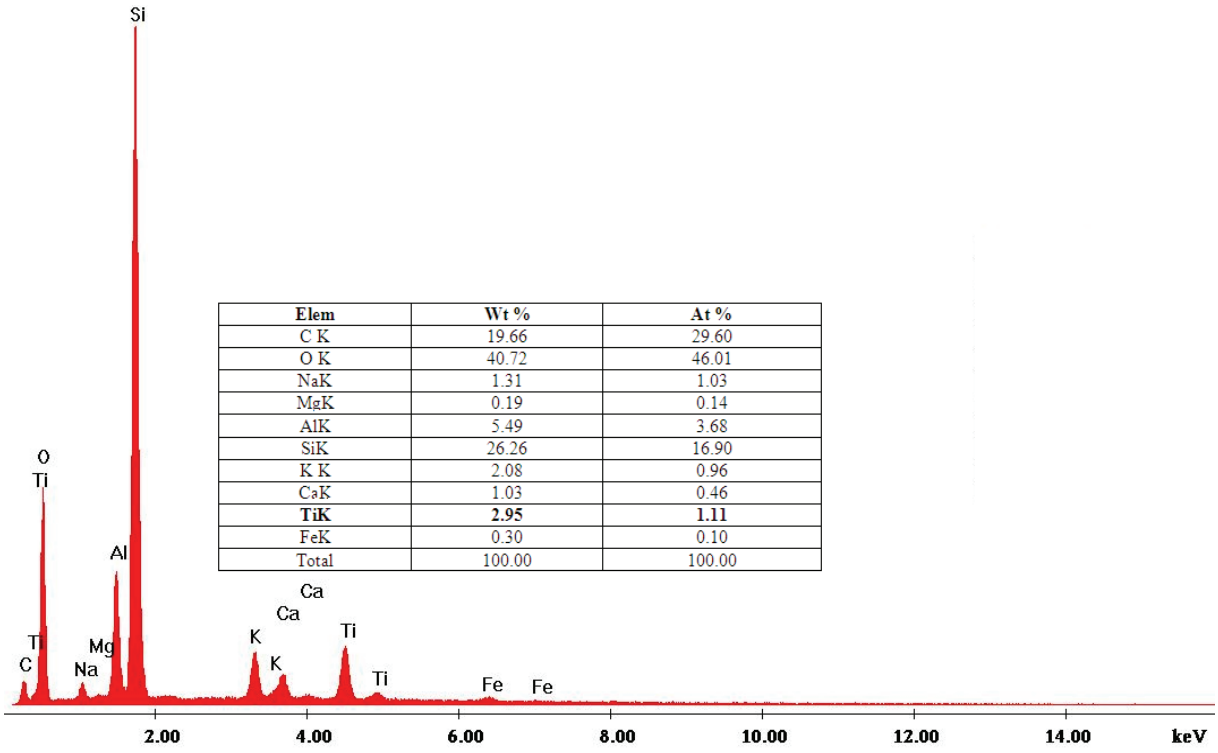
The analysis of titanium element was performed by energy dispersive spectroscopy (EDAX), shown in Figs. 5 and 6. It is clearly observed that titanium particles have been dispersed on the sample; the presence of nitrogen is also observed for both samples.

The EDAX spectra confirm the presence of the N and Ti ions in the materials obtained by sol-gel and hydrothermal methods. From EDAX quantification it is observed that the amounts of titanium and nitrogen ions are larger within the hybrid material obtained by the sol-gel versus hydrothermal method.



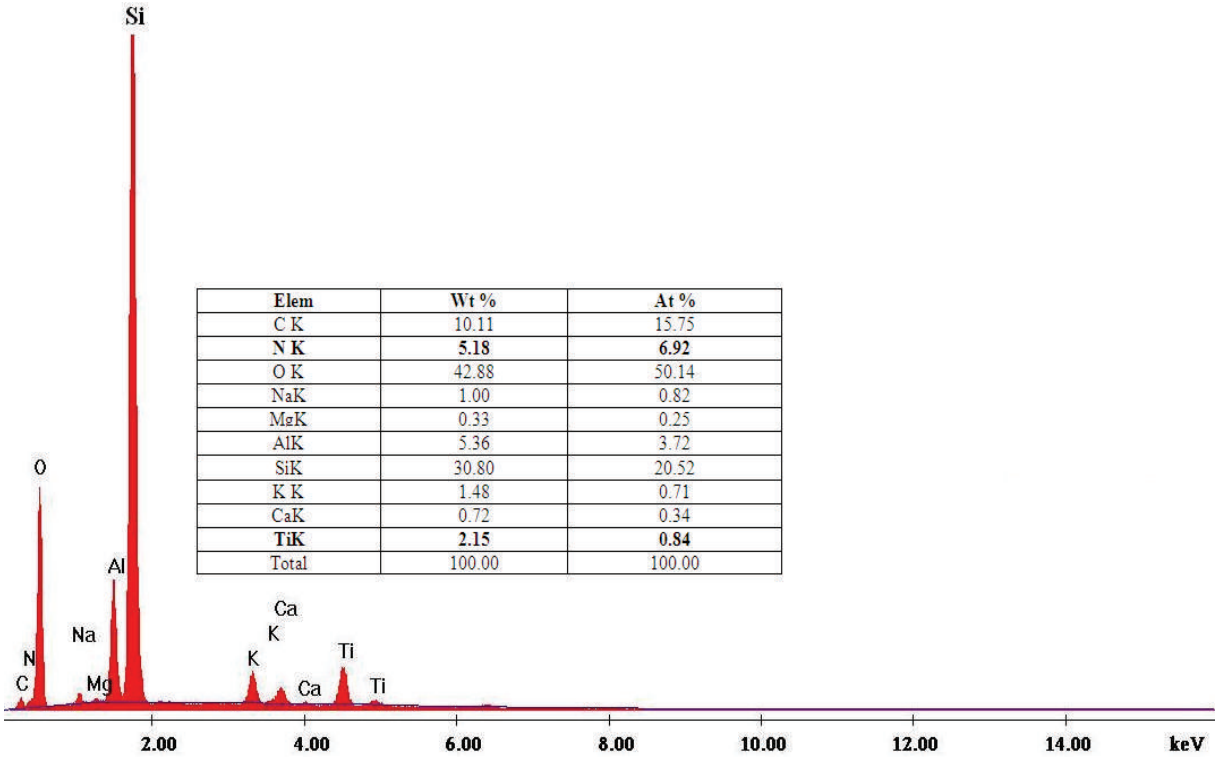
Elem	Wt %	At %
CK	12.85	21.24
OK	36.69	45.53
NaK	0.72	0.62
AlK	5.10	3.75
SiK	34.56	24.43
KK	2.16	1.10
CaK	1.04	0.52
TiK	**6.03**	**2.50**
FeK	0.85	0.30
Total	100.00	100.00

Fig. 5a. EDAX image of undoped Z-TiO_2-SG.



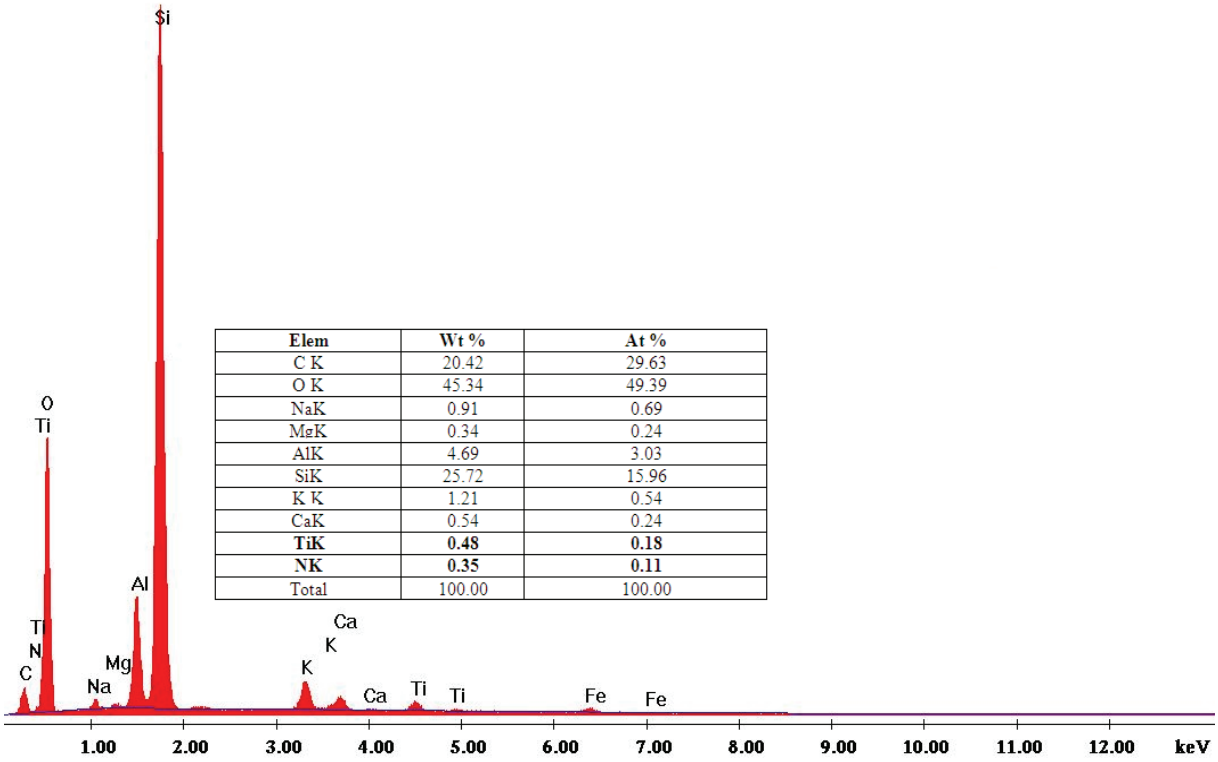
Elem	Wt %	At %
C K	19.66	29.60
O K	40.72	46.01
NaK	1.31	1.03
MgK	0.19	0.14
AlK	5.49	3.68
SiK	26.26	16.90
K K	2.08	0.96
CaK	1.03	0.46
TiK	**2.95**	**1.11**
FeK	0.30	0.10
Total	100.00	100.00

Fig. 5b. EDAX image of undoped Z-TiO_2-H.



Elem	Wt %	At %
C K	10.11	15.75
N K	**5.18**	**6.92**
O K	42.88	50.14
NaK	1.00	0.82
MgK	0.33	0.25
AlK	5.36	3.72
SiK	30.80	20.52
K K	1.48	0.71
CaK	0.72	0.34
TiK	**2.15**	**0.84**
Total	100.00	100.00

Fig. 6a. EDAX image of Z-TiO_2-N-SG.



Elem	Wt %	At %
C K	20.42	29.63
O K	45.34	49.39
NaK	0.91	0.69
MgK	0.34	0.24
AlK	4.69	3.03
SiK	25.72	15.96
K K	1.21	0.54
CaK	0.54	0.24
TiK	**0.48**	**0.18**
NK	**0.35**	**0.11**
Total	100.00	100.00

Fig. 6b. EDAX image of Z-TiO_2-N-H.

Conclusions

TiO_2 and zeolite functionalized with undoped/N ions-doped TiO_2, have been prepared by sol-gel and hydrothermal methods. XRD, SEM, and EDAX results showed that the TiO_2 supported on zeolite was in the anatase form and was formed on mainly the outer surface of zeolite. IR approved the presence of TiO_2 within the zeolite lattice. No peak corresponding to the nitrogen presence was found by XRD method, but EDAX quantification proved its presence. Morphological studies and quantitative analyses reveal that the sol-gel method is more efficient in titanium and nitrogen ions retained in hybrid material matrix versus hydrothermal method.

Acknowledgements

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