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Some physicochemical properties of silver loaded clinoptilolite from Beli plast, East Rhodopes by spray pyrolysis method

K. Genov[1], V. Blaskov[1,*], S. Vassilev[2], I. Boevski[1], M. Shipochka[1], I. Stambolova[1]

[1]*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.*
[2]*Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.*

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Silver loaded zeolite was obtained by the spray pyrolysis method. The material was characterized by DC arc atomic emission spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), IR spectroscopy and scanning electron microscopy (SEM). The concentration of Ag in the final samples, calculated from the XPS spectra, corresponds to that in the precursor solution. The SEM photographs reveal both separate silver particles and agglomerates located on the zeolite surface and inside the channels.

Keywords: Ag coated, HEU, Spray pyrolysis, zeolite, SEM

1. INTRODUCTION

The Bulgarian clinoptilolite (CAS No:12173-10-3) is a natural zeolite with HEU–type framework. Its structure and properties are widely investigated and discussed in the literature [1-7]. As a representative of the zeolite class, clinoptilolite can be used as a catalyst support, adsorbent and ion exchanger. Our interest in silver loaded clinoptilolite was provoked by these facts: clinoptilolite is a natural mineral and is cheaper than synthetic zeolites; Ag loaded zeolites can be used as catalysts for several types of reactions (e.g., oxidation with ozone [6]) or as materials with antibacterial properties [8].

Over the last decades spray pyrolysis has been one of the mainstream chemical methods applied for the formation of thin layers and particles (powders) of different compounds [9-11]. The method is cheap and requires simple equipment in comparison with the physical methods (vacuum evaporation, magnetron sputtering, etc.). Spray pyrolysis allows mixing of the initial components at a molecular level. It allows doping with any chemical element in various proportions; a distinctive feature of sprayed catalysts is the homogeneous distribution of the ingredients throughout the entire particle since all ingredients are formed in a homogeneous solution [12-15].

The aim of this article was to prepare Ag loaded natural clinoptilolite (Ag/CL) via spray pyrolysis method and to investigate the physicochemical properties of the samples.

* To whom all correspondence should be sent:
e-mail: vblaskov@abv.bg

2. EXPERIMENTAL PROCEDURES

General methods

An aqueous $AgNO_3$ precursor solution was used to obtain a final product with 7.5 wt % silver. Clinoptilolite (CL) 10 g (fraction 3-5 mm), obtained from Beli Plast deposit by Bentonit AD, was put in a ceramic crucible and was heated in a hot furnace at 250-300°C. The temperature was sufficient to decompose the precursor.

The aerosol of the precursor solution was generated by a pneumatic glass nebulizer and was transported to the substrate. The spray coating was repeated 5 times in 10-second intervals. The sample was mechanically stirred in order to obtain homogeneous distribution of the drops over the whole surface of zeolite particles. The final treatment at 350°C was carried out for 60 min.

The silver content of the Ag/CL sample was analyzed by a D.C. arc - AES method on a spectrograph PGS-2 (Carl Zeiss - Jena), equipped with a ruled grating 650 grooves mm^{-1} and λ blaze 570 nm. D.C. power generator was used for spectra excitation in electrodes RW–0, Ringsdorff. The electrode spacing was 4.0 mm, and the amount of sample - 10 mg.

The crystalline phase composition of the samples was studied on a X-ray diffractometer Philips PW 1050 with CuK_α-radiation.

The chemical composition was determined on a VG ESCALAB II electron spectrometer using AlK_α radiation with energy of 1486.6 eV. The binding energies were determined with an accuracy of

±0.1 eV utilizing the C1s line at 285.0 eV (from an adventitious carbon) as a reference. The chemical composition of the samples was investigated on the basis of areas and binding energies of C1s, O1s, Ag3d photoelectron peaks (after linear subtraction of the background) and Scofield's photoionization cross-sections.

The morphology of the samples was investigated by SEM (JSM-5510 of JEOL).

3. RESULTS AND DISCUSSION

The D.C. arc - AES method proved the presence of Ag in the samples. The photographic plate is shown on Fig. 1. The characteristic Ag lines at 328.068 pm and 338.289 pm can be seen. Two characteristic lines of Al (308.215 and 309.271 pm) and of Si (288.157 pm) are also seen. This method indicated that the silver was successfully coated on the zeolite, but gave no information on the distribution of the Ag particles.

Fig. 1. Ag/CL spectral plate from D.C. arc – AES analysis.

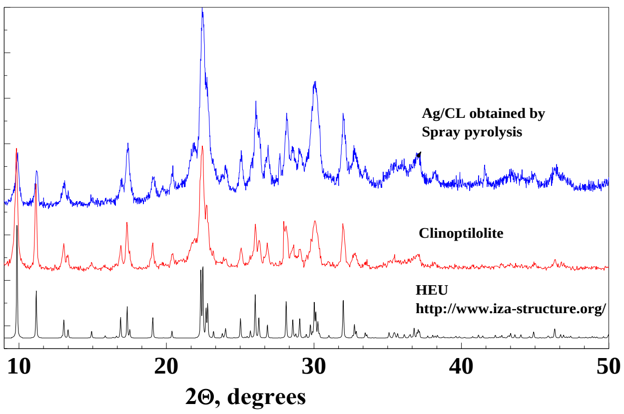

Fig 2. XRD diffractogram of CL, Ag loaded CL and HEU type structure according to zeolite data base atlas.

XRD analysis (Fig. 2) revealed that the natural Bulgarian clinoptilolite contains less than 17 % impurities of cristobalite, quartz, albite and microcline. The increased intensity of the diffraction peak at 2Θ =30 is a result of the presence of silver. XRD analysis did not detect any Ag phases, although the samples contain over 5 wt % silver. Probably, some of the silver particles are incorporated inside the zeolite channels, due to the porous structure of the zeolite.

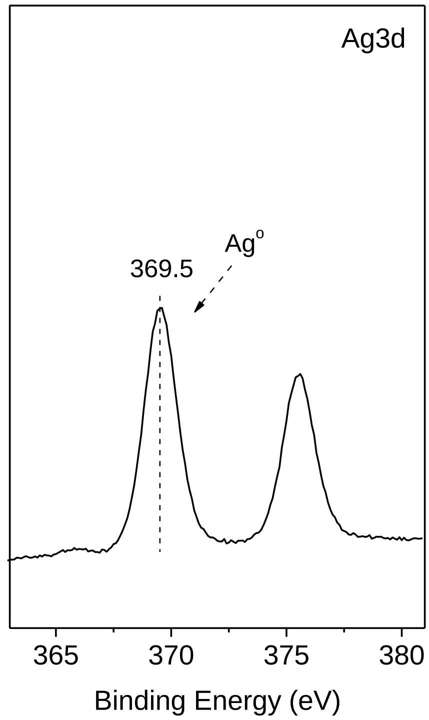

Fig 3. Ag 3d photoelectron spectra of the Ag loaded CL.

The chemical composition of CL and Ag/CL was investigated on the basis of areas and binding energies of C1s, O1s, Si2s, Si2p, Al2s, Al2p and Ag3d photoelectron peaks. The surface atomic concentrations of O, Al, Si, Ag, Na, K and Ca were estimated as well and are shown in Table 1. It can also be seen that the concentration of silver in the zeolite (Fig. 3, Table 1) corresponds to that in the spray precursor solution.

Fig. 4 presents the morphology of the Ag loaded zeolite. It can be seen that single Ag particles (indicated by black arrows) and aggregate heaps of Ag particles (indicated by white arrows) are situated on its surface. A thin silver layer is probably formed in some sections of the (010) zeolite plane. The IR spectrum of the Ag/CL sample is presented on Fig. 5. The main vibrational absorbance peaks are presented in Table 2. They correspond to Si-O-Si or Si-O-Al vibrations. The typical silanol vibrations (950 and 570 cm^{-1}) can not be observed because natural clinoptilolite is not in H form. The possible ~O-H vibrations were shifted to higher wavelenghts at 465, 604 and 3453 cm^{-1} , due to the presence of

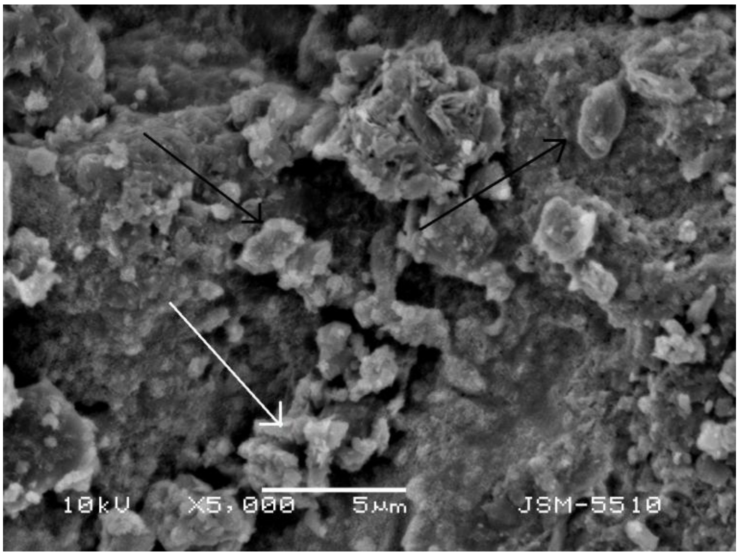

Fig.4. SEM image of Ag loaded CL.

Table 1. Chemical composition of the samples according to the data of the XPS analysis

Chemical composition	O [at.%]	**SI [AT.%]**	Al [at.%]	Na [at.%]	K [at.%]	Ca [at.%]	Ag [at.%]
clinoptilolite	60.5	31.6	4.2	<0.5	1.9	1.5	-
Ag/clinoptilolite	55.5	27.0	8.8	<0.5	0.5	0.8	7.3

Table 2. Key infrared bands of the samples according to values, given in [6].

Wavelength, cm^{-1}	Assignment
1200, 1070	ν_{as} (Si-O-Si)
950	ν (Si-OH)
798	ν_s (Si-O-Si)
570	ν (Si-OH)
450	δ (Si-O-Si)

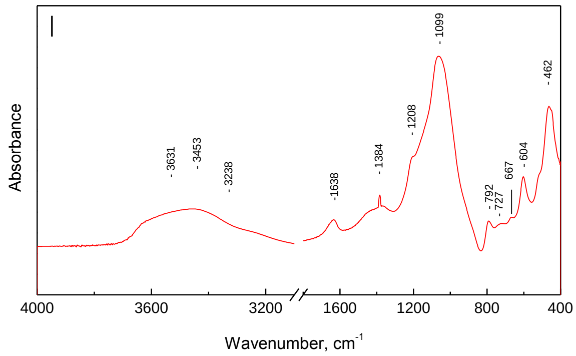

Fig.5. IR absorbance spectra of Ag loaded CL.

silver, as has been found before [16]. The band at 1390 cm^{-1} was attributed to NO_3^- ions which should decompose after annealing at a temperature of 350°C. This peak can also be assigned to polluted air.

4. CONCLUSIONS

Spray pyrolysis is a faster and more flexible way for coating metals on alumino-silicate media in comparison with ion-exchange or wet impregnation methods. We have successfully applied the spray pyrolysis to produce Ag loaded clinoptilolite. Silver ions or particles located inside the channels, as well as on the outer zeolite fragments were found. The samples may find application as catalysts, antibacterial substances, etc., due to their high surface area and low price.

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НЯКОИ ФИЗИКО-ХИМИЧНИ СВОЙСТВА НА КЛИНОПТИЛОЛИТ ОТ БЕЛИ ПЛАСТ, ИЗТОЧНИ РОДОПИ, ПОКРИТ СЪС СРЕБРО ЧРЕЗ СПРЕЙ ПИРОЛИЗА

Кр. Генов[1], Вл. Блъсков[1,*], С. Василев[2], Ив. Боевски[1], М Шипочка[1], Ир. Стамболова[1]
[1)]Институт по обща и неорганична химия, Българска академия на науките, София 1113, България
[2)] Институт по електрохимия и енергийни системи, Българска академия на науките, София 1113, България

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(Резюме)

Получен е нанесен със сребро зеолит чрез спрей пиролиза. Материалът е охарактеризиран с атомно-емисионна спектроскопия (AES), рентгенова фотоелектронна спектроскопия (XPS), рентгенова дифракция (XRD) и сканираща електронна микроскопия (SEM). Концентрацията на сребро в образците, изчислена от XPS спектрите, отговаря на тази в изходния разтвор. На SEM фотографията се наблюдават както отделни сребърни частици, така и агломерати от тях, разположени върху повърхността и вътре в каналите на зеолита.