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Ag COATED BULGARIAN NATURAL GLASS PERLITE VIA SPRAY PYROLYSIS FOR DECOMPOSITION OF OZONE

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ABSTRACT

The Bulgarian natural alumino-silicate glass (A deposit of "The Broken Mountain" near the village of Vodenicharsko, municipality of Djebel) perlite was coated with Ag via the Spray pyrolysis method. Direct current arc Atomic Emission Spectroscopy (DC arc-AES), Scanning Electron Microscopy (SEM), X-ray photoelectron Spectroscopy (XPS), Infrared Spectroscopy (IR) and X-ray Diffraction (XRD) methods were used for Ag detection. The XRD analysis revealed the presence of Ag particles and quartz. The spray pyrolysis method allows distribution of the Ag inside and outside of the core shell surfaces. The aim of this work is to obtain a silver loaded alumino-silicates catalyst for ozone decomposition.

Keywords: perlite glass, Ag loading, coating, ion-exchange, Ag thin film.

INTRODUCTION

Perlite is a natural amorphous sodium potassium aluminium silicate glass, (CAS No 93763-70-3 for expanded and CAS No 130885-09-5 for the natural (crude) form) and it is widely used in construction and industry. The raw (crude) perlite has a bulk density - 1100 kg m^{-3}, but when it is rapidly heated to 871°C, the rock "pops" in a manner similar to popcorn and creates expanded perlite with a low density of around 30-150 kg m^{-3}. This expansion is due to the presence of two to six percent entrained or bound (combined) water in the crude perlite rock. The typical and according to literature [1] chemical analysis of perlite is given in Table 1. It is noteworthy that the expanded perlite is a natural alumino-silicate; rich in SiO_2 and Al_2O_3. Since perlite granules are highly porous media, they can naturally act as a good adsorbent. Also, according to a previous investigation of our colleagues, the Ag loaded on some silicates and alumino-silicates materials is suitable for catalytic decomposition of ozone under ambient condition. In [2] Naydenov et al., published that 5 % mass. Ag supported on amorphous SiO_2 (fraction 0.1- 0.2 mm) convert ca. 100 % ozone at 27°C. Nikolov et al. also found in their studies [3], that Ag supported Bulgarian natural zeolite - clinoptilolite decomposes O_3 to O_2 at room temperature with a relatively high activity (ca 85 %). Consequently, from this perspective we choose the expanded perlite as the precursor for loading of silver 'over its surface' and future use as a catalytic centre for ozone decomposition. There are different methods for loading atoms of transition elements over the surface of amorphous or crystalline silicates or alumino-silicates (gels, cogels, zeolites, mica, glasses, and ceramics). For example, Ag could be easy loaded via wetness impregnation or Tollen's reagent method, where the latter one is

Table 1. Typical approximate composition analysis of perlite.

Constituent	Typical, %	According to literature [1], %
SiO_2	70 - 75	75.22
Al_2O_3	12 - 15	13.08
Na_2O	3 - 4	3.00
K_2O	3 - 5	4.95
Fe_2O_3	0.5 - 2	1.83
MgO	0.2 - 0.7	0.10
CaO	0.5 - 1.5	1.43
Chemically bound H_2O	3 - 5	

widely used in human life for many ages [4]. However, over the last decades spray pyrolysis has been one of the mainstream chemical methods applied for formation of thin layers and particles (powders) of different compounds, alongside with the sol-gel method. One of the reasons for the interest towards this method is the fact that it is cheap and incorporates simplified equipment in comparison to the physical methods for formation of thin layers (vacuum evaporation, magnetron sputtering, etc.) The method allows mixing of initial components at a molecular level. It also enables easy formation of multi-component oxide compounds having a complex chemical and phase composition, such as ferrites, superconductors, spinel types, etc. for application as catalysts, sensors, optical elements, and others. Spray pyrolysis allows doping, in practice, with any chemical element and in various proportions [5-7].

The aim of this work is to investigate the possibilities for silver particles deposition over aluminous-silicate via the easy and quick method of spray pyrolysis, and to present analyses data for the expanded perlite and Ag/Perlite samples obtained in the Institute of General and Inorganic Chemistry – a research centre of the Bulgarian Academy of Sciences.

EXPERIMENTAL

Spray pyrolysis

10 g substrate – (Perlite (P), crushed fraction 3 - 5 mm) obtained from Bentonit AD (deposits from "The Broken Mountain" for perlite mining, near the village of Vodenicharsko, municipality of Djebel), were put in a crucible, placed in a hot furnace and heated up to the precursor - $AgNO_3$ (Valerus) decomposition temperature. The aerosol of the precursor solution in water was generated with a pneumatic glass nebulizer and transported to the substrate. The spray coating process was repeated 5 times at 10-second intervals while the samples were mechanically stirred in order to obtain homogeneous distribution of the drops over the whole surface of the zeolite particles.. The final treatment at 350^{o}C was carried out for 60 min for decomposition of the rest of nitrogen from NO_3^- and calcination. The aqueous $AgNO_3$ precursor solution was calculated to obtain a final product containing 7.5 % mass silver coated over the zeolites particles.

Analysis of the samples

XRD. The crystalline phase composition of the samples was studied by XRD, using a X-ray diffractometer Philips PW 1050 with CuK_a-radiation.

SEM. JSM-5510 of JEOL was used for morphology observations of the samples.

D.C. arc - AES method. This method was applied with a spectrograph PGS-2 (Carl Zeiss - Jena) equipped with a ruled grating 650 grooves mm-1 and λ blaze 570 nm. The spectrum registered is from the 2nd order. A D.C. power generator was used for spectra excitation in electrodes RW–0, Ringsdorf with electrode shape: crater 3.5 mm diameter 4.0 mm depth (the electrode with sample was set as anode); electrode spacing 4.0 mm, amount of sample 10 mg; spectral plates WU-2 (ORWO). The Ag/P sample was analyzed by this method to prove its silver contents.

XPS. The measurements were performed in a VG ESCALAB II electron spectrometer, using AlK_α radiation with an 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 Ag/P was investigated on the basis of the areas and binding energies of C1s, O1s, Ag3d photoelectron peaks (after linear subtraction of the background) and Scofield's photoionization cross-sections.

IR-spectrometry. A Nicolet 6700 FT-IR spectrometer (Thermo Scientific) was used to measure the infrared absorption. The IR range covered was 400 to 4000 cm-1 with an incremental step of 0.9643 cm^{-1}. The spectra were recorded and scrutinised with the original OMNIC™ software.

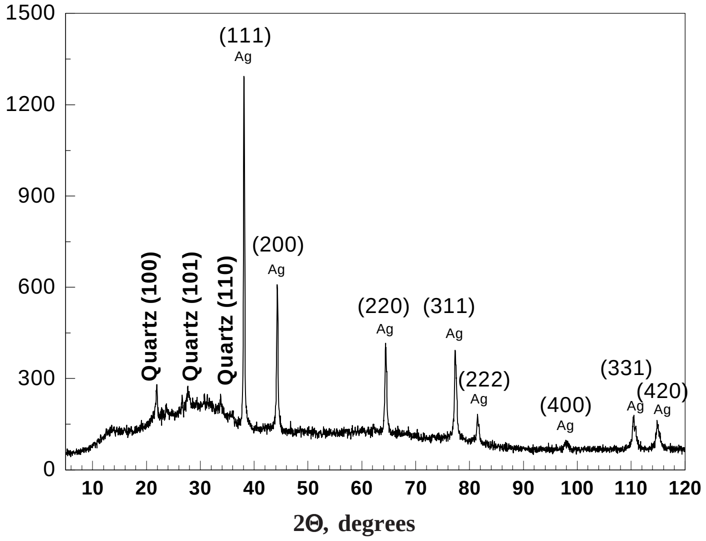

Fig. 1. XRD of Ag/P.

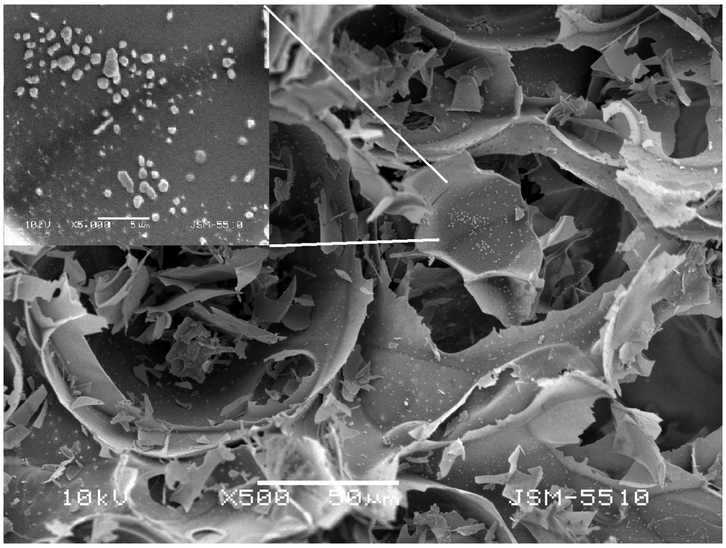

Fig. 2. SEM of Ag/P.

RESULTS AND DISCUSSION

The X-ray diffractograms of the Ag/P samples consist of two parts: an amorphous part, which belongs to the natural perlite and clearly visible characteristic peaks of the silver Ag^o (Fig. 1). Wide peaks attributed on crystalline quartz (100),(101) and (110) were registered. A possible reason for the quartz present in the glass structure, might be the metamorphous processes proceeding when the natural perlite was formed.

The images of the perlite surface (Fig. 2) confirm the high porosity of the perlite granules as a good support for Ag. The inset picture in Fig. 2 shows Ag particles with various shapes and sizes. The dimensions are in the sub- or micron range – typically obtained by spray pyrolysis. This method allows distribution of the Ag inside and outside of the core shell surfaces. So this sample might be suitable as a catalyst for various processes in comparison with Ag loaded samples, obtained via another methods.

The chemical composition of the Ag/P were investigated on the basis of areas and binding energies of C1s, O1s, Si 2s, Si 2p, Al 2s, Al 2p andAg3d photoelectron peaks (after linear subtraction of the background) and Scofield's photoionization cross-sections. Aluminum and silicon measurements were made using the integrated line

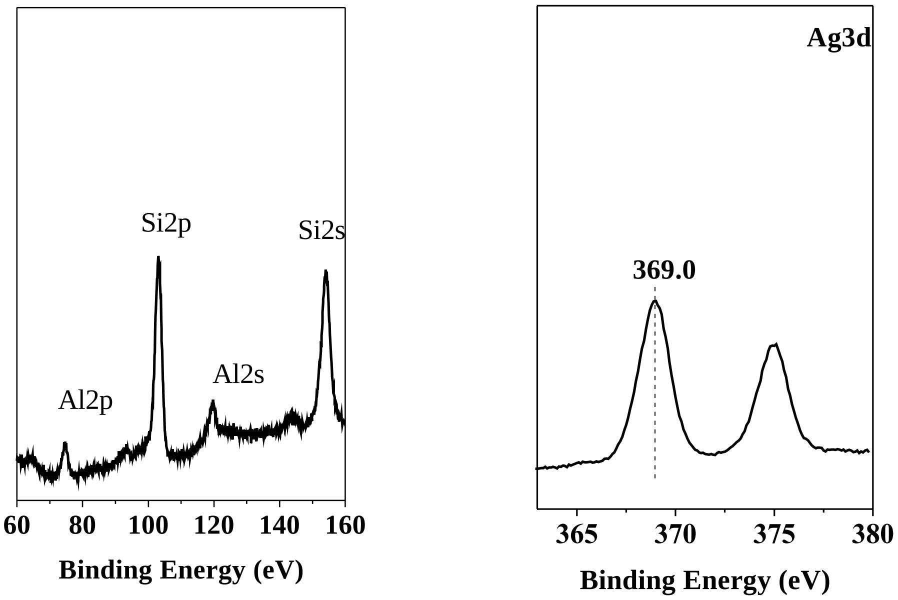

Fig 3. XPS spectra of Ag/P.

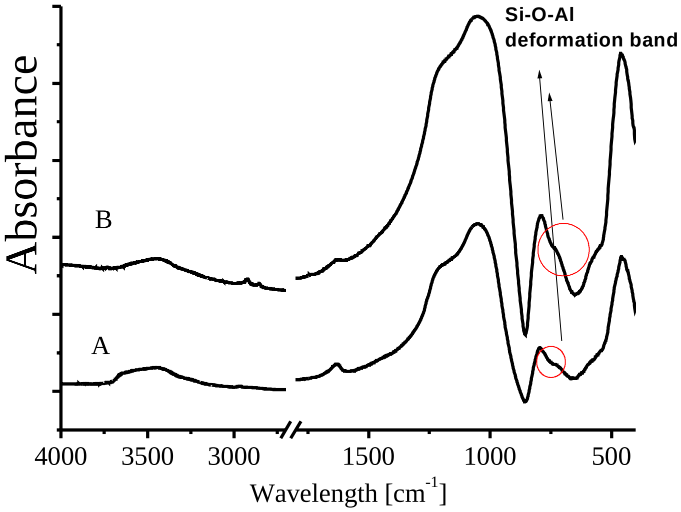

Fig. 4. IR specra of Perlite (A) and Ag/P (B).

intensities of the Al(2s) and Si(2p) photoelectron lines (Fig. 3). The surface atomic concentrations of O, Al, Si, Ag, Na, Ka and Ca estimated from these data, along with the binding energy values of different photoelectron lines are shown in Table 2.

The DC arc - AES analysis of the Ag/P samples shows clearly that silver was loaded successfully on to the medium. Characteristic Ag lines at 328.0683 pm and 338.2891 pm are observed. Within the spectrographic plate the two analysis lines of Al at 308.2155 and 309.2713 pm, and the additional one of Si at 288.1578 pm also exist.

The IR spectroscopy was particularly informative in our investigation. In Fig. 4 the presented IR spectra show pure expanded perlite (A), loaded with Ag (B) having characteristic vibrational signals. Notably, all samples present show the typical infrared vibration for aluminum-silicates, described before in the literature [8, 9].

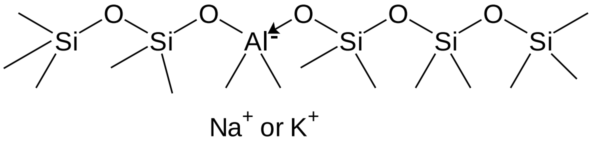

Fig. 5. A scheme of aluminous-silicate structure.

Table 3. IR bands of aluminosilicates.

Wavelength, cm^{-1}	Assigment
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)

The spectrum (B) does not indicate a band at 1384 cm^{-1} which is typical for NO_3. This means that during the spray pyrolysis process all of NO_3^+ groups from silver nitrate were decomposed. The characteristic vibrations for Si-O-Si or Si-O-Al (Si-OH) are given in Table 3. In Fig. 4, a weak shoulder on the high-frequency side near 690 cm^{-1} is observed. These bands are assigned to Si-O-Al deformation [10]. In Fig. 5. a scheme of the alumino-silicate structures is given. As can be seen, the negative Broenstedt acidic aluminium sites are compensated with Na^+, or K^+ ions which is typical for alumino-silicates, as a class of minerals.

CONCLUSIONS

The spray pyrolysis allows obtaining a catalyst with high active surface area (based on the perlite) loaded with numerous silver particles serving as catalytic centers. An Ag loaded alumino-silicate is obtained. It was established that the method is suitable for Ag coating of glass granules. The XRD analysis revealed presence of Ag particles and quartz. Scanning electron microscopy showed Ag particles with various shapes and sizes with sub- or micron range dimensions, distributed inside and outside of the core shell surfaces. XPS detects the concentration of silver on the perlite surface. The IR spectra do not have NO_3^+ signal. This work proposes the using of cheaper natural glass as a medium and an economical and simple method for deposition of catalytic centers.

Acknowledgements

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