

Ozone Decomposition over Silver-Loaded Perlite

Krassimir Genov, Vladimir Georgiev, Todor Batakliiev, and Dipak K. Sarker

Abstract—The Bulgarian natural expanded mineral obtained from Bentonite AD perlite (A deposit of "The Broken Mountain" for perlite mining, near by the village of Vodenicharsko, in the municipality of Djebel), was loaded with silver (as ion form - Ag^+ 2 and 5 wt% by the incipient wetness impregnation method), and as atomic silver - Ag^0 using Tollen's reagent (silver mirror reaction). Some physicochemical characterization of the samples are provided via: DC arc-AES, XRD, DR-IR and UV-VIS. The aim of this work was to obtain and test the silver-loaded catalyst for ozone decomposition. So the samples loaded with atomic silver show ca. 80% conversion of ozone 20 minutes after the reaction start. Then conversion decreases to ca. 20 % but stay stable during the prolongation of time.

Keywords—aluminum-silicates, Ag/perlite expanded glass, ozone decomposition

I. INTRODUCTION

ACCORDING to work already published [1], ozone a highly toxic gas, is harmful for all living organisms and particularly dangerous for the human health. The World Health Organization (WHO) recommends concentration of ozone of < 45 ppm in the biosphere. Ozonation widely used industrially and in the laboratory for purification and sterilization of waste and natural waters as well as air decontamination is a very valuable process across many branches of science (such as medicine). Today, ecological problems are not only to protect the earth stratosphere from a decrease of ozone concentration, but also to decompose excesses of ozone in the biosphere. The ozone easily decomposes to oxygen following the reaction (1):



Inconveniently, the potentially explosive reaction runs with unfettered gaseous expansion, when the temperature and pressure of the system is increased. The way to solve this problem is to find and research new catalysts, which decompose ozone at ambient temperature. Accordingly, in reference to both literature and our previous investigations [1-6], the transition metal loaded over various porous media (zeolites and ALPO) can be suitable as a catalyst for low temperature ozone decomposition. In Naydenov et al.[4],

published work suggest that 5% wt. Ag supported on amorphous SiO_2 (fraction 0.1-0.2 mm) can convert ca. 100 % ozone at 27 °C. In Kumar, Konova et al. [2, 3] it is reported that for Ag-modified alumino-silicates, Beta and MCM-41 zeolites showed a very high decomposition of ozone (~98% conversion for the 5 wt% Ag/MCM-41 catalyst and ca 44% for 5 wt% Ag modified Beta zeolite). We also found in studies [7], that Ag on a Bulgarian natural zeolite - clinoptilolite support permits decomposition of O_3 to O_2 at room temperature with a relatively high activity (ca. 85 %).

Consequently, from this perspective and its successes we chose the expand perlite use as the precursor for loading of silver 'over its surface' and future use as catalytic centre for ozone decomposition. The 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 low density of about 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 make-up and according to literature [8] chemical analysis of perlite is given in Table 1.

TABLE I
TYPICAL PROXIMATE COMPOSITIONAL ANALYSIS OF PERLITE

Constituent, %	Typical	According to literature [8]
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	-

It is noteworthy that the expanded perlite is a natural alumino-silicate; rich in SiO_2 and Al_2O_3 .

II. EXPERIMENTAL

A. Loading of Ag.

The modification of 10 g perlite obtained from Bentonite AD (A deposit of "The Broken Mountain" for perlite mining, near by the village of Vodenicharsko, Djebel Municipality), with Ag^+ was carried out by the incipient wetness impregnation method. The procedure was the same as

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described previously from Naydenov [4], Nikolov et al.[7] for obtaining successful Ag/SiO₂ surface coverage. The reaction is allowed to proceed in the absence of light, at ambient temperature for 24 h in a rotatory evaporator device using an aqueous solution of silver nitrate (Merck). The amount of AgNO₃ used was such, as to permit a 2 wt %, and 5 wt % mass of silver to be loaded on the sample (Ag/P). Ag⁰ was loaded over perlite using a Tollen's reagent method described in literature according to Lim et al. [9]. The procedure was identical, but instead of H₂-C=O, a 10 % w/v glucose-in-water solution (ActavisTM) was used. After filtration over a sintered glass filter (3 MO 4) and exhaustive washing with distilled water, the samples were dried at 110 °C and calcined at 600 °C.

A. Analysis of the samples.

DC arc - AES method. This method, was conducted on spectrograph PGS-2 (Carl Zeiss - Jena) equipped with a ruled grating (650 grooves mm⁻¹) and λ blaze of 570 nm. The spectrum recorded is in the form of a 2nd order derivative. A DC power generator was used for spectral excitation within electrodes (RW-0, Ringsdorf). The electrode shape was that of a annulus of dimensions 3.5 mm diameter and 4.0 mm depth (the electrode with sample being set as the anode). Electrode spacing was set at 4.0 mm, with a 10 mg amount of sample and using WU-2 spectral photographic plates. Any Ag samples were analysed by this method, to prove the extent of silver loading.

XRD. The analysis was undertaken on a Bruker-AXS XRD diffractometer, D8 Advance with CuK α radiation, (1.54180 Å) and SolX detector within the 2 θ range 5-30 degrees and a constant incremental step 2 θ of either 0.02 or 0.04 degrees.

IR. A Nicolet 6700 FT-IR spectrometer (Thermo Scientific) was used to measure in the infrared. The IR range covered was 400 to 4000 cm⁻¹ with incremental step: 0.9643 cm⁻¹. The spectra were recorded and scrutinised using original OMNICTM software.

UV-VIS method. An Evolution 300 BB, UV-VIS spectrophotometer (Thermo Scientific) was used for UV-Visible spectrophotometric recording of sample absorbance. The wavelength used was from 190 to 600 nm (step 1 nm), and F(R ∞) was normalized to 1.

B. Catalytic experiments.

Room temperature ozone decomposition experiments were investigated via an isothermal plug flow reactor under steady-state conditions (without temperature gradients). The 1 g of catalyst particles (diameter ca.1 mm) was chosen, taking into account the reactor diameter 6 mm, Ozone was synthesized in a flow of oxygen (99.7 %), dried with silica gel, using an ozone generator (with a silent discharge of 15-20 kV between the electrodes). The inlet concentration of ozone in the flow of oxygen was 24000 ppm and the volume rate 6 L/h. Ozone concentration was analyzed with an ozone analyzer BMT 964 (Germany) with an accuracy of ± 3 ppm. The reaction temperature was ambient (25 °C) and was maintained with an

accuracy of ± 0.2 °C. The activity of the catalysts was measured at start, then every 5 min and after 1 h every 30 min. The ozone conversion was calculated on the basis of equation (2), where C refers to concentration:

$$\text{Conversion}[\%] = 100 \times \left[\frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}} \right] \quad (2)$$

III. RESULTS AND DISCUSSION

A. Analysis of the samples.

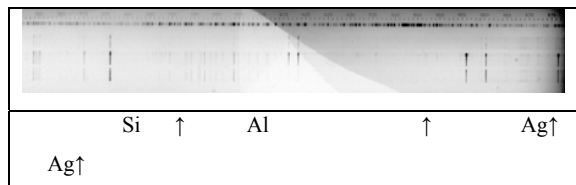


Fig. 1 Ag/Perlite Spectral plate from DC arc – AES – showing key resonance lines

Figure 1 presents the main DC arc - AES analysis of the Ag-Perlite (Ag/P) samples. It shows clearly that silver was successfully loaded on to the samples. Characteristic Ag lines at 3280.683 pm (655 nm at scale) and 3382.891 pm (675 nm) are observed. Within the spectrographic plate the two analysis lines of Al at 3082.155 and 3092.713 pm (at 615 and 620 nm in scale), and additional one of Si at 2881.578 pm (575 nm at scale) also exist. This analysis is not 'revealing' enough to show where and how the silver was distributed over the perlite surface. The spectra presented in Fig. 2 show the amorphous glassy structure of expanded perlite form (A), which is also stable after Ag⁰ and Ag ion and cluster loading.

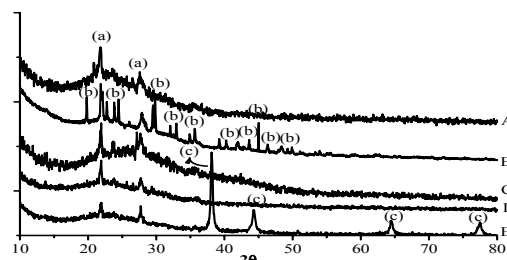


Fig. 2 XRD spectra of expanded perlite (A) and silver loaded perlite – (B) 5 % wt sample before calcinations. (C) – calcined sample loaded with 2 % wt Ag. (D) – calcined perlite loaded with 5 % wt silver. (E) XRD of sample loaded with Tollen's reagent via the silver mirror reaction. (a) - some crystal SiO₂ structure, possible α -cristobalite, (b) AgNO₃ - ICDD-PDF-2# 43-649, (c) Ag-3C - PDF# 04-0783

XRD analysis shows, in addition that this form of the Bulgarian mineral contains the impurity of some SiO₂ crystal structure, which is possibly - cristobalite, at less than 17 %. The XR diffractogram of the 5% wt sample before washing and calcinations was also represented (B). One can clearly see the spectrally resolved presence of AgNO₃ diffractions (b). After washing and calcinations these diffraction peaks were

not observed on diffractograms (C and D). The last spectral 'form' (E) presents the Ag⁰ signals very clearly, and proves the samples contained an elemental silver load on the glass itself, using the silver mirror reaction.

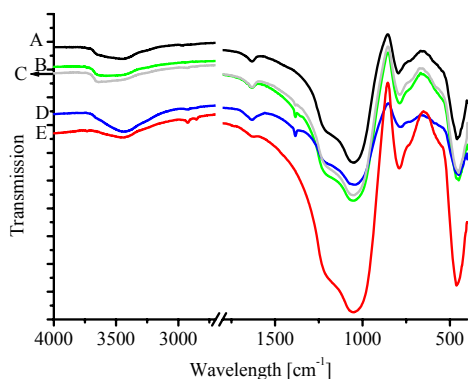


Fig. 3 The IR spectra of the five tested samples (A-E).

IR analyses were interesting and particularly informative in our investigation. In Fig. 3 the presented IR spectra show pure expanded perlite (A), loaded with 2 and 5 wt % Ag⁺ (B and C) and loaded with Ag⁰ (Tollen's reagent method) – before calcinations (D) and after calcinations (E) having characteristic vibrational signals. Notably, all samples present show the typical infrared vibration for aluminum-silicates, described in literature [10,11]. The spectra (B), (C) and (D) in Fig. 3 indicate a band at 1384 cm⁻¹ which is typical for NO₃⁻ (asymmetric stretching mode). Although XRD do not show the presence of AgNO₃ (or NO₃⁻ groups) in calcined 2 and 5 wt % samples, here the band is shown clearly and it is also included in the spectrum for dried, fresh Ag⁰/Perlite sample. After calcinations the band is no longer present (Fig. 3 (E)). It may be here that the band is presented as NH₄NO₃ where the region of 3330 to 2800 cm⁻¹ is the denotation for NH₄⁺ with ν₁' , ν₃' , and (ν₂' + ν₄') vibrations, correlated to the ν₁' as symmetric stretching mode; ν₂' as symmetric deformation mode; ν₃' as asymmetric stretching mode and ν₄' as asymmetric deformation mode. This can be reasoned since, after heating to 600°C, the NH₄NO₃ decomposes, and the band disappears. In Fig. 4 the UV-VIS spectra of the samples are given and show a number of interesting features. As one can see, all samples present the typical peak for aluminosilicates at 230 nm. This peak appears not only for the amorphous system as with (alumino)silica gels, but also exists in all crystal (alumino)-silicate structures, such as zeolites. The samples loaded with the silver exhibit another notable peak at 400-450 nm, which increases in the calcined Ag⁰/P sample and may be the possible reason for appearance of this peak were the Ag⁺ and/or Ag⁰ ion particles and clusters, formed over the perlite surface.

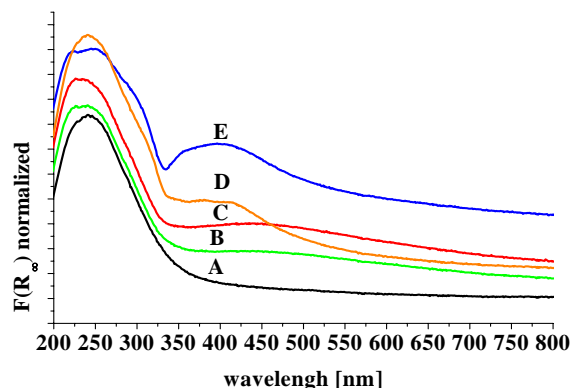


Fig. 4 UV-VIS Spectra for Perlite (A), 2% wt Ag/P(B) 5% wt Ag/P (C), fresh Ag⁰/P(D) and calcined Ag⁰/P (E)

B. Catalytic experiments.

The results of a catalytic test for ozone decomposition run over Ag/P samples are also interesting.

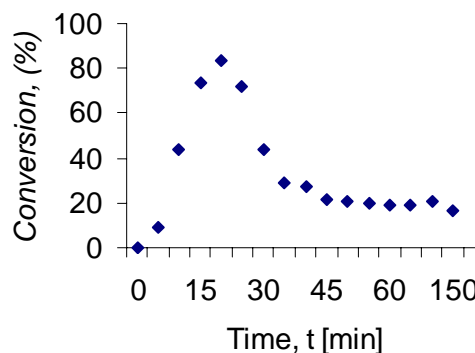


Fig. 5 Conversion 2O₃ → 3O₂ at 25 °C over Ag⁰/P

Ag/P samples loaded with 2 and 5 % wt silver did not show any activity or activity was very low (less than 4% conversion for 5 % wt sample). The possible reason may be the presence of NO₃⁻ groups. As we know, the presence of NO_x inhibits the process and in this case we generate the ozone from the pure oxygen not from the air. This was not the situation where the sample had been loaded with silver through the silver-mirror reaction (Ag⁰/P). The catalytic result and conversion of ozone is presented in Figure 5. Here, we observed the very high conversion up to 80%, 20 min. after reaction start. Then the activity of catalyst decreases to ca 20 %, (from 20 to 45 minute) and stays stable during the reaction time duration. So in this respect, the reaction began (started) with the very high activity due to the free catalytic centers which quickly convert ozone to oxygen. Then the reaction speed the conversion decreased, respectively. The flow of ozone streams over the catalyst and when the new free centers are accessible the catalyst then converts the O₃ molecules. According to data in the literature [4,12] silver is not oxidized by oxygen at room temperature, but in presence of ozone silver surfaces are oxidized stepwise from Ag₂O to AgO. It has been suggested

that the dissociative adsorption of O_3 produces surface chemisorbed atomic oxygen. Thus, the step-wise mechanism of the reaction can be suggested in Fig. 6:

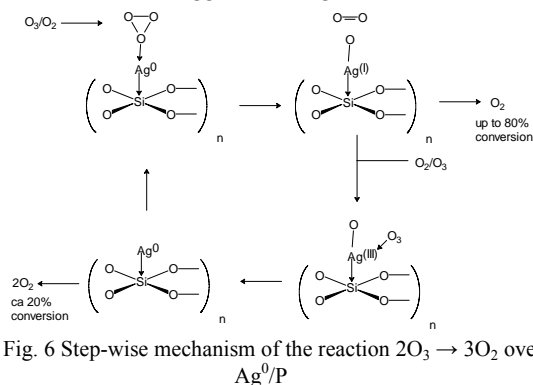


Fig. 6 Step-wise mechanism of the reaction $2O_3 \rightarrow 3O_2$ over Ag^0/P

In the first step: Ag^0 is coordinated and converts ozone with high yield of O_2 , with a change the state to $Ag(I)$. During the second step: $Ag(I)$ is coordinated to another O_3 molecule (changing its state to $Ag(III)$) and convert ozone with low percentage of O_2 yield. Finally, in a concluding step of the cycle, Ag is returned to a zero coordination state, thereby facilitating Ag^0 to take part in the first step 1 yet again.

IV. CONCLUSION

The Bulgarian glass mineral from Bentonite AD has two mineral components: amorphous perlite and an impurity of crystal SiO_2 structures corresponding, according to XRD evidence, to cristobalite.

With our method of DC arc – AES we are able to deduce and prove the existence of silver, loaded on perlite. This method is still valuable for semi-micro qualitative analysis of some elements in solid samples and Al, Si, and Ag are the elements that are easily detected.

XR Diffractograms show that 'silicate' glass structure is not broken in the process of loading with Ag and after calcinations to $600^\circ C$. The residue of $-NO_3$ groups (presented as NH_4NO_3) in the Ag^0/P sample can be easily removed during calcination and may in fact be removed during the self-catalysed reaction carried-out on the Ag-based particles.

The amount of silver in the Ag^0/P is 20 and 50 times higher than the amount of silver in the Ag^+/P but it is a more suitable catalyst for decomposition of ozone in ambient temperature because of higher surface area.

APPENDIX

Appendixes, if needed, appear before the acknowledgment.

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