



Ozone decomposition on Ag/SiO₂ and Ag/clinoptilolite catalysts at ambient temperature

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ABSTRACT

Silver modified zeolite (Bulgarian natural clinoptilolite) and Ag/silica catalysts were synthesized by ion exchange and incipient wet impregnation method respectively and characterized by different techniques. DC arc–AES was used for Ag detection. XRD spectra show that Ag is loaded over the surface of the SiO₂ sample and that after the ion-exchange process the HEU type structure of clinoptilolite is retained. UV–VIS (specific reflection at 310 nm) and IR (band at 695 cm⁻¹) spectroscopy analysis proved that silver is loaded as a T-atom into zeolite channels as Ag⁺, instead of Na⁺, Ca²⁺, or K⁺ ions, existing in the natural clinoptilolite form. The samples Ag/SiO₂ and Ag-clinoptilolite were tested as catalysts for decomposition of gas phase ozone. Very high catalytic activity (up to 99%) was observed and at the same time the catalysts remained active over time at room temperature.

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1. Introduction

Ozone is used as an oxidant for waste water treatment and drinking water sterilization [1]. The exhaust gases from such processes contain residual ozone, which is above the acceptable value, and due to the fact that ozone itself is very toxic, an additional air pollution problem must be solved. The most effective method for nullification of ozone is via heterogeneous catalytic decomposition. During the process, highly reactive oxygen species are produced and these are able to completely oxidize the toxic compounds (organic or inorganic) at room temperatures [2,3]. The behaviour of silver catalysts in the above mentioned reaction is the subject of several insightful publications [4,5]. Imamura et al. [4], concluded that Ag-containing catalysts show highest activity when compared with the oxides of Co, Ni, Fe, Mn, Ce, Cu, Pb, Bi, Sn, Mo, V and Si. Our earlier investigations regarding ozone decomposition over Ag-modified zeolite, silica and mesoporous molecular sieve catalysts are presented elsewhere [6,7]. The Bulgarian clinoptilolite is a natural zeolite with HEU-type framework and its structure

and some properties have been widely investigated and are discussed in the literature from the last century to present [8–11]. As a member of the zeolite class, clinoptilolite can be used as catalyst support, adsorbent and ion-exchange medium. Our interest in silver exchanged clinoptilolite is based on these facts: clinoptilolite is a naturally occurring mineral and it is cheaper than new synthetic zeolites; Ag⁺ loaded into the channels can be used as catalytic center for several types of reaction (i.e. oxidation with ozone). Here, we report our method of Ag-exchange over natural clinoptilolite (CL), some characterization of its silver loaded form (Ag-CL) and its application for the gas phase catalytic decomposition of ozone at ambient temperature, in comparison with a Ag/SiO₂ catalyst.

2. Experimental

2.1. Catalyst preparation

2.1.1. Ag surface impregnation onto SiO₂ structures

The modification of SiO₂ (Merck) with Ag was carried out by the incipient wetness impregnation method [6]. The reaction proceeded for 24 h at room temperature in a rotator evaporator device using an aqueous solution of silver nitrate (Sigma–Aldrich). After impregnation, the sample was dried at 110 °C and calcined at

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500 °C. The mass ratio of SiO₂ to AgNO₃ was fabricated in a manner to obtain 5 wt.% Ag/SiO₂.

2.1.2. Exchange of clinoptilolite T-atoms with Ag⁺

10 g clinoptilolite obtained from Bentonit AD in Beli Plast deposit, were put in Erlenmeyer flask with a magnetic stirrer, sealed and mixed with 250 mL of an aqueous solution of ammonia (Valerus, Bulgaria) overnight. After filtration over sintered glass filter (3 MO 4) and washing with distilled water, the NH₄⁺ form (NH₄-CL) was isolated. A subsequent step involved the sample being calcined at 600 °C (24 h) to become the H⁺ form (H-CL). This form was exchanged once again on magnetic stirrer using a 0.5 M aqueous solution of AgNO₃ until the acidity of the solution tended to low pH—so that the Ag⁺ form (Ag-CL) was obtained.

2.2. Analysis of the samples

DC arc–atomic emission spectroscopy (AES) method was conducted on spectrograph PGS-2 (Carl Zeiss-Jena) equipped with a ruled grating (650 grooves mm⁻¹ and λ blaze 570 nm) described in details by Boevski and Daskalova [16]. Ag-CL and Ag/SiO₂ samples were analyzed by this method to prove the silver exchange or loading.

X-ray diffraction (XRD) was undertaken on a XRD diffractometer (Bruker-AXS, D8 Advance with CuKα radiation (1.54180 Å)) and SolX detector.

A UV–VIS method used a Thermo Scientific, Evolution 300 BB, UV–VIS spectrophotometer and was used for UV–VIS spectrometry of samples, the value of reflectance $F(R_{\infty})$ was normalized to 1.

Infrared (IR) spectrometry using a Thermo scientific, Nicolet 6700 FT-IR spectrometer was used, with a resolution of 0.9643 cm⁻¹ to define compositional differences in samples.

2.3. Catalytic experiments

The catalytic activity and long-term stability in respect of the heterogeneous decomposition of ozone were investigated in an isothermal plug flow reactor under steady state conditions without temperature gradients. The catalyst particles size (0.5–0.6 mm) was chosen taking into account the reactor diameter (4.0 mm) and the volume rate (mean value 133,333 h⁻¹ calculated on the total catalyst bed volume) in order to reduce the effect of external diffusion. Pre-treatment of the catalysts included heating at 110 °C for 1.5 h in a steady air flow. The rate of the gas flow was 5.6 L/h and the catalyst volume, 0.042 cm³.

Ozone was synthesized in a flow of oxygen (99.7%), dried with silica gel, using an ozone generator with a silent discharge of 4–6 kV between the electrodes. The inlet concentration of ozone was 4390 ppm. Ozone concentration was analyzed with an Ozomat GM (Anseros, Germany) analyzer with an accuracy of ±50 ppm. The carrier gas for the evolved ozone assessed was oxygen. The reaction temperature was set at ambient (23 °C) and was maintained with an accuracy of ±0.2 °C. The activity of the catalysts was calculated on the basis of the equation:

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

where C is the concentration and the subscripts simply refer to the sampling point.

3. Results and discussion

3.1. Physicochemical analyses

3.1.1. DC arc–AES

The DC arc–AES analysis of the Ag/SiO₂ and Ag-CL samples show that silver was successfully loaded or exchanged. The characteristic Ag lines at 3280.683 pm (655 nm at ruled grating scale) and 3382.891 pm (675 nm) can be observed. At the spectral plates the two analysis lines of Al–3082.155 and 3092.713 pm (only for CL), and one of Si 2881.578 pm also exist.

3.1.2. XRD

The spectra presented in Fig. 1a show that the HEU-type crystalline structures of the CL natural form can be stable also after ion exchange. XRD analysis also shows that the natural form of Bulgarian clinoptilolite contains impurities of cristobalite, quartz, albite and microcline (less than 17%), and the diffraction peak at 22° 2θ, increased for the Ag-CL sample. As it is clearly visible (Fig. 1b) XRD spectra for the Ag-CL before and after ozonation are very similar.

The X-ray powder diffraction patterns of fresh and ozonated samples of 5 wt.% Ag/SiO₂ are presented in Fig. 2. In the fresh sample one sees silver present as a metal phase (Ag⁰). The major Ag diffraction peaks correspond to the values in JCPDS–PDF # 00–004–0783. The two broad peaks centered at 11.6° and 22° are due to the amorphous support (SiO₂). After ozone treatment, the XRD trace of the same sample reveals that the amount of the metallic Ag⁰ phase decreases and in the ozonated samples it is insignificantly present. After ozonation, silver is presented mainly in its oxidized form. The X-ray spectrum of the ozonated sample contains lines corresponding to monoclinic AgO (JCPDS–PDF #00–051–0945) in addition to a cubic phase with unit cell parameter $a = 0.4959(3)$ nm,

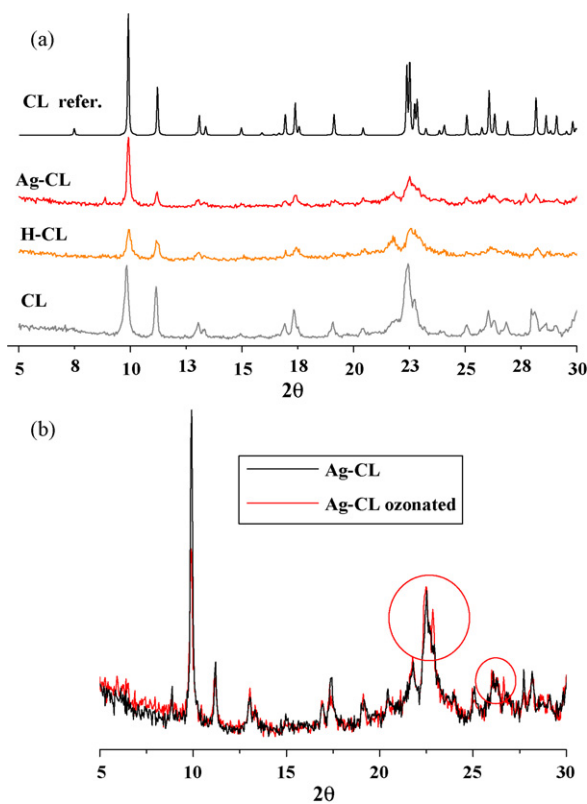


Fig. 1. X-ray diffraction showing intensity against scattering angle, 2θ (degrees). The figure shows (a) XRD traces of CL, H-CL, Ag-CL and XRD from reference (CL reference) generated on <http://www.iza-structure.org/databases/>; (b) XRD spectra of a fresh and ozonated Ag-CL samples.

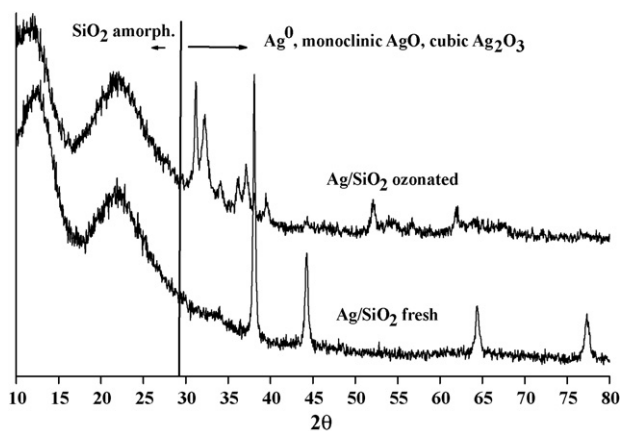


Fig. 2. A plot of X-ray diffraction showing intensity against scattering angle, 2θ (degrees). Illustrated are XRD spectra of Ag/SiO₂—both fresh and ozonated.

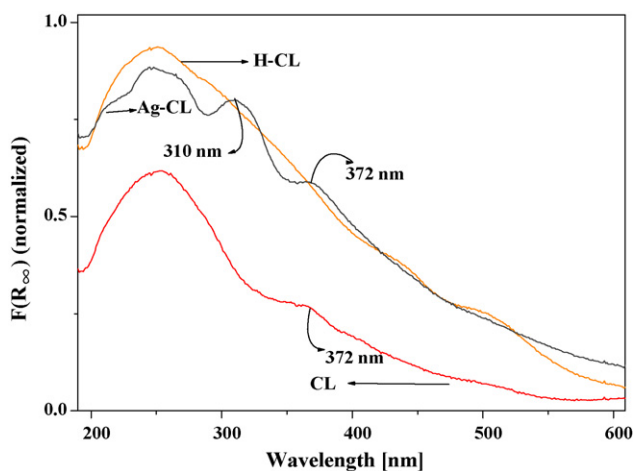


Fig. 3. Normalized (fit to 1), reflectance ($F(R_{\infty})$) versus excitation wavelength, using DRUV–VIS spectra of the zeolite samples. The arrowed areas of the spectra represent key reflectance wavelengths.

which is slightly higher than 0.4904 nm as reported in the literature (JCPDS–PDF #00–072–0607) for a cubic Ag₂O₃ phase.

3.1.3. UV–VIS

The spectral analysis of zeolite is shown in Fig. 3. All the presented samples have clear peaks at 250 nm. The reflectance peak at 310 nm corresponds to Ag⁺ clusters inside the framework of zeolite and this is in accordance with the literature [13]. Peaks around 372 nm (CL and Ag-CL) can be affiliated to quasi-colloidal particles of Ag⁰ (size ~1 nm) or other metal formed at the external surface of clinoptilolite crystals. This peak is not observed for H-CL sample, leading to our deduction that some of the silver is present as a superficial-framework particle covering.

Table 1

Key infrared assignation bands for Ag/SiO₂ and CL samples, according to values cited in literature [12] for common functional groups.

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)

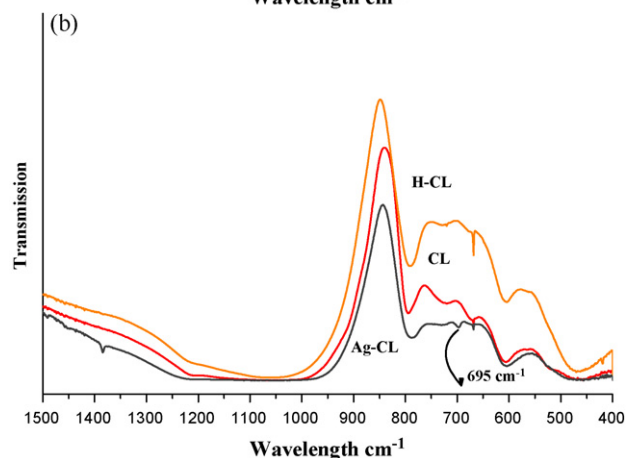
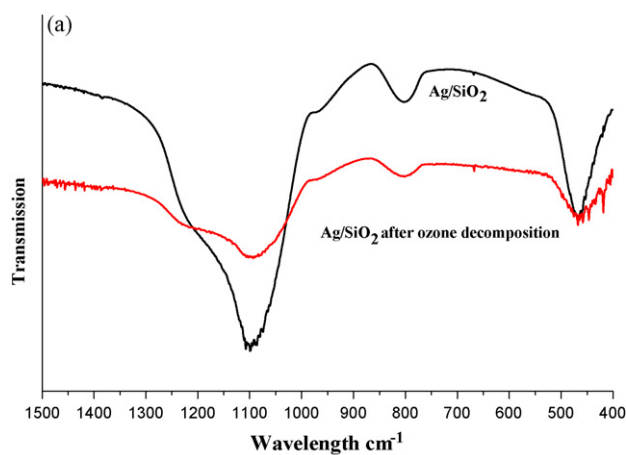


Fig. 4. A plot showing infrared (IR) transmittance (%) spectra as a function of scanning wavelength (wavenumber) of (a) Ag/SiO₂ and clinoptilolite—natural and Ag-exchanged form (b).

3.1.4. IR spectroscopy

Due to the fact that silver cannot be observed in the IR spectra of the Ag/SiO₂ sample, in Fig. 4a only the silver loaded SiO₂ (before and after catalytic process) is shown. The main vibrational transmissions present are elucidated in Table 1 and they correspond to Si–O–Si, or Si–O–H vibration [12], but only a very weak silanol vibration (950 cm⁻¹) can be observed. In Fig. 4b the spectra in a region from 1500 to 400 cm⁻¹ of CL and exchanged forms are presented. This region is considered as important for Ag-exchange processes. These results are also congruous with the literature [14,15], where it is stated that two bands exist in this range at ca. 675 cm⁻¹ (related to 5-membered ring vibrations) and 695 cm⁻¹ (originates from bending vibrations of two 4-membered rings, vibrating alternately). These bands can be found only in our Ag loaded samples. However, in the spectra only the band at 695 cm⁻¹ (of the Ag-CL sample) occurred. Other IR vibrations present are due to the SiO₂ structure of CL, and are also described in Table 1. Here the silanol vibrations are clearly visible (570 cm⁻¹ band shifts to 600 cm⁻¹), and the reason for the presence of Si–OH groups is the aluminum present within zeolite.

3.2. Catalysis

In Fig. 5a the ozone decomposition over Ag/SiO₂ starts with about 95% conversion, and after 45 min a 99% conversion is obtained. From 45 to 150 min, the conversion is very high (close to 100%), then a slow decrease was observed. The plausible explanation for this insignificant deactivation is the formation of physically adsorbed oxygen on the surface, perhaps in addition to the for-

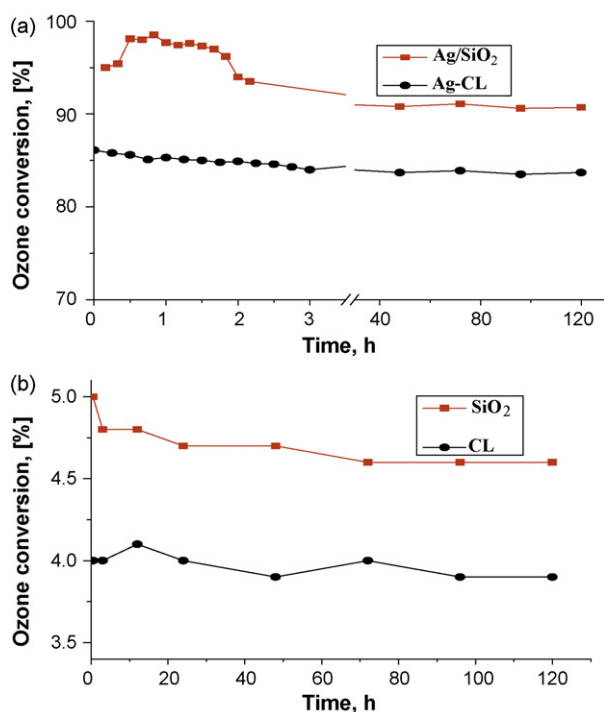


Fig. 5. Ozone conversion as a function of exposure time for samples (a) on Ag/SiO₂ and Ag-CL and (b) on pure SiO₂ and CL. The symbols and trend lines pertaining to the identified samples are represented in the graph legends.

mation of higher silver oxides (higher oxidation states). However, the deactivation is not considerable and the catalyst is suitable for such an application, and may be appropriate for practical use, which was proved with a longer duration-exposure test of 120 h. The AgO or Ag₂O₃ formed in the process of ozonation easily decompose to metallic silver and oxygen under ambient conditions [1].

The behaviour of the Ag-clinoptilolite catalyst is interesting for analysis, because silver is not loaded onto the surface as in the case of Ag/SiO₂, the Ag-CL samples were ion exchanged. In this case, the Ag is located as T-ions in zeolite channels. As shown in Fig. 5a the observed ozone conversion (~85%) is constant until the end of the measurement—for up to 5 days. Notwithstanding that, in this case, the conversion was slightly lower than Ag/SiO₂, and we did not observe any deactivation. A possible reason is the location of the silver—inside zeolite channels. The activity of the supports for ozone decomposition were also investigated (Fig. 5b). Pure SiO₂ converts less than 5% of the ozone present; the natural form of clinoptilolite has about 4% ozone conversion.

4. Conclusions

According to the DC arc-AES method existence of silver, loaded onto the media was proved. XRD diffractograms show that the HEU structure of clinoptilolite samples is not disrupted in the process of loading, first with NH₄⁺ and then with Ag⁺. Firstly, silver is loaded

universally over the silica surface and during the reaction is oxidized itself.

The UV-VIS analysis of Ag-CL show that the silver is loaded as ion (T-atom) or ion clusters into the zeolite framework (reflection at 310 nm). The band at 695 cm⁻¹ is presented in the Ag-CL sample, and in this case one can conclude that silver was loaded into the 4-membered rings. Ag-CL showed a marginally lower activity for ozone decomposition (~85% conversion) compared to Ag/SiO₂ but chemical deactivation of the former is not observed. Thus, it could be used practically as catalyst for neutralization of waste gases containing ozone and could also be applied to ozone-catalytic incineration of volatile organic carbons (VOCs).

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References

- [1] A. Naydenov, P. Konova, P. Nikolov, F. Klingstedt, N. Kumar, D. Kovacheva, P. Stefanov, R. Stoyanova, D. Mehandjiev, Decomposition of ozone on Ag/SiO₂ catalyst for abatement of waste gases emissions, *Catal. Today* 137 (2–4) (2008) 471–474.
- [2] A. Naydenov, D. Mehandjiev, Complete oxidation of benzene on manganese dioxide by ozone, *Appl. Catal. A* 97 (1) (1993) 17–22.
- [3] A. Naydenov, R. Stoyanova, D. Mehandjiev, Ozone decomposition and CO oxidation on CeO₂, *J. Mol. Catal. A* 98 (1) (1995) 9–14.
- [4] S. Imamura, M. Ikebata, T. Ito, T. Ogita, Decomposition of ozone on a silver catalyst, *Ind. Eng. Chem. Res.* 30 (1) (1991) 217–221.
- [5] G.N. Waterhouse, G.A. Bowmaker, J.B. Metson, Oxidation of a polycrystalline silver foil by reaction with ozone, *Appl. Surf. Sci.* 183 (3–4) (2001) 191–204.
- [6] N. Kumar, P. Konova, A. Naydenov, T. Salmi, D.Yu. Murzin, T. Heikkilä, V.-P. Lehto, Ag-modified H-Beta, H-MCM-41 and SiO₂: influence of support, acidity and Ag content in ozone decomposition at ambient temperature, *Catal. Today* 119 (1–4) (2007) 342–346.
- [7] N. Kumar, P. Konova, A. Naydenov, T. Heikkilä, T. Salmi, D.Yu. Murzin, Synthesis of novel Ag modified MCM-41 mesoporous molecular sieve and beta zeolite catalysts for ozone decomposition at ambient temperature, *Catal. Lett.* 98 (1) (2004) 57–60.
- [8] M. Kanazirski, J. Janev, Physicochemical analysis of mineral paragenesis of zeolitized perlitites in the Borovicka area in the eastern Rhodope Mts, *Compt. Rend. Acad. Bulg. Sci.* 36 (12) (1983) 1571–1574.
- [9] O. Petrov, T.A. Karamaneva, G. Kirov, Cation distribution in clinoptilolite structure: natural samples, *Compt. Rend. Acad. Bulg. Sci.* 37 (3) (1984) 785–788.
- [10] Z. Milakovska, Red thermal oxidation aureoles around limestone clasts incorporated within oligocene clinoptilolite rocks (NE Rhodopes, Bulgaria), *Compt. Rend. Acad. Bulg. Sci.* 59 (11) (2006) 1173–1180.
- [11] P. Vassileva, D. Voikova, Investigation on natural and pretreated Bulgarian clinoptilolite for ammonium ions removal from aqueous solutions, *J. Hazard. Mater.* 170 (2–3) (2009) 948–953.
- [12] H.-J. Jeon, S.-C. Yi, S.-G. Oh, Preparation and antibacterial effects of Ag-SiO₂ thin films by sol-gel method, *Biomaterials* 24 (27) (2003) 4921–4928.
- [13] B. Concepcion-Rosabal, G. Rodriguez-Fuentes, N. Bogdanchikova, P. Bosch, M. Avalos, V.H. Lara, Comparative study of natural and synthetic clinoptilolites containing silver in different states, *Microporous Mesoporous Mater.* 86 (1–3) (2005) 249–255.
- [14] W. Mozgawa, M. Król, T. Bajda, Application of IR spectra in the studies of heavy metal cations immobilization on natural sorbents, *J. Mol. Struct.* 924–926 (2009) 427–433.
- [15] W. Mozgawa, T. Bajda, Application of vibrational spectra in the studies of cation sorption on zeolites, *J. Mol. Struct.* 792–793 (2006) 170–175.
- [16] Iv. Boevski, N. Daskalova, A method for determination of toxic and heavy metals in suspended matter from natural waters by inductively coupled plasma atomic emission spectrometry (ICP-AES). Part I. Determination of toxic and heavy metals in surface river water samples, *J. Univ. Chem. Tech. Metall.* 42 (4) (2007) 419–426.