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Decomposition of ozone on Ag/SiO_2 catalyst for abatement of waste gases emissions

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Abstract

A silica-supported Ag system made by the incipient wetness impregnation method was investigated in the reaction of heterogeneous catalytic decomposition of ozone. It was established that the catalytic ozone decomposition on Ag/SiO_2 proceeded in the temperature interval −40 °C to 25 °C as a first order reaction with activation energy of 65 kJ/mol (pre-exponential factor $5.0 \times 10^{14}\ s^{-1}$). Based on the results from the instrumental methods (SEM, XRD, XPS, EPR, TPD) it can be concluded that in presence of ozone the silver is oxidized to a complicated mixture of Ag_2O_3 and AgO. Due to the high activity and stability of the Ag/SiO_2 catalyst, it is promising for neutralization of waste gases containing ozone.

Keywords: Ozone decomposition; Ag/SiO_2; Waste gases; Silver oxide; Silica

1. Introduction

Ozone is known as a strong oxidizing agent for waste and drinking water treatment, sterilization and deodoration [1–4]. The exit gases from such processes contain residual ozone and due to the fact that the ozone itself is very toxic [1], an additional air pollution problem must be solved. The most effective method for neutralization of waste gases containing ozone is the heterogeneous catalytic decomposition [2–4]. The disadvantage of this method is the deactivation of the catalysts due to presence of nitrogen oxides formed during ozone synthesis [5], the presence of water vapour and carbon dioxide [6,7]. Therefore, it is of importance to develop a new reliable and active catalyst for ozone decomposition. The behavior of silver catalysts in the reaction of ozone decomposition was a subject of several investigations [8–11]. 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 [8]. During the catalytic decomposition of ozone, a highly reactive oxygen species is produced and it is able to oxidize completely the toxic compounds at room temperatures [12–14].

The aim of the present paper is to investigate the kinetics and the mechanism of ozone decomposition on silver-modified SiO_2 with a view to its further application to the neutralization of waste gases containing residual ozone and possible use for decontamination of polluted gases from toxic volatile organic compounds (VOCs) by applying of ozone-catalytic method [12].

2. Experimental

The modification of SiO_2 (delivered commercially from Merck company) with Ag was carried out by the incipient wetness impregnation method. The reaction proceeded at ambient temperature for 24 h in a rotator evaporator device using an aqueous solution of silver nitrate. After impregnation, the sample was dried at 110 °C and calcined at 500 °C. The specific surface area of the supported catalyst was determined by low-temperature nitrogen adsorption using Sorptomatic 1900 (Carlo Erba Instruments). The BET equation was used for calculation of the surface area. The morphology of the samples was investigated by a scanning electron microscope (Cambridge Leica 360). The metal content of the sample was

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determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) with a Jobin Yvon 38 (France). Phase composition and particle sizes of the samples were studied by X-ray powder diffraction. XRD spectra were recorded at room temperature using a Bruker D8 Advance powder diffractometer with Cu Kα radiation and SolX detector. Data were collected in the 2θ range from 10° to 80° with a step 0.04° and counting time of 2 s/step. The XPS studies were performed in a VG Escalab II electron spectrometer using AlKα radiation with energy of 1486.6 eV. The residual gas pressure in the analysis chamber was 10^{-7} Pa. Binding energy values (BE ±0.2 eV) were referenced to the C 1s line at 285.0 eV. Oxygen TPD – spectra were recorded by using of a fast response Teledyne (3000 P) O_2 – gas analyser in argon (99.999%) flow (9.0 l/h), the catalyst sample being 0.2 g. The EPR spectra were recorded as a first derivative of the absorption signal of an ERS-220/Q (ex-GDR) spectrometer within the temperature range of −195 to 130 °C. The g-factors were determined with respect to a Mn^{2+}/ZnS standard. The catalytic activity of the sample in the reaction of ozone decomposition was investigated in a plug flow reactor system permitting isothermal operation. The reactor was made of glass and had an inner diameter of 4.1 mm. The catalyst particle sizes were varying: 0.1–0.2 mm and 0.5–0.6 mm. The volume rate was 120,000 h^{-1}. Ozone was synthesized in a flow of oxygen (99.7%) dried with silica gel using an ozone generator with silent discharge and coaxial electrodes. The inlet concentration of ozone was varying from 5 to 15 g/m^3 (0.1–0.3 mol/m^3). Ozone concentration was measured by an Ozomat GM (Anseros, Germany) ozone analyzer with a resolution of ±0.1 g/m^3. The reaction temperature was −35 to 25 °C and was maintained with an accuracy of ±0.2 °C.

3. Results and discussion

The metal content was measured to be 4.85 wt.% and the surface area (BET), 342 m^2/g. The pore size distribution curve can be decomposed to four different peaks with maxima at 1.6, 2.3, 2.9 and 3.7 nm, i.e. the main part of the pores are in a narrow range from 1.5 to 5.5 nm. The scanning electron micrograph (SEM) of the Ag-SiO_2 catalyst reveals a uniform particle size distribution of Ag over the silica support, the average particle size of Ag clusters ranging from 0.5 to 1 μm.

Fig. 1, curve a, presents the temperature-conversion dependence of 5 wt.% Ag/SiO_2 catalyst in the temperature interval −35 to 25 °C, measured after the reaching of steady state conditions. As can be seen, the conversion is 50% at −13 °C and reaches almost 100% at room temperature. The lowering of the conversion observed with the higher particle diameter (Fig. 1, curve b, $d_p = 0.5–0.6$ mm) reveals that there is a significant increase of the effect of the internal diffusion.

A reactor model was used to obtain the values of the integrated reaction rates and, taking into account the diffusion effects, to establish the kinetics parameters [15]. On the basis of the prediction for the effectiveness factor and fitting with the experimental data, the following values for the kinetic parameters have been obtained in the temperature interval from −35 to 25 °C: $E_a = 65$ kJ/mol; $k_o = 5.0 \times 10^{14}$ s^{-1}.

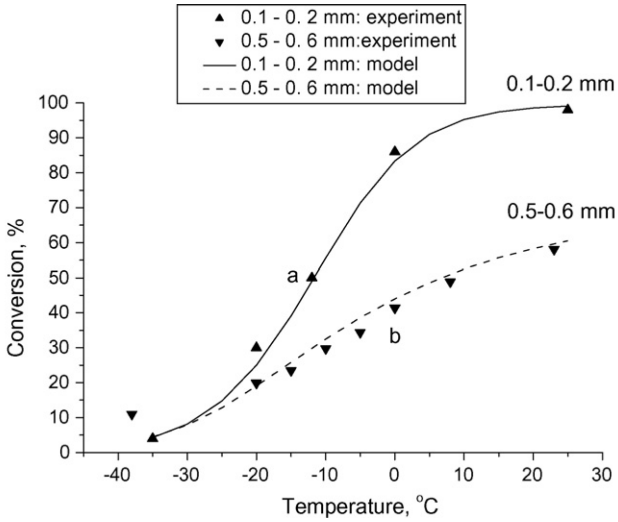

Fig. 1. Conversion–temperature dependences for the reaction of ozone decomposition over an 5 wt.% Ag/SiO_2 catalyst, $C_{O_3\,\mathrm{inlet}} = 0.25$ mol/m^3 (12 g/m^3), GHSV = 120,000 h^{-1}.

The X-ray powder diffraction patterns of fresh, ozonated and subjected to TPD samples of 5 wt.% Ag/SiO_2 are presented in Fig. 2. As can be seen, in the fresh sample silver is present as a metal phase (Ag^0). The major Ag diffraction peaks correspond

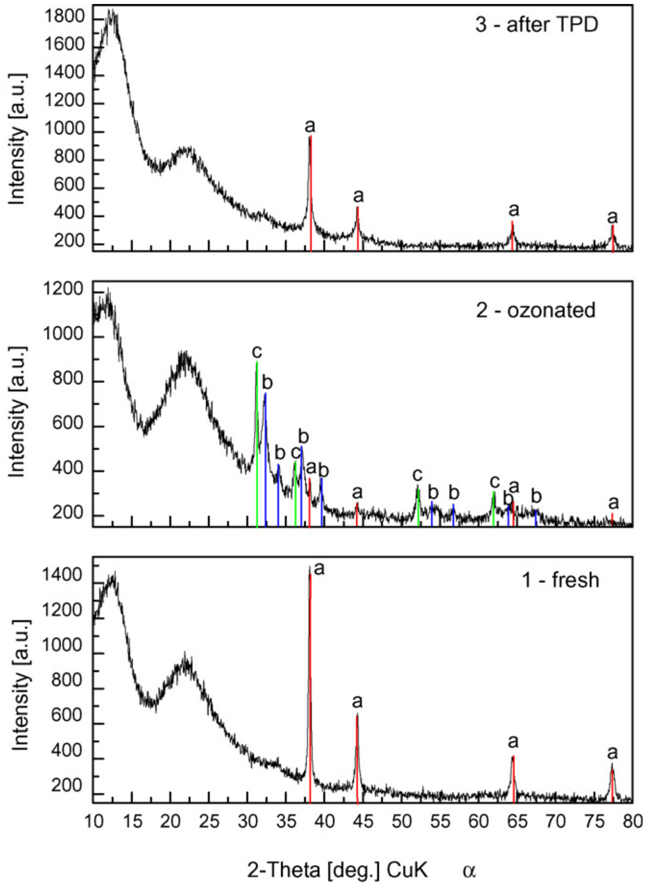

Fig. 2. X-ray powder diffraction patterns of fresh, ozonated and after TPD samples of 5 wt.% Ag-SiO_2: (a) metallic silver, (b) monoclinic AgO, (c) cubic Ag_2O_3.

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. After treatment with ozone, the XRD pattern of the same sample reveals that the amount of the metallic Ag^0 phase decreases and in the ozonated samples it is insignificant. After ozonation, silver is presented mainly in its oxidized form. The X-ray pattern of the ozonated sample contains lines of monoclinic AgO (JCPDS - PDF #00-051-0945) as well as of a cubic phase with unit cell parameter $a = 0.4959(3)$ nm, which is slightly higher than 0.4904 nm as reported in the literature (JCPDS - PDF #00-072-0607) for a cubic Ag_2O_3 phase. The formal oxidation state of silver in the first phase is 2+ but crystal structure determination has established it to be present in this phase in the form of silver (I, III) [16]. The formal oxidation state of silver ions in the second phase is 3+ but some authors claim that the material is in fact $Ag_2O(O_x)$, where (O_x) is trapped oxygen and the oxidation state of silver in this phase remains uncertain [17]. Fig. 3 presents the TPD spectra obtained after treatment of the catalyst at room temperature in pure oxygen and in an ozone oxygen mixture. With the ozonated sample there are two desorption peaks, at 115 °C and 180 °C, while with the sample treated in oxygen no significant desorption was observed up to 300 °C. According to data in the literature [18], silver is not oxidized by O_2 at 27 °C, but in presence of ozone silver surfaces are oxidized stepwise from Ag_2O to AgO (silver I, III oxide) at the same temperature. It was suggested that the dissociative adsorption of O_3 produces surface chemisorbed atomic oxygen. The recombinative desorption of chemisorbed oxygen is observed at 307 °C. At higher temperatures (above 416 °C), a process of desorption of bulk-dissolved (subsurface) oxygen starts [19]. Therefore, the oxygen peaks observed at low temperatures (50–200 °C) are result of associative desorption of the surface oxygen produced by the treatment with ozone. It has been established that the crystallite size (obtained by analysis of the diffraction line broadening) decreases from about 50 nm for the fresh sample to about 30–35 nm for the sample exposed to the ozone and heated to 380 °C in agron flow (i.e. after TPD). As result of the thermal treatment, the initial state of silver is restored and only a metal phase is observed. It is known that the thermal stability of Ag_2O (being decomposed completely at 200 °C) is higher than that of AgO, which is transformed to its initial elements at 100 °C [19]. Ag_2O_3 is extremely unstable compound. Therefore the first peak (110 °C) in O_2-TPD can be attributed to the oxygen obtained during Ag_2O_3 and AgO decomposition, while the second peak (at 180 °C) is due to Ag_2O.

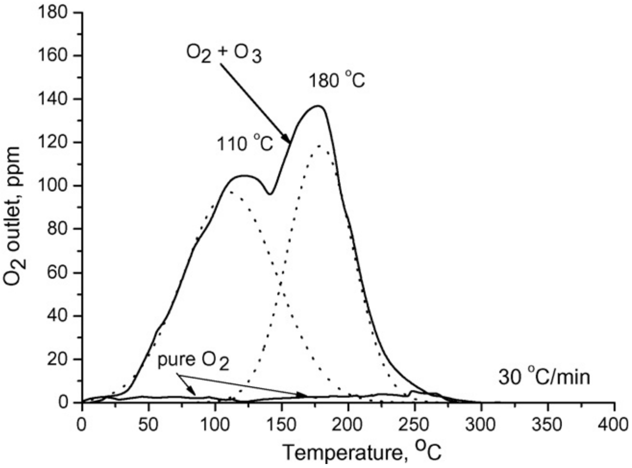

Fig. 3. TPD spectra of 5 wt.% Ag/SiO_2 catalyst.

In order to investigate the chemical state of the silver particles, the Ag 3d photoelectron spectra of fresh and worked with ozone catalysts as well as that of Ag foil scribed in air were obtained (not shown). The latter shows an Ag 3d peak at 368.2 eV, which is in accordance with the binding energy value for a silver foil obtained by Waterhouse et al. [11] and attributed to Ag^0. The fresh and ozone-treated Ag/SiO_2 samples show peaks with maxima at 368.4 eV and 368.6 eV, respectively. Due to the fact that the binding energies are very close and it is difficult to determine the oxidation state of the Ag particles, an additional study was performed on Ag MVV Auger transition [20–23]. Fig. 4 shows Ag MVV Auger spectra of fresh and applied to ozone decomposition Ag/SiO_2 catalysts and Ag foil. The Ag foil scribed in air has a peak with a kinetic energy of 358.2 eV, typical for Ag^0 [11]. The kinetic energy of the fresh Ag/SiO_2 sample shifts to a lower value of 357.5 eV which indicates surface oxidation of the silver particles. The Auger peak of the ozonated Ag/SiO_2 sample exhibits a double structure which can be resolved into two peaks centered at 355.6 and 356.7 eV, respectively. The latter could be attributed to Ag^+ oxidation state [11] while the peak at lower kinetic energy is probably due to formation of carbonate species on the surface of the silver particles.

EPR spectroscopy has been applied to obtain additional information on the formation of Ag clusters and Ag nanoparticles, as well as on the adsorption of oxygen species on the catalyst surfaces [24–27]. While the fresh 5 wt.% Ag/SiO_2 sample does not display any EPR signal, three types of signals can be resolved in the EPR spectra of treated samples (not shown). At higher registration temperature, a broad asymmetric signal with $g \approx 2.15$ (Si1) is visible in the EPR spectra of both samples, treated in pure oxygen and in ozone–

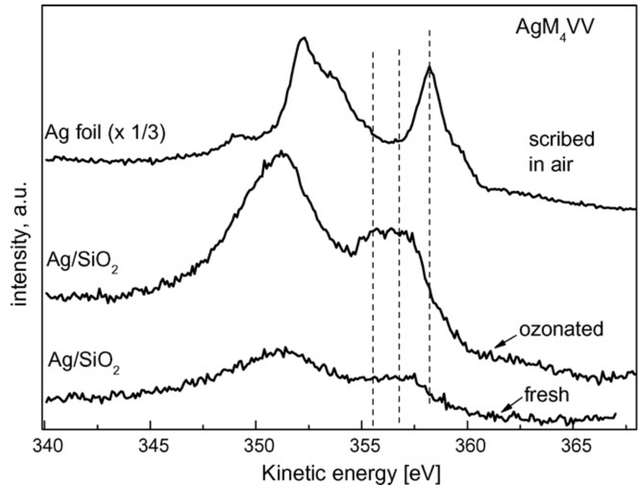

Fig. 4. Ag M4VV Auger spectra of fresh and worked in reaction of ozone decomposition samples of 5 wt.% Ag/SiO_2 and Ag foil.

oxygen mixture. On cooling, the asymmetric signal is broadened and disappears at −170 °C. It is noticeable that the intensity of the asymmetric signal for the O_2-treated sample is about three times higher than that for the $(O_3 + O_2)$-treated sample. Based on the previous EPR studies of supported Ag catalysts [23,24], this signal can be assigned to Ag clusters with a general composition $Ag_n^{\delta+}$, where $(n - \delta+)$ is an odd number and $n \leq 10$. The larger line width does not permit determining of the hyperfine structure, as a result of which the number of Ag species is not clear. The relative part of these Ag clusters is sensitive whether the sample is treated with O_2 or O_3. At lower registration temperature (−170 °C), only the EPR spectrum of O_3-treated 5 wt.% Ag/SiO_2 displays an additional narrow signal with a low intensity, $g \approx 2.03$ and a line width of about 3 mT (SiO_2). At first sight, the EPR parameters allow attributing this signal to conduction electrons in the Ag nanoparticles [27]. However, taking into account that this signal appears in the EPR spectrum of O_3 treated sample only, this signal can be associated with adsorbed O_2^- species rather than with conduction electrons in Ag nanoparticles [28]. The low-temperature spectra of both O_2 and O_3 treated samples display the signal with $g = 4.3$, which is typical for Fe^{3+} ions in a rhombic crystal field. It seems that Fe^{3+} ions are obtained from the iron traces in the carrier (SiO_2) after the oxidation. It is known, that Ag_2O and Ag_2O_3 are brown-black and black coloured, respectively. On the contrary, the AgO is grey to white in colour [29]. In our case the color of the fresh sample was light-brown, since the ozonated sample was deeply black coloured, which could be taken as an additional indication of absence of AgO.

4. Conclusion

The catalytic ozone decomposition on 5 wt.% Ag/SiO_2 proceeds in the temperature interval −40 °C to 25 °C as first order reaction rate with activation energy of 65 kJ/mol and pre-exponent value of 5.0×10^{14} s^{-1}. Based on the results from the instrumental methods and data from the literature it can be concluded that in the fresh 5 wt.% Ag/SiO_2 catalyst the silver is mainly in a metal form while in presence of ozone a complicated mixture of Ag_2O_3 and AgO is formed. The surface oxygen, produced during ozone decomposition, is mobile and takes part in the catalytic cycle. As a result, a very active 5 wt.% Ag/SiO_2 catalyst is synthesized. Due to the high activity and stability of the 5 wt.% Ag/SiO_2, we can conclude that this catalyst is promising for neutralization of waste gases containing ozone and also can be applied to ozone-catalytic incineration of VOCs.

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