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Single and bi-metallic silver modified ZSM-5 for waste gases neutralization

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Abstract Single and bi-metallic silver modified ZSM-5 catalysts were synthesized using three methods of preparation, characterized by different techniques: X-ray powder diffraction (XRD), scanning electron microscopy (SEM), nitrogen physisorption, X-ray fluorescence (XRF), inductively coupled plasma atomic emission spectrometry (ICP-AES) and tested in heterogeneous catalytic decomposition of ozone at ambient temperature. The highest degree of ozone decomposition was observed over 5Ag(Imp)-H(IE)-ZSM-5 catalyst, which exhibit 97% conversion and does not show any deactivation with the time. The method of preparation, amount of supported silver and the presence of modifiers as Cu, Ce, and Zr were found to be important for the ozone decomposition reaction.

Introduction

Catalytic processes are used for removing harmful components from waste gases. Ozone treatment is a widely used method for purification and sterilization of waste and natural waters, as well as oxidation of organic substances. As a result of oxidation the waste gases contain residual concentration of ozone, which is above the admissible values, and it must be decomposed. Ozone decomposition has been reported to be effective over metal oxide catalysts [1–4]. However, there are only a few investigations reported in the literature regarding ozone decomposition over Ag modified zeolite catalysts [5–7]. The synthetic zeolites are among the most important crystalline materials commercially available due to such properties as unique structures at subnanolevel, thermal stability, acidity, shape-selectivity, etc. Metal modified and proton form zeolites are widely used as supports and catalysts in oil refinery, petro-chemical industry and have potential applications in the synthesis of fine chemicals and environmental catalysis [8]. ZSM-5 is a highly siliceous zeolite, which has a 10-membered [oxygen] ring system. Its framework contains two perpendicularly intersecting channel systems with sizes 0.54 nm × 0.56 nm and 0.51 nm × 0.54 nm, respectively [9].

The aim of the present work is to investigate the catalytic behaviour and activity of the several different types of silver modified ZSM-5 zeolite catalysts with respect to catalytic decomposition of ozone.

Experimental

Catalyst preparation

Na-ZSM-5 zeolite was prepared according to the procedure described in Refs. [10, 11] with some modifications. Solution A was prepared by mixing fumed silica (Aldrich) with distilled water. Solution B was prepared by dissolving NaOH (Merck) and $Al(OH)_3$ (Aldrich) in distilled water and was added to solution A. Solution C was prepared by dissolving tetrapropyl ammonium bromide (Fluka) in distilled water. Solution C was added to initial mixture and stirred for a required amount of time. The gel formed was

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transferred in a Teflon cup and inserted in an autoclave. The synthesis was carried out in oven at 423 K. After completion of the synthesis, the crystalline product was filtered, washed with distilled water, dried at 373 K and calcined at 823 K to remove the organic template. Proton form of ZSM-5 was obtained by ion-exchange of Na-ZSM-5, using 1 M NH_4Cl or 1 M NH_4NO_3 (denoted as n further in the catalyst notation) solution at room temperature for 48 h. After that the catalyst was washed with distilled water, dried at 383 K and calcined in a muffle oven at 773 K. The modification of the samples with Ag, Cu, Ce, and Zr was carried out by two different methods: impregnation and ion-exchange. Additionally silver was introduced in situ during zeolite synthesis. The silver loading was aimed to be 2 or 5 wt%. Therefore, the anticipated metal concentration is given prior to the catalyst's names. The real Ag concentration, deposited in the zeolite depending on the applied method is calculated on the basis of the metal amount that was extracted with hot HNO_3 and measured by ICP technique.

In situ method

In situ method was performed during the zeolite syntheses with direct adding of the required amount of silver nitrate into the prepared gel followed by above mentioned procedure for the parent H-ZSM-5. The catalysts prepared by in situ method were denoted as Ag(IS)-H-ZSM-5.

Impregnation method

An incipient wetness impregnation of H-ZSM-5 catalyst was carried out at ambient temperature for 24 h in a rotator evaporator device using an aqueous solution of silver nitrate. After impregnation the samples were dried at 383 K and calcined at 773 K. The catalysts prepared by impregnation method were denoted as Ag(Imp)-H-ZSM-5.

Ion-exchange method

Introducing of the second metal was done by ion-exchange of the proton form of the zeolite powder using Zr-, Ce-, or Cu-nitrate solutions at room temperature for 48 h. After that the catalyst was filtered, washed with distilled water, dried at 383 K and calcined at 773 K. The catalysts prepared by ion-exchange method were denoted as Ag(IE)-H-ZSM-5 or Ag-M(IE)-ZSM-5, where M is a corresponding metal ion.

Catalysts characterization

The specific surface area of the supported catalysts was determined by nitrogen adsorption using Sorptomatic 1900 (Carlo Erba Instruments). The Dubinin equation was used for calculation of the surface area.

To verify the crystal structure of the synthesized zeolites, X-ray powder diffraction measurements was applied on a Bragg–Brentano $\theta/2\theta$ reflection geometry based Philips PW1820 diffractometer using Cu K_α ($\lambda = 1.54184$ Å) radiation. The Cu X-ray tube voltage was set to 40 kV and the current to 50 mA. The divergence of the primary X-ray beam was limited by an automatic divergence slit (ADS) and a 15 mm mask. The irradiated sample length was set at a fixed 12 mm. On the diffracted side there was a 0.2 mm receiving slit and a 1° anti-scatter slit. The diffracted X-ray beam was filtered with a Ni $K\beta$ filter. The measured diffractograms were analyzed using X'Pert HighScore software (Philips, 2001) and the Powder Diffraction File (PDF) database (PDF-2, sets 1-46, 1996 release, ICDD). The PDF database was used to identify the sample peaks and the corresponding phases.

The morphology of the samples was studied using a scanning electron microscope (Cambridge Leica 360). The Si/Al ratio of Na-ZSM-5 was determined by X-ray fluorescence and was found to be 31. The metal content of the different samples was determined by the inductively coupled plasma atomic emission spectrometry (ICP-AES) with a Jobin Yvon 38-France.

Catalytic experiments

The catalytic activity of the samples in reaction of ozone decomposition was investigated in an isothermal plug flow reactor permitting operation under steady state conditions without temperature gradients. The catalyst grain size (0.2–0.4 mm) was chosen taking into account the reactor diameter (6.0 mm) and the gas hourly space velocity (GHSV) of 133,333 h^{-1} (calculated on the total catalyst bed volume and STP for the gas) in order to reduce the effect of external diffusion. The activity of the catalysts was measured after 15 min and was calculated on the basis of equations:

$$\text{Conversion}\ [\%] = 100 * [(C_{\text{inlet}} - C_{\text{outlet}})/C_{\text{inlet}}];$$

$$\text{Rate constant}\ [\text{h}^{-1}] = -\text{GHSV} * \ln[1 - ((C_{\text{inlet}} - C_{\text{outlet}})/C_{\text{inlet}})],$$

where C_{inlet} and C_{outlet} are the ozone concentrations in inlet and outlet of the reactor and GHSV is calculated on the basis of the volumetric gas flow per hour, re-calculated to STP (0 °C and 101 kPa).

Pre-treatment of the catalysts included heating at 110 °C for 1.5 h in air flow. The rate of the gas flow was 5.6 L/h and the catalyst volume was 0.042 cm^3.

Ozone was synthesized in a flow of oxygen (99.7%) dried with silica gel using ozone generator with a silent discharge of 4–6 kV between the electrodes. The inlet concentration of ozone was 10 g/m^3. Ozone concentration was analyzed with an Ozomat GM (Anseros, Germany) ozone analyzer with an accuracy of ±0.1 g/m^3. The reaction temperature was ambient (23 °C) and was maintained with an accuracy of ±0.2 °C.

Results and discussion

Catalyst synthesis and characterization

According to the X-ray analysis the diffraction pattern of Na-ZSM-5 zeolite (Fig. 1a) indicates a synthesis of a pure structure, similar to those reported in the literature. The X-ray powder diffraction patterns of freshly prepared single and bi-metallic silver modified ZSM-5 catalysts were similar to that of the parent Na-ZSM-5, indicating that the modification with Ag, Zr, Ce, and Cu did not influence the structure of the zeolite (Fig. 1b).

The sizes of the Ag crystallites in the samples obtained by impregnation were calculated using Scherrer equation. The first three, most intense Ag peaks were taken for investigation.

$$\text{Average crystallite size} = \frac{K\lambda}{B\cos\theta},$$

where B describes the structural broadening B (size) = $B_{\text{observed}} - B_{\text{standard}}$, which is the difference in integral profile widths or the full width at half maximum (FWHM) between a standard Si reference sample and the studied sample. Si peak at 28.4°2θ with a FWHM of 0.115° was used as the reference peak. The λ is the wavelength of the X-ray radiation and the position of the peak is 2θ. The K is the shape factor, which varies with crystal shape. A shape factor of 0.9 was used for these calculations. The average crystallite size of Ag was calculated to be 39.2 nm.

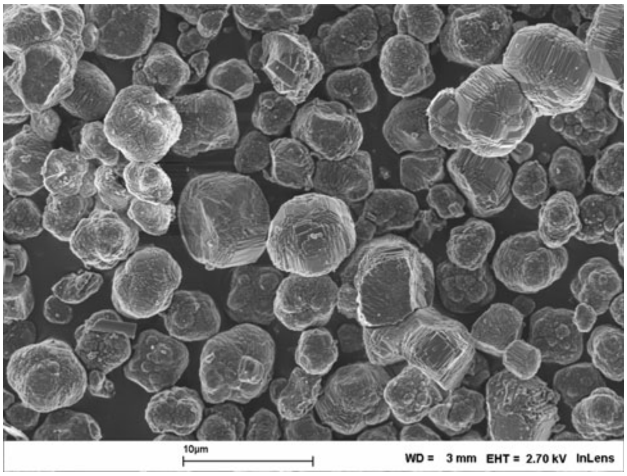

Fig. 2 SEM photograph of Ag deposited on ZSM-5 by impregnation (5Ag(Imp)-H(IE)-ZSM-5). Silver loading is 2.74 wt%

The SEM photograph of Ag modified ZSM-5 catalyst prepared by impregnation is presented in Fig. 2. The SEM investigation reveals that the Ag particles are spherical with a uniform distribution and a mean diameter of 30–50 nm [12].

The specific surface area, the total pore volume, and the metal content of the supported catalysts are presented in Table 1. The notations of the catalysts are formed of the number showing the introduced amount of silver and in a parenthesis after the transition metal—the applied method of introduction. As can be seen, depending on the method of preparation, the metal content in the zeolites ranges from 0.7 for IS and IE to 2.8 wt% for the impregnated samples. Although in the latter case this amount corresponds also to the metal located on the outer surface, however, using the IS and IE methods of preparation, the greater part of the silver is introduced in the zeolite framework in the form of Ag ions. On the contrary, when the modification of the

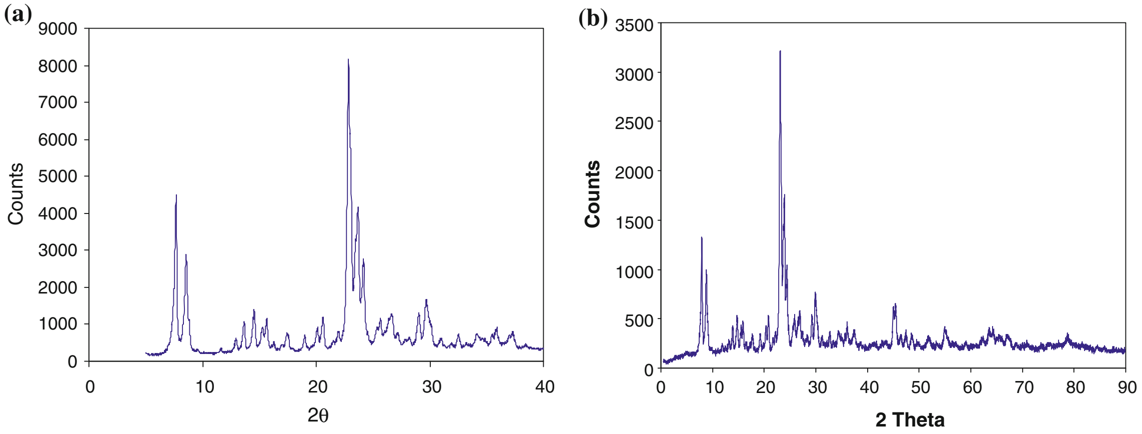

Fig. 1 X-ray powder diffraction pattern of **a** Na-ZSM-5 and **b** 5Ag(IE)-H(IE)-ZSM-5

Table 1 Metal contents, total pore volumes, and surface areas of the prepared catalysts

No.	Catalysts	Me loading (wt%)				Total pore volume (cm^3/g)	Surface area (m^2/g)
		Ag	Zr	Ce	Cu		
1	5Ag(IE)-H(IE)-ZSM-5	0.9	–	–	–	0.18	472
2	2Ag(Imp)-H(IE)-ZSM-5	1.2	–	–	–	0.17	472
3	5Ag(Imp)-H(IE)-ZSM-5	2.7	–	–	–	0.15	431
4	5Ag(Imp)-H(IE-n)-ZSM-5	2.6	–	–	–	0.16	458
5	5Ag(Imp)-Zr(IE)-ZSM-5	2.2	0.31	–	–	0.16	450
6	5Ag(Imp)-Ce(IE)-ZSM-5	2.6	–	0.25	–	0.15	442
7	5Ag(Imp)-Cu(IE)-ZSM-5	2.8	–	–	0.30	0.16	449
8	2Ag(IS)-H(IE)-ZSM-5	0.3	–	–	–	0.17	488
9	5Ag(IS)-H(IE)-ZSM-5	0.7	–	–	–	0.17	366

zeolite is made by impregnation method the substantial amount of silver is on the surface.

Ozone decomposition

Figure 3 presents the degree of heterogeneous decomposition of ozone over the different silver modified supported catalysts at ambient temperature, measured 15 min after the beginning of the process. As can be seen the catalytic activity depends on methods of synthesis, silver content, and presence of different additives, such as Cu, Ce, and Zr.

One can see that the highest decomposition of ozone was observed over 5Ag(Imp)-H(IE-n)-ZSM-5 (97%) and 5Ag(Imp)-H(IE)-ZSM-5 (96%) catalysts, which were prepared by impregnation of silver and contains 5 wt%. The only difference between the two catalysts is the type of solutions (NH_4Cl or NH_4NO_3—denoted as n) used for ion-exchange of Na-ZSM-5 to obtain the proton form. Using nitrate instead chloride gives higher surface area of the catalyst and a little bit higher activity.

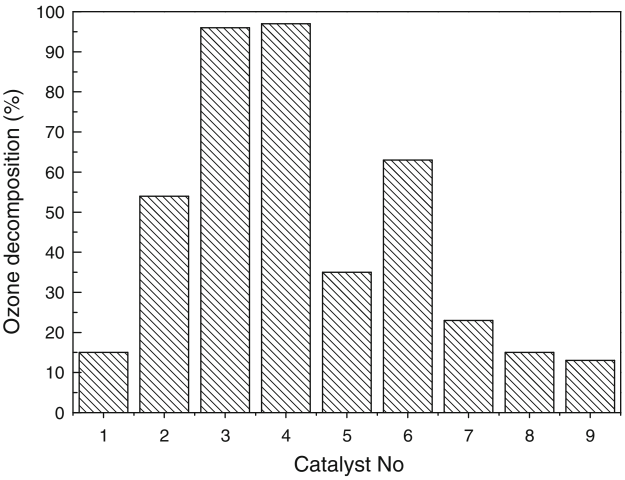

Fig. 3 Degree of ozone decomposition at room temperature (23 °C) over different silver modified supported catalysts (the numbers of the catalysts correspond to Table 1): *1* 5Ag(IE)-H(IE)-ZSM-5, *2* 2Ag(Imp)-H(IE)-ZSM-5, *3* 5Ag(Imp)-H(IE)-ZSM-5, *4* Ag(Imp)-H(IE-n)-ZSM-5, *5* 5Ag(Imp)-Zr(IE)-ZSM-5, *6* 5Ag(Imp)-Ce(IE)-ZSM-5, *7* 5Ag(Imp)-Cu(IE)-ZSM-5, *8* 2Ag(IS)-H(IE)-ZSM-5, *9* 5Ag(IS)-H(IE)-ZSM-5

A very important factor for production of highly active towards ozone decomposition catalysts is the method of their synthesis. For example, the activity of 5Ag-H-ZSM-5 catalyst differs 7.4 times depending on its method of synthesis (Fig. 3):

$$\text{5Ag(IS)-H(IE)-ZSM-5}(13\%) < \text{5Ag(IE)-H(IE)-ZSM-5}(15\%) < \text{5Ag(Imp)-H(IE)-ZSM-5}(96\%)$$

$$\text{2Ag(IS)-H(IE)-ZSM-5}(15\%) < \text{2Ag(Imp)-H(IE)-ZSM-5}(54\%)$$

As can be seen the highest decomposition of ozone was observed when the silver is introduced by impregnation method. The lowest ozone decomposition degree was observed when the catalysts were prepared by so called in situ method during the zeolite syntheses.

The activity of the microporous catalysts towards ozone decomposition depends on the silver content. With increase in the silver loading the activity of the catalysts becomes higher (Fig. 3):

$$\text{2Ag(Imp)-H(IE)-ZSM-5}(54\%) < \text{5Ag(Imp)-H(IE)-ZSM-5}(96\%)$$

An exception from this rule is the case when silver is supported by in situ (IS) method, where the metal is directly added to the initial gel during support synthesis. Probably the bigger amount of supported silver (5 wt%) applied in this synthesis blocks part of zeolite pores and leads to lower catalytic activity. This assumption is confirmed by the fact, that sample 5Ag(IS)-H(IE)-ZSM-5 has surface area with 120 m^2/g lower than that of sample 2Ag(IS)-H(IE)-ZSM-5 (Table 1).

Table 2 Rate constants of different silver modified supported catalysts

No.	Catalysts	k (10^5 h^{-1})
1	5Ag(IE)-H(IE)-ZSM-5	0.22
2	2Ag(Imp)-H(IE)-ZSM-5	1.04
3	5Ag(Imp)-H(IE)-ZSM-5	4.29
4	5Ag(Imp)-H(IE-n)-ZSM-5	4.68
5	5Ag(Imp)-Zr(IE)-ZSM-5	0.57
6	5Ag(Imp)-Ce(IE)-ZSM-5	1.33
7	5Ag(Imp)-Cu(IE)-ZSM-5	0.35
8	2Ag(IS)-H(IE)-ZSM-5	0.22
9	5Ag(IS)-H(IE)-ZSM-5	0.19

Besides methods of preparation and silver content, the activity of the catalysts in reaction of ozone decomposition also depends on the presence of a second metal, such as Ce, Zr, or Cu. As can be seen the highest decomposition of ozone was observed with Ce-modified silver catalyst and the lowest one for 5Ag(Imp)-Cu(IE)-ZSM-5 catalyst. However, introducing the second metal in our case leads to decrease of the initial activity of the catalysts (Fig. 3):

$$\text{5Ag(Imp)-H(IE)-ZSM-5}(96\%) > \text{5Ag(Imp)-Zr(IE)-ZSM-5}(35\%);$$

$$\text{5Ag(Imp)-H(IE)-ZSM-5}(96\%) > \text{5Ag(Imp)-Ce(IE)-ZSM-5}(63\%);$$

$$\text{5Ag(Imp)-H(IE)-ZSM-5}(96\%) > \text{5Ag(Imp)-Cu(IE)-ZSM-5}(23\%).$$

For comparison of the activities of different microporous catalysts, their calculated rate constants for reaction of ozone decomposition are presented on Table 2.

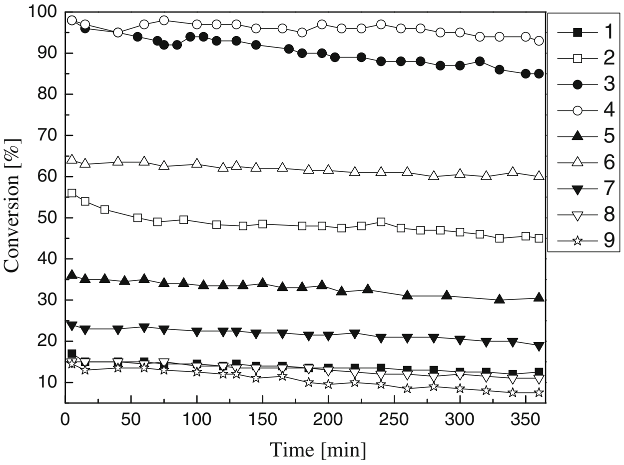

Fig. 4 Long-term stability in reaction of ozone decomposition at room temperature over different silver modified catalysts. The numbers of the catalysts correspond to Table 1

The time–conversion dependence measured for 360 min over the different silver catalysts is given in Fig. 4. One can see that the conversion is stable and almost constant with time on stream at room temperature.

Conclusions

Single and bi-metallic silver modified ZSM-5 catalysts are very promising for heterogeneous catalytic decomposition of ozone due to high catalytic activity at room temperature and, at the same time, they remain active with the time. The most active 5Ag(Imp)-H(IE)-ZSM-5 catalyst exhibit sufficiently high conversion of 97% at room temperature.

Three main factors were found to have an influence on the catalytic activity in reaction of ozone decomposition: (i) choice of the preparation method, giving the needed structure, surface area, and metal located on the catalyst surface; (ii) silver loading; (iii) modifying the catalyst with other metals.

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