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ROLE OF THE PREPARATION METHOD ON CATALYTIC ACTIVITY OF Ag/CeO_2 FOR OXIDATION OF CO, CH_3OH AND $(CH_3)_2O$

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ABSTRACT

The catalytic activity of Ag/ceria catalysts for oxidation of CO, CH_3OH and $(CH_3)_2O$ has been studied. Two different techniques were used for preparation of the catalysts – deposition-precipitation and modified version of deposition – precipitation. HRTEM combined with EDS, X-ray diffraction, FTIR of CO at 90 and 300 K and XPS measurements were employed to obtain information about the effect of different synthesis procedures on the surface and on the bulk structure of the catalysts and to explain the differences observed in their catalytic performance.

Key words: *Silver catalysts, complete oxidation, CO, VOCs, ceria*

INTRODUCTION

The removal of volatile organic compounds (VOCs) emitted from industrial and domestic processes have drawn a lot of attention due to increasing social and political concern in environment. A cheap and efficient way of VOCs removing is their complete catalytic oxidation to harmless products such as H_2O and CO_2. Supported Pt and Pd are well established as efficient catalysts for VOCs combustion. However, due to the high cost and limited reserve of such noble metals, the quest for cheaper and more environmentally friendly catalytic materials are of an ever-increasing importance for tomorrow's applications. Recently, the promotion effect of Ag on the performance of NiO_x and CoO_x in reaction of total oxidation of CH_3OH as well as of mixture of CH_3OH, $(CH_3)_2O$ and CO – main components of waste gases from production of formaldehyde has been reported [1]. It was found that catalytic behaviour depends on the selection of support and NiO_x is more suitable support than CoO_x. CeO_2 is known as a very attractive support material, because of its ability to maintain a high dispersion of the active components and to change the oxidation state of the cation between +3 and +4 depending on the redox conditions [2].

The aim of present study was to examine the catalytic activity of Ag/CeO_2 catalysts for abatement of air pollutants – CH_3OH, $(CH_3)_2O$ and CO in waste gases from formaldehyde production. HRTEM, X-ray diffraction, FTIR of CO at 90 and 300 K and XPS measurements were employed to obtain information about the effect of different synthesis procedures on the surface and on the bulk structure of the catalysts and to explain the differences observed in their catalytic activity.

EXPERIMENTAL

1. Catalyst preparation

Two different techniques were used for preparation of Ag/ceria catalysts: deposition-precipitation (DP) and modified version of deposition-precipitation (MDP). Deposition-precipitation took place by precipitation of a desired amount of $AgNO_3$ (at pH 9.0) with K_2CO_3 at 333 K on ceria suspended in water by ultrasound. Ceria, used as a support and also as reference was laboratory-made by precipitation of $Ce(NO_3)_3.6H_2O$ with K_2CO_3 at 333 K (pH 9.0), ageing in a course of 1 h at the same temperature, drying and calcination in air at 673 K for 2 hours. The MDP involved precipitation of $AgNO_3$ at the pH value indicated above on cerium (III) hydroxide freshly precipitated and aged 1 hour at 333 K. In both cases, the resulting precipitates were aged 1 h at 333 K, then filtered and washed until no NO_3

– could be detected. Further, the precipitates were dried in vacuum at 353 K and calcined in air at 673 K for 2 hours. All the samples were synthesized in a „Contalab“ laboratory reactor enabling complete control of the reaction parameters (pH, temperature, stirrer speed, reactant feed flow, ect). The Ag loading for each catalyst was 3wt. %. „Analytical grade“ chemicals were used for catalysts preparation.

Depending on the preparation method, the samples were labelled as AgCeDP and AgCeMDP.

2. Characterization techniques

The BET surface areas of the catalysts were determined on a „Flow Sorb II-2300“ device.

HRTEM analysis was performed using a Jeol JEM 2010 (200 kV) microscope equipped with an EDS analytical system Oxford Link. The powdered samples were ultrasonically dispersed in isopropyl alcohol and the obtained suspensions were deposited on a copper grid, coated with a porous carbon film.

X-ray diffraction patterns were obtained on a DRON-3 automatic powder diffractometer using Cu Kα radiation.

X-ray photoelectron data were recorded on a VG Scientific ESCALAB-210 spectrometer using unmonochromatized Mg Kα radiation (1253.6 eV) from an X-ray source operating at 15 kV and 20 mA. The binding energy scale of the spectrometer was calibrated by setting the Ag $3d_{5/2}$ peak of a sputtered Ag foil to 368.27 eV. The working pressure was below 8.10^{-9} mbar. The hemispherical analyzer works at a constant pass energy of 20 eV for Ce 3d, Ag 3d, O 1s, C 1s regions and VB. All spectra were recorded at a photoelectron take-off angle of 90°. Charging effects were corrected by using the Ce $3d_{3/2}$ U''' line at 917.00 eV as reference [3]. Quantitative calculations were made using MULTILINE program [4].

The FTIR spectra were taken on a Perkin-Elmer 1760 spectrometer (equipped with a MCT detector) with the samples in self-supporting pellets introduced in a cell allowing thermal treatments in controlled atmospheres and spectrum scanning at controlled temperatures (from 90 to 300 K). The experiments were performed on sample preliminarily heated up to 673 K in dry oxygen and cooled down in the same atmosphere (oxidised sample) or reduced in hydrogen at 373 K and outgassed at RT (reduced sample). Band integration and curve fitting were carried out by „Curvefit“, in Spectra Calc

(Galactic Industries Co.) by means of Lorentzian curves. All the spectra were normalised on the weight of the pellets.

3. Catalytic activity measurements

The catalytic activity of the samples in CO and CH_3OH oxidation was measured using continuous flow equipment with fixed bed stainless steel reactor at atmospheric pressure. The following conditions were chosen: catalyst bed volume – 0.5 cm^3 (particle size 0,6 – 1.0 mm), inlet CO and CH_3OH concentrations – 2.0 % balanced with air and space velocity 20000 h^{-1}.

Two types of equipments for DME oxidation measurements were used: (i) flow-line equipment with an isothermal reactor, allowing precise control of the methanol dehydration to $(CH_3)_2O$ on Al_2O_3 and (ii) flow–line equipment with stainless steel reactor for deep oxidation of the preliminarily purified DME. The feed gas was 1.0 % DME balanced with air and the space velocity was 20000 h^{-1}.

The reactant and product gases were analyzed for methanol, DME, CO, CO_2, O_2 and N_2 by HP 5890 Series II gas-chromatograph, equipped with flame ionization and thermal conductivity detectors and Porapak Q and MS-5A columns.

RESULTS AND DISCUSSION

1. Physicochemical characterization of the catalysts

The XRD patterns of the catalysts prepared by different methods are shown in Fig. 1. They showed the presence of CeO_2 in the cubic crystal structure of fluorite-type. The average size of ceria particles calculated from the peak at $2\theta = 28.6$ is 4.5 nm, according to Scherrer's equation. This size remains almost unchanged after the deposition of Ag – 4.3 nm. AgMDP catalyst also contains ceria crystallites with similar size. No peaks related to the presence of Ag were discernible in the diffraction patterns. The absence of a signal for Ag could be attributed to the fact that the particles size is too small and also that the measurement is under the detection limit of the instrument.

HRTEM measurements confirm that in both samples ceria is highly crystalline after calcination at 673 K (Fig. 2). The analysis of the fringes observed in the micrographs revealed that the support has a cubic structure and that it mainly exposes the (111) face. The surface of AgCeDP is covered by an AgOx layer, according to FTIR data (see below). Since silver is unstable under the electronic beam of the microscope, an agglomeration into metallic silver particles occurs during the first few minutes of exposure, thus producing a lot of small silver particles that coalesce to form big particles by increasing the time under the electronic beam. However, the results agree well with XRD data for presence of very small silver particles.

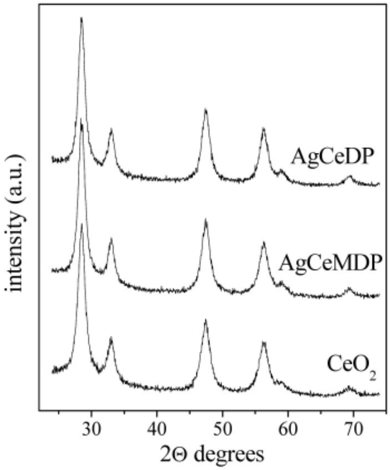

Figure 1. *XRD patterns of studied samples*

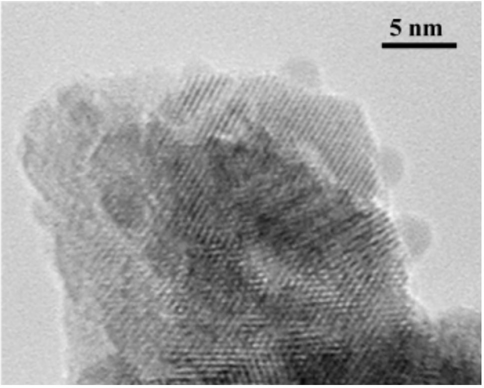

Figure 2. *HRTEM image of AgCeDP(magnification of 800,000).*

The absorption spectra of CO adsorbed at 90 K (fine curve) and at RT (bold curve) on AgCeDP oxidized sample are reported in Fig. 3. An intense band at 2149 cm^{-1} and a weaker one at 2168 cm^{-1} are observed in the spectrum in carbonylic region (Fig. 3a). On the basis of data already reported, the band at 2149 cm^{-1} can be assigned to CO on Ce^{4+} cations and on OH groups, while that at 2168 cm^{-1} is due to CO adsorbed on Ce^{4+} sites with a different coordinative unsaturation [5]. A very weak band at 2100 cm^{-1} could be seen in the spectrum, too. The low intensity of this band is in agreement with the reduction of Ag by the inlet of CO. This band could be tentatively assigned to Ag^0 sites stabilized by the support. However, a contribution of CO adsorbed on Ag$^{\delta+}$ sites to the band at 2168 cm^{-1} could also be suggested and supported by XPS measurements (see below). The formation of different carbonate and bicarbonate structures was observed in the carbonate region 1800–800 cm^{-1} (Fig. 3b). The appearance of bands at 1560, 1480, 1357, 1285, 1216 and 854 cm^{-1} after CO adsorption could be an indication for the reduction of Ag$_x$O.

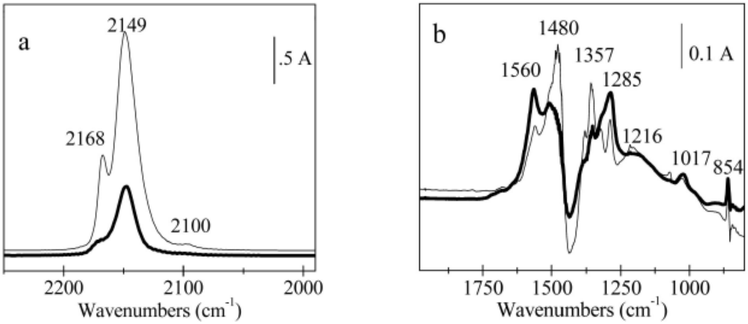

Figure 3. *FTIR spectra of 5.0 mbar CO adsorbed at 90 K (fine curve) and at RT (bold curve) on oxidized AgCeDP in the carbonylic region (a) and in the carbonate region (b).*

The inlet of CO at 90 K on AgCeDP catalyst reduced at 523 K (bold curve) produces in the carbonylic region a strong band at 2155 cm^{-1} that can be assigned to CO adsorbed on Ce^{3+} sites; another one at 2139 cm^{-1} due to liquid-like CO and a broadening from the low frequency side (Fig. 4). The reduction of the CO pressure causes a simultaneous decrease of the intensity of all the components and at RT only a very weak band at 2121 cm^{-1} is present (fine curve). The broad and weak adsorption at lower frequencies can be tentatively related to Ag^0 sites, possibly stabilised by ceria and able to adsorb small amounts of CO.

Very similar spectroscopic feature were observed in the corresponding spectra of oxidized and reduced AgCeMDP, however bands were with lower intensity. These observations implied lower numbers surface sites, able to activate CO.

The admission of oxygen at RT on preadsorbed CO on the reduced samples produces a band at 2162 cm^{-1} (not shown). According to previous results on Ag/titania, the band at 2162 cm^{-1} can be assigned to CO on Ag$^{\delta+}$ sites exposed at the surface of the Ag$_x$O layer [6].

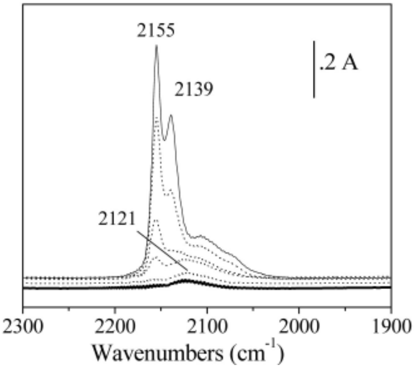

Figure 4. *FTIR absorbance spectra of 5.5 mbar CO adsorbed on reduced AgCeDP during a gradual increase of the temperature from 90 up to 300 K (between fine and bold curves) in carbonilyc region.*

XPS technique was used to characterise the nature of the surface of the Ag/ceria catalysts. The analysis of Ce 3d XPS spectra of fresh (as-prepared) catalysts indicates the presence of stoichiometric CeO$_2$ on the surface. The binding energies of six peaks, corresponding to the three pairs of spin-orbit doublets obtained by curve fitting are in good agreement with the data for stoichiometric CeO$_2$ [7,8]. Upon reduction, two new peaks appear at 885.23 and 904.04 eV. Moreover, in combination with the appearance of these peaks, the relative areas of the peaks at 889.16 and 907.68 eV, as well as that at 917 eV, decrease. These changes are caused by the reduction of Ce^{4+} and the appearance of Ce^{3+}. The XPS spectra of Ce 3d core electron levels of fresh and reduced silver-containing catalyst prepared by deposition-precipitation are illustrated in Fig. 5. The spectrum of pure ceria is also shown for comparison.

There are 8 peaks assignments in the spectra, labeled according to the convention established by Burroughs [9]. The peaks U, U″, U‴ and V, V″, V‴ refer to $3d_{3/2}$ and $3d_{5/2}$, respectively. These peaks are characteristic of the Ce(IV) 3d final state. At the same time, the peaks U′ and V′ (at about 903 and 885 eV) refer to $3d_{3/2}$ and $3d_{5/2}$, respectively. They are present for the Ce(III) 3d final state [10]. The increased intensity of the peaks at 884.93 and 903.53 eV in the XPS spectrum of reduced AgCeDP in comparison with those observed on the fresh catalyst is clearly seen. The decreased intensity of the peak at 917 eV is observed, too. The reduction of MDP-prepared silver-promoted catalyst causes similar changes on the surface, but Ce^{3+} content is lower than that on the surface of DP-prepared ones (not shown).

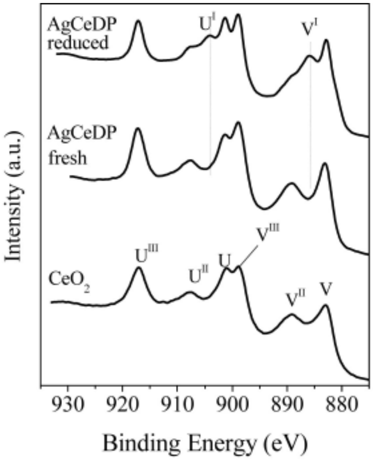

Figure 5. *Ce 3d XSP spectra of fresh CeO_2 and AgCeDP – fresh and reduced.*

The calculation of the Ce^{3+} concentration, according to equations in [10] evidences that the atomic content of Ce^{3+} on the catalysts surface increases after reduction (Table 1). The presence of Ce^{3+} on the surface of fresh samples may be caused by X-ray induced reduction of CeO_2, in agreement with the data from the literature [10]. The promotion by silver enhances the oxygen mobility and facilitates the creation of surface oxygen vacancies. Moreover, the data reveal that the preparation method influences the surface reduction of ceria and this effect is stronger on the catalysts prepared by deposition-precipitation.

Table 1. *Surface concentration of Ag and Ce^{3+}, calculated by XPS data*

Catalysts	Surface concentration of Ag, (at. %)		Surface concentration of Ce^{3+}, (at. %)	
	fresh	reduced	fresh	reduced
AgCeDP	2.19	2.16	0.19	0.44
AgCeMDP	0.60	0.60	0.18	0.31

The Ag 3d XPS peaks of fresh and reduced Ag/ceria catalysts are presented in Fig. 6. The BE of the 3d$_{5/2}$ and 3d$_{3/2}$ peaks (368.6 and 374.6 eV, respectively) of fresh and reduced samples are in agreement with those reported in the literature for metallic silver [11]. No shift of the peaks is observed after reduction. The only difference is that the peaks of fresh AgCeDP are broader (FHWM = 2.4) compared to that of the reduced sample (FHWM = 1.7). The decrease in the width of the peaks after reduction may be attributed to the presence of partially oxidized Ag cations or adsorbed oxygen species, as suggest our FTIR data. Moreover, structures due to chemisorbed and subsurface O species are observable in O 1s spectra of fresh silver/ceria catalysts (not shown). XPS measurements evidence also that the atomic concentration of Ag on the surface of the DP-prepared catalysts is higher than that observed on the catalyst prepared by MDP (Table 1). These results, as well as the higher Ce^{3+} surface concentration over reduced DP-prepared catalyst support the suggestion that nanosized metallic particles in close contact with oxygen defects on ceria are responsible for the higher catalytic activity of this catalyst.

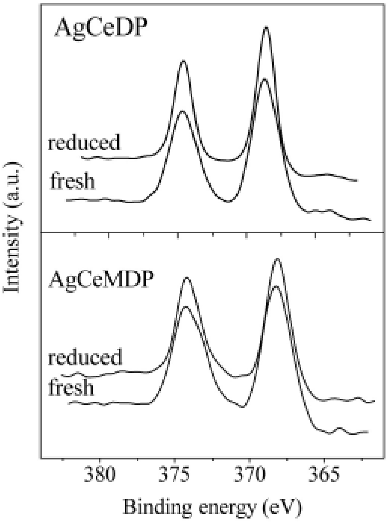

Figure 6. *Ag 3d XPS spectra of fresh and reduced Ag/ceria catalysts prepared by DP and MDP methods.*

2. Catalytic activity

Figs. 7–9 show the conversion curves vs. temperature over Ag/ceria catalysts. The figures demonstrate the role of two different synthesis procedures on the CO, CH_3OH and $(CH_3)_2O$ oxidation activity of these catalysts. Ag/CeO_2 sample prepared by DP shows higher CO and CH_3OH oxidation activity than that of MDP – prepared. The most pronounced effect of different preparation methods was registered in the CO oxidation reaction (Fig. 7). The activity increased with increasing temperature and reached 50 % CO conversion at 373 K over DP-prepared sample and at 433 K over MDP-prepared. Almost 100 % CO oxidation was achieved over AgCeDP sample at 423 K and at 493 K over AgCeMDP.

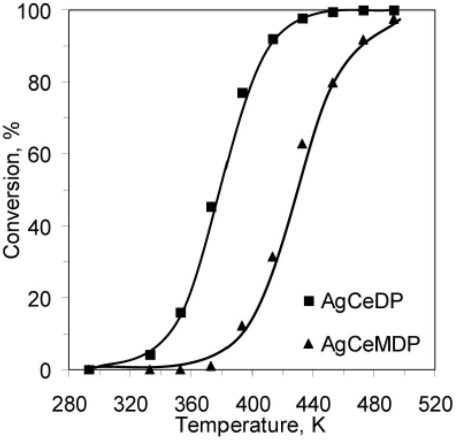

Figure 7. *Temperature dependence of CO conversion over Ag/ceria catalysts prepared by DP and MDP methods.*

The comparison of CH_3OH oxidation activity data for both investigated samples confirmed better behavior of AgCeDP. The results have shown that at 373 K were attained 90 and 15 % conversion over DP – and MDP-prepared Ag/CeO_2, respectively (Fig. 8).

The catalytic performance for $(CH_3)_2O$ oxidation of the samples is demonstrated in Fig. 9. Both catalysts reached maximum conversion at about 413 K, 11 % and 6 % over MDP – and DP-prepared Ag/CeO_2, respectively. The increase of the reaction temperature to 540 K slightly improves the catalytic activity of AgCeDP.

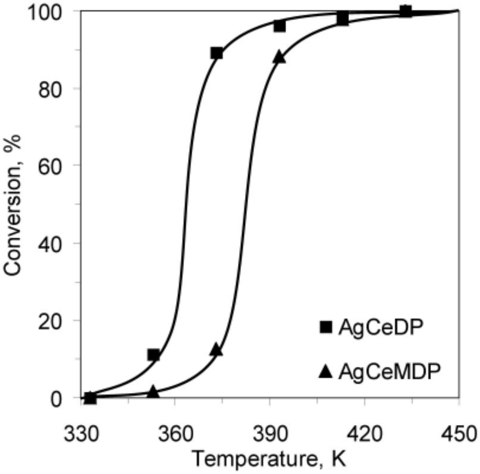

Figure 8. *Temperature dependence of* CH_3OH *conversion over Ag/ceria catalysts prepared by DP and MDP methods.*

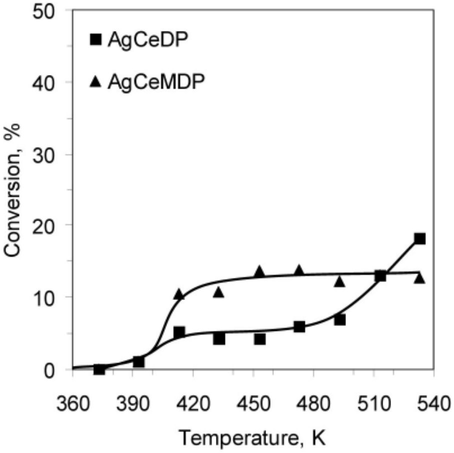

Figure 9. *Temperature dependence of* $(CH_3)_2O$ *conversion over Ag/ceria catalysts prepared by DP and MDP methods.*

The catalytic data analysis reveals that deposition-precipitation is more suitable methods for synthesis of active ceria-based catalysts. Deposition-precipitation has the advantage over coprecipitation to allow preparation of catalysts with metallic particles localized mainly on the surface of the supports, avoiding encapsulation of active sites within the support. Recently, catalytic combustion of VOCs and preferential oxidation of CO (PROX) was studied over IB metal/ceria catalysts [12]. It was proposed that the presence of smaller crystallites of both IB metal and ceria result in a larger enhancement of mobility/reactivity of surface ceria oxygens, involved in both reactions through a Mars–van Krevelen mechanism.

The impact of the preparation method on the performance of Ag/ceria catalysts can be reasonably rationalized on the basis of different surface concentration of both silver nanoparticles and reactive ceria oxygens sites. It could be suggested that differences in perimeter interface around silver particles, acting as the site for oxidation reaction, affect the activity of the studied catalysts.

CONCLUSION

The application of two different preparation methods of Ag/CeO_2 catalysts leads to significant differences in their catalytic activity for oxidation of CO, CH_3OH and $(CH_3)_2O$. The experimental results revealed that deposition-precipitation is more suitable method for synthesis of Ag/ceria catalysts because it allowed significant part of metal promoter to be exposed at the catalyst surface. FTIR spectra of CO adsorbed on oxidized and reduced catalysts and XPS measurements evidenced higher concentration of Ag on the surface of the catalyst prepared by DP than that on the catalyst prepared by MDP. The higher surface concentration of silver nanoparticles and Ce^{3+} over reduced DP-prepared catalyst supports suggestion that nanosized metallic particles in close contact with oxygen defects on ceria are responsible for better catalytic performance of this catalyst.

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