

Silver-based catalysts for preferential CO oxidation in hydrogen-rich gases (PROX)

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Silver samples were prepared by impregnation of different supports (SiO₂, CeO₂, and MnO₂) with aqueous solution of AgNO₃. The catalysts were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, temperature-programmed reduction, temperature-programmed desorption of oxygen, high resolution SEM, in situ diffuse reflectance infrared Fourier transform spectroscopy of adsorbed CO, and tested in the reaction of preferential CO oxidation in H₂-rich gases. A 15%Ag/SiO₂ sample pretreated in pure oxygen showed the best catalytic performance. It is suggested that oxidative pretreatment leads to the formation of surface and subsurface oxygen species, which rearrange the silver surface thus increasing significantly silver catalyst activity for CO oxidation in hydrogen-rich gases.

Key words: Ag/SiO₂ catalyst, Ag/CeO₂ catalyst, Ag/MnO₂ catalyst, CO oxidation, PROX.

INTRODUCTION

CO preferential oxidation in hydrogen-rich gases (PROX process) has been studied for application to polymer electrolyte membrane fuel cells (PEMFCs) to reduce CO in the fuel gases below 10 ppm. The catalysts, proposed so far for the PROX process, are based mainly on noble metals such as Pt, Rh, and Ru, deposited on different supports with or without promoters [1–9]. The working temperature of these catalysts is within the range of 130–200 °C [10–12]. It seems to be too high to match subsequent reaction in a PEMFC, which is usually carried out at 50–125 °C [13]. Decreasing the reaction temperature and search for more economic catalysts for PROX are challenging objectives for the near future. IB-group metals, supported on suitable metal oxides, are very promising as PROX catalysts. Highly dispersed gold exhibits an extraordinarily high activity in low-temperature CO oxidation [14–19], however, it deactivates rapidly during long-term operation [20–22]. A very promising catalytic system that has received a great attention during the last years is the copper-cerium mixed oxide composites [23–24]. These oxides show a practically constant and high selectivity towards CO oxidation within a wide temperature interval. However, satisfactory CO conversion (about 90%) is obtained at a temperature above 150 °C [25–28]. Silver, another member of group IB, has been scarcely investigated as a PROX catalyst in spite of its high activity in low temperature CO oxidation in absence of hydrogen [29–31]. Reports

concerning utilization of Ag as catalyst for selective CO oxidation are few and they examine only mono-metallic silver supported on SiO₂ or carbon [32–34] and composites like Ag/Co and Ag/Mn oxides [35, 36]. Qu and co-workers [31–33] have observed that SiO₂ and siliceous mesoporous materials, such as MCM-41 and SBA-15, are suitable supports for active PROX catalysts. An increase in Si/Al ratio of H-ZSM-5-supported catalysts results in a decrease in activity due to strong interaction between Ag atoms and Al ions in the zeolite framework. The authors communicate a maximal conversion of about 40% at 45 °C. Zhang et al. [37] have found that the Si/Al ratio of the support has an important effect on the structure of Ag catalysts and as a consequence on the catalytic activity and selectivity in preferential CO oxidation. Derekaya and co-authors found that a 50/50 (mol.%) Ag-Co mixed oxide sample calcined at 200 °C was the most active catalyst and a 50/50 (mol.%) Co-Ce mixed oxide sample calcined at 200 °C was the most selective catalyst for PROX process [35]. Very active and stable Ag/OMS-2 catalysts were obtained by Hu *et al.* [38] through a simple reflux method. It was found that addition of a small amount of Al is beneficial to the formation of small sized highly dispersed Ag metal particles.

This paper is a first part of our research targeting at the influence of metal oxides of high oxygen capacity as CeO₂ and MnO_x on the properties of silver catalysts in the reaction of selective CO oxidation in hydrogen-rich gases. Preliminary catalytic tests showed that silica is the most suitable support. The main objective of the present study is to investigate the effect of silver loading on the activity and selectivity of Ag/SiO₂ in PROX process.

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EXPERIMENTAL

Catalysts preparation

Silver catalysts were prepared by addition of respective support (SiO₂, CeO₂ or MnO₂) to an aqueous solution of AgNO₃ to obtain 5, 10, and 15 wt.% Ag on SiO₂ (Aerosil, S_{BET} = 147 m²/g), and 5 wt.% Ag on CeO₂ (S_{BET} = 130 m²/g) and MnO₂ (Fluka, S_{BET} = 58 m²/g). Reference data [32] and preliminary catalytic measurements showed that pretreatment in oxygen at high temperatures increased the catalytic activity. For this reason, all samples were calcined and pretreated in pure O₂ for 2 h at 450 °C before the catalytic tests.

Catalyst characterization

Powder XRD patterns were collected at room temperature in a step-scan regime (step = 0.05°, count time = 2 s) on a Siemens D-501 diffractometer using CuK_α radiation (λ = 1.5718 Å). XRD data processing was performed by using X'Pert HighScore program. SEM images were recorded by a field emission scanning electron microscope (FE-SEM) model S5200. Temperature-programmed reduction (TPR) was carried out by an equipment described elsewhere [38] using a flow mixture of 5% H₂ in Ar at a flow rate of 10 ml/min, and a temperature ramp of 10 °C/min up to 900 °C. Prior to TPR experimental run the samples were treated in He for 30 min at 150 °C. Temperature-programmed desorption of oxygen (TPD-O₂) experiments were performed on the same experimental setup. Oxygen desorbed from the samples was determined by means of a mass spectrometer (QMS-422 Baltzers) and a thermal conductivity detector. Before TPD-O₂ experiment each sample was pretreated in oxygen flow for 2 h at 450 °C, cooled down to room temperature in oxygen followed by 30 min in He. Desorption of O₂ was carried out in He flow until reaching 900 °C at a ramp rate of 20 °C/min.

X-ray photoelectron measurements were conducted on an ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of 5.10⁻¹⁰ mbar using a twin anode MgKα/AlKα X-ray source with excitation energies of 1253.6 and 1486.6 eV, respectively. Passing through a 6-mm slit (entrance/exit) of a hemispherical analyser, electrons of 20 eV energy were detected by a channeltron. Because of small concentration and natural width of the AgMNN peak, 50 eV pass energy was used. The spectra were recorded with a total instrumental resolution (as measured with the FWHM of Ag3d_{5/2} photoelectron line) of 1.06 and 1.18 eV for MgKα and AlKα excitation sources, respectively. The energy

scale was calibrated by normalizing the Si2p line to 103.3 eV. Spectra processing included subtraction of X-ray satellites and Shirley-type background [39]. Peak positions and areas were evaluated by a symmetrical Gaussian-Lorentzian curve fitting. Relative concentrations of the different chemical species were determined by normalization of the peak areas to their photoionization cross-sections calculated by Scofield's approach [40].

Carbon monoxide adsorption on 15% Ag/SiO₂ catalyst was studied by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Nicolet 6700 spectrometer equipped with a high temperature/vacuum chamber installed in Collector II accessory (Thermo Spectra-Tech). The CO was adsorbed from CO + Ar mixture flow at room temperature. Experiments were carried out on oxidized or calcined samples, being pretreated in O₂ + Ar for 2 h at 450 °C or in air for 2 h at 450 °C, respectively.

Catalytic activity measurements

The catalytic activity tests were carried out in a continuous flow type glass reactor at atmospheric pressure with a catalyst bed loading of about 0.8 cm³ (fraction 0.25–0.31 mm). The gas mixture consisted of 1 vol.% CO, 1 vol.% O₂, 40 vol.% H₂, and He as balance to 100 vol.%. External mass transfer limitations were minimized by working at high GHSV (18750 h⁻¹). The reaction temperature was measured by an internal thermocouple. Converted gas mixture analysis at the outlet was performed by a HP5890 series II gas chromatograph equipped with a thermal conductivity detector and Carboxen-1000 column. Helium was used as a carrier gas. Aalborg mass flow controllers were used to regulate gas flow rates. Before catalytic test each sample was calcined and pretreated in oxygen for 2 h at 450 °C.

Carbon monoxide conversion was calculated based on changes in CO concentration:

$$\text{CO}_{\text{conversion}} = ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) * 100 / [\text{CO}]_{\text{in}}, \quad \%$$

Oxygen conversion degree was based on O₂ consumption:

$$\text{O}_{2\text{conversion}} = ([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}) * 100 / [\text{O}_2]_{\text{in}}, \quad \%$$

Finally, the selectivity for CO oxidation (S_{CO}) was calculated based on the oxygen mass balance as follows:

$$S_{\text{CO}} = 0.5 * ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) * 100 / ([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}) \quad \%$$

RESULTS AND DISCUSSION

Preliminary tests with 5% Ag on a different

support, SiO₂, CeO₂, and MnO₂, indicated that 5% Ag/SiO₂ and 5% Ag/CeO₂ samples reached a maximal activity in the temperature range of 60–100 °C (Fig. 1A). A maximum of catalytic activity (20% CO conversion) with Ag/MnO₂ was observed at a higher temperature – 130 °C. Since the catalyst of better performance was Ag/SiO₂, silica was the selected support for future preparation of samples of different Ag loading (5, 10, 15 wt.%). As it was mentioned in the Experimental section, all samples

were pretreated in oxygen before catalytic tests. Figure 1B presents CO and O₂ conversions, and selectivity to CO₂ with temperature on silica-supported catalysts of different Ag loading. The conversion curves are ‘volcano-shaped’ and a maximum was reached within the temperature interval of 70–100 °C. The activity increased with the increase in Ag loading. For all samples, the selectivity to CO₂ decreased with temperature rise.

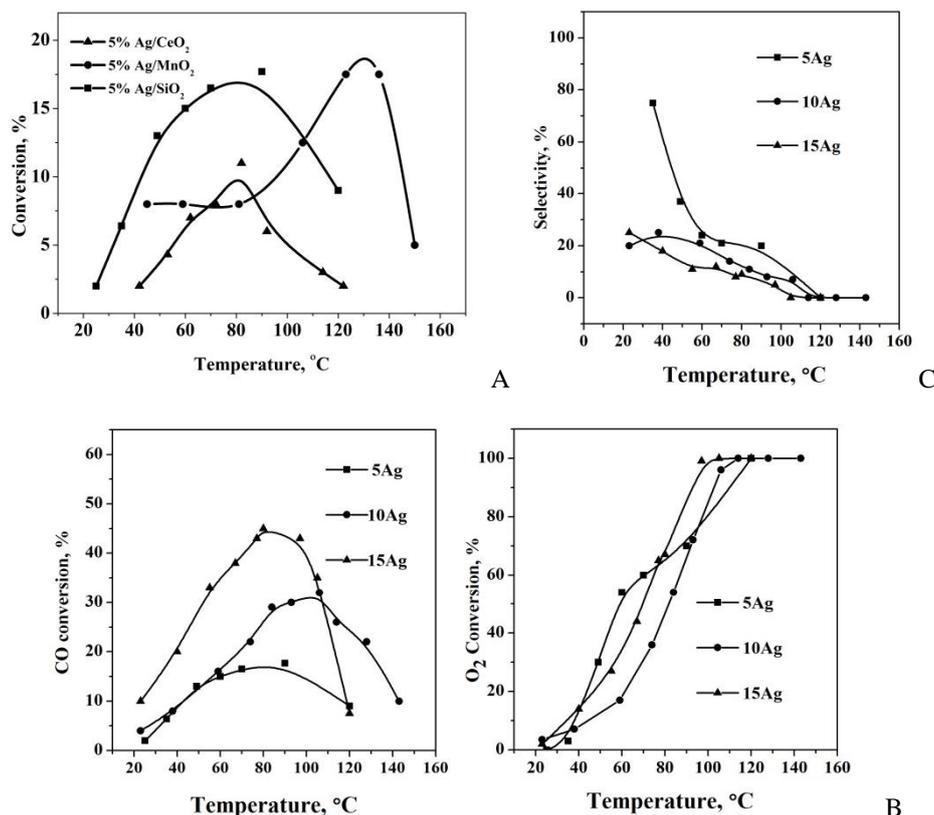


Fig. 1. A. CO conversion degree with catalyst bed temperature on Ag supported on different oxides; B. CO (a) and O₂ (b) conversion degrees with temperature on silica-supported catalysts of different Ag loading; (c) selectivity to CO₂.

A drop in CO₂ selectivity observed with all samples and compatible with results reported in the literature is attributed to the fact that the activation energy of H₂ oxidation was found to be considerably higher than that of CO oxidation [41,42]. A sample of the most active catalyst, 15% Ag/SiO₂, reached a maximum activity of 60% within 70–90 °C, i.e. it dropped down. This catalyst was further examined by different physicochemical methods.

According to XRD data, silver was in the form of Ag⁰ (01-087-0719) in all silver samples after pretreatment in oxygen. Calculated silver particles size by using Scherrer equation showed increasing values with increasing loading from 5 nm for 5% Ag up to 23 and 47 nm for 10% Ag and 15% Ag, respectively (Fig. 2).

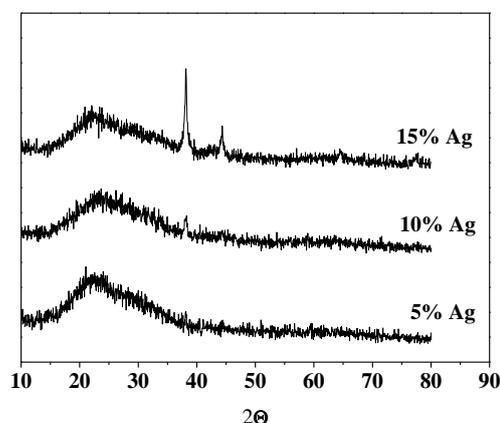


Fig. 2. XRD patterns of monometallic silver samples after treatment in oxygen flow at 450 °C.

Figure 3 displays SEM images obtained from backscattered electrons for 15% Ag. As is known, these images depend on the atomic number contrast among the different constituents of the sample. Bright zones represent heavy elements, while dark ones correspond to light elements. Thus, the bright zones can be assumed to be silver, while the dark counterparts correspond to the support. Spherical silver particles with mean diameter of 20–40 nm are visible in the micrograph of 15% Ag/SiO₂ sample and this manifests good coincidence with XRD data.

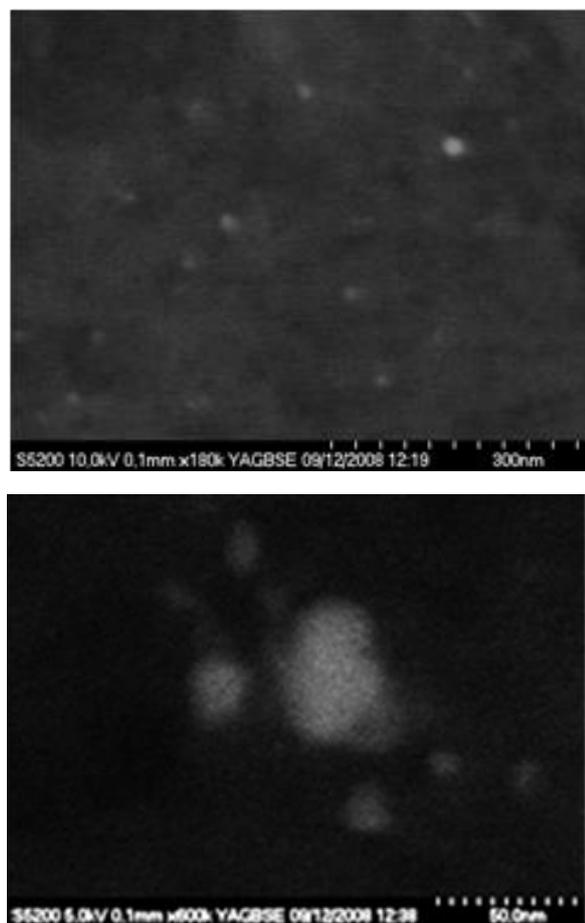


Fig. 3. SEM images of 15% Ag/SiO₂ after calcination.

O₂-TPD was used to study oxygen interaction with the silver surface. Four desorption peaks are visible in the spectrum (Fig. 4A): a very low intensity peak at 130 °C, and peaks at 410, 493, and 750 °C. Desorption temperatures of molecular, atomic, and lattice oxygen have been reported to be 150–470, 550–650, and over 750 °C, respectively [43–44]. Qu *et al.* observed two desorption peaks of oxygen in the TPD spectrum of Ag/SiO₂ catalyst pretreated with oxygen at 500 °C [32]. A peak at about 500 °C is assigned to desorption of bulk oxygen species (O_β), which diffuses *via* an interstitial diffusion mechanism.

The desorption peak at higher temperatures (≈ 700 °C) is attributed to subsurface oxygen (O_γ) [45–46]. Based on the results cited above, we suppose that the low temperature peaks at 120 and 401 °C arise from desorption of adsorbed molecular oxygen, the peak at 493 °C originates from atomic oxygen desorption, and the peak at 750 °C comes from desorption of subsurface oxygen species. Two reduction peaks at 92 and 113 °C are observed in the TPR profile of 15% Ag/SiO₂ catalyst (Fig. 4B). According to some authors [47], a peak at 108 °C can be ascribed to reduction of oxygen species on finely dispersed silver. Taking into account that XRD data are pointing to the presence of metallic silver only, hydrogen consumption at 92 and 113 °C is ascribed to the reduction of surface oxygen species.

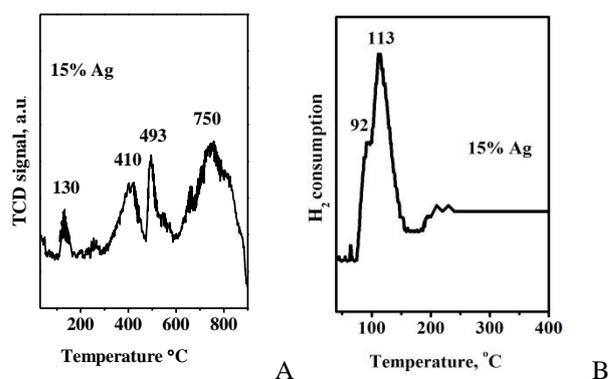


Fig. 4. O₂-TPD (A) and TPR (B) patterns of 15% Ag/SiO₂ catalyst pretreated with oxygen at 450 °C.

XPS experiments were carried out on calcined and oxidized 15% Ag/SiO₂ samples in order to estimate silver oxidation state on the surface (Fig. 5). As the characteristic 3d states of oxidized and metallic silver are closely positioned together (within 0.5 eV) [46], the binding energy values of Ag3d do not identify unambiguously silver particle oxidation state.

Auger parameter ($\alpha = EK(\text{AgMNN}) + EB(\text{Ag}3d_{5/2})$) was used for precise determination of the chemical state of Ag, thus eliminating surface effects of electrostatic charging [49,50]. Two Auger peaks are visible in the XPS spectrum of 15% Ag sample oxidized for 2 h at 450 °C and the α parameters are 724.0 eV (356.1 + 367.9 eV) and 726.1 eV (358.2 + 367.9 eV), respectively. Since the Auger parameters of Ag⁰ and Ag⁺ are 726.0 eV and 724.5 eV [50], it is clear that part of the surface silver species in the 15% Ag sample after pretreatment in oxygen are in the form of Ag⁺ and some occur as Ag⁰, i.e. both Ag⁺ and Ag⁰ species are present on the surface of the monometallic silver sample after oxidative pretreatment.

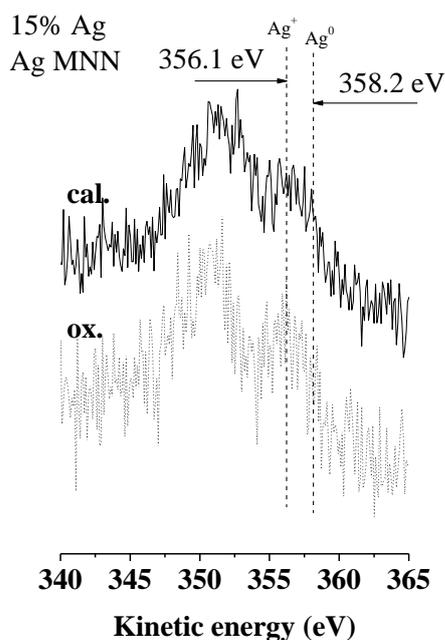


Fig. 5. XP spectra of Ag MNN registered on oxidized (2 h, 450 °C in oxygen) and calcined silver samples.

Qu *et al.* [32] claim that oxygen pretreatment leads to the formation of subsurface oxygen, which induces rearrangement of the silver surface, facilitates the formation of active sites for CO oxidation, and enhances the ability of the catalyst to adsorb CO and activate oxygen. Carbon monoxide was found to interact directly with subsurface oxygen species at room temperature, which might be one of the reasons for high activity of the catalyst for CO oxidation. In view of this, DRIFT spectroscopy of adsorbed CO was applied to shed some additional light on the state of the catalyst surface.

It is well known that in situ DRIFT spectroscopy is one of the most powerful techniques to obtain information about the type of the active sites, their stability and reactivity, chemical state of the surface under static and dynamic conditions within a wide temperature range and after different kinds of pretreatment. The most frequently used probe molecule to study supported catalysts is carbon monoxide due to $\nu(\text{C}-\text{O})$ sensitivity to the chemical state of the metal atom(s) to which it is being coordinated.

We made an attempt to gain further information on the state of the catalyst surface by adsorption of CO after various pretreatments. The IR spectra of CO adsorbed on calcined and oxidized 15% Ag/SiO₂ samples are shown in figure 6. Only gas-phase spectra are visible after CO adsorption from CO + N₂ mixture on the calcined sample. After 20 h exposure at room temperature a band for gaseous CO₂ appeared (2300–2400 cm⁻¹) indicating that the CO oxidation occurred at room temperature.

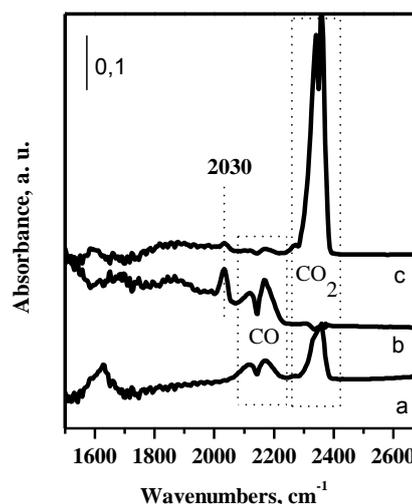


Fig. 6. Diffuse-reflectance infrared spectra of CO adsorbed at room temperature on 15% Ag/SiO₂ after different pretreatments: a - 20 h exposure to CO after calcination; b - 1 h exposure to CO after oxidation; c - 20 h exposure to CO after oxidation.

Most probably, CO reacted with surface or sub-surface oxygen formed during calcination in air. No O₂-TPD was carried out after calcination, however, it can be assumed that some oxygen surface and subsurface species were formed after this pretreatment. The picture was completely different after adsorption of CO on oxidized surface: the band at 2030 cm⁻¹ is visible in the IR spectra. There are few FTIR studies dedicated to the adsorption of CO on supported Ag⁰ particles as summarized by Müslehiddinolu and Vannice [51]. Before their study, literature data mainly concluded about the absence of IR bands after adsorption of CO at 300 K. [52–54]. According to Müslehiddinolu and Vannice about 10% of the total amount of Ag⁰ sites are able to adsorb CO and they are either on very specific planes or on steps [51]. Gravejat *et al.* [55] have established by volumetric measurements that the total amount of adsorbed CO species count for a small fraction of the superficial sites of reduced Ag particles implying that they are adsorbed on defect sites. According to the above-mentioned data [51–55] a band in the frequency range of 2020–2055 cm⁻¹ is due to formation of monocarbonyl CO-Ag⁰ species depending on pretreatment or CO partial pressure. Surface faceting has been observed in the case of thin films, single crystals, and supported catalysts after oxygen treatment [56,57]. Morphological changes of silver following a high-temperature treatment in oxygen have been directly observed in SEM micrographs by Nagy *et al.* [58].

Based on the assumption given above we can state that pretreatment in oxygen at 450 °C gave rise to silver surface rearrangement leading to the forma-

tion of sites suitably exposed to linear CO bonding. After 20 h exposure at room temperature in CO + N₂ mixture, the band for CO–Ag⁰ decreased its intensity along with the appearance of a band due to gaseous CO₂ to demonstrate interaction between adsorbed CO and subsurface oxygen. The band of linearly adsorbed carbon monoxide disappeared completely after a purge thus revealing its low stability.

CONCLUSIONS

According to the results presented above, we can conclude that supported silver catalysts are promising systems for selective oxidation of CO at low temperatures. Among all studied supports, silica was the most suitable. Oxidation pretreatment led to the formation of surface and subsurface oxygen species that rearranged the silver surface and significantly affected silver catalyst activity for CO oxidation in hydrogen-rich gases.

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КАТАЛИЗАТОРИ НА ОСНОВАТА НА СРЕБРО ЗА СЕЛЕКТИВНО ОКИСЛЕНИЕ НА СО В БОГАТИ НА ВОДОРОД СМЕСИ

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(Резюме)

Получени са сребърни катализатори посредством импрегниране на различни носители (SiO_2 , CeO_2 и MnO_2) с воден разтвор на AgNO_3 . Те са охарактеризирани с помощта на различни методи: рентгенова дифракция, рентгенова фотоелектронна спектроскопия, температурно програмирана редукция, температурно програмирана десорбция на кислород, сканираща електронна спектроскопия с висока резолюция, *in situ* дифузно-отражателна инфрачервена спектроскопия на адсорбиран СО. Образците са тествани в реакция на селективно окисление на СО в богати на водород смеси. Установено е, че проба с най-добра каталитична активност е предварително обработен в чист кислород образец Ag/SiO_2 . Предполагано е, че използването на окислителна предварителна обработка води до образуване на повърхностни и подповърхностни кислородни форми и преструктуриране на повърхността на сребърните частици, което значително увеличава активността на катализатора в изследваната реакция.