

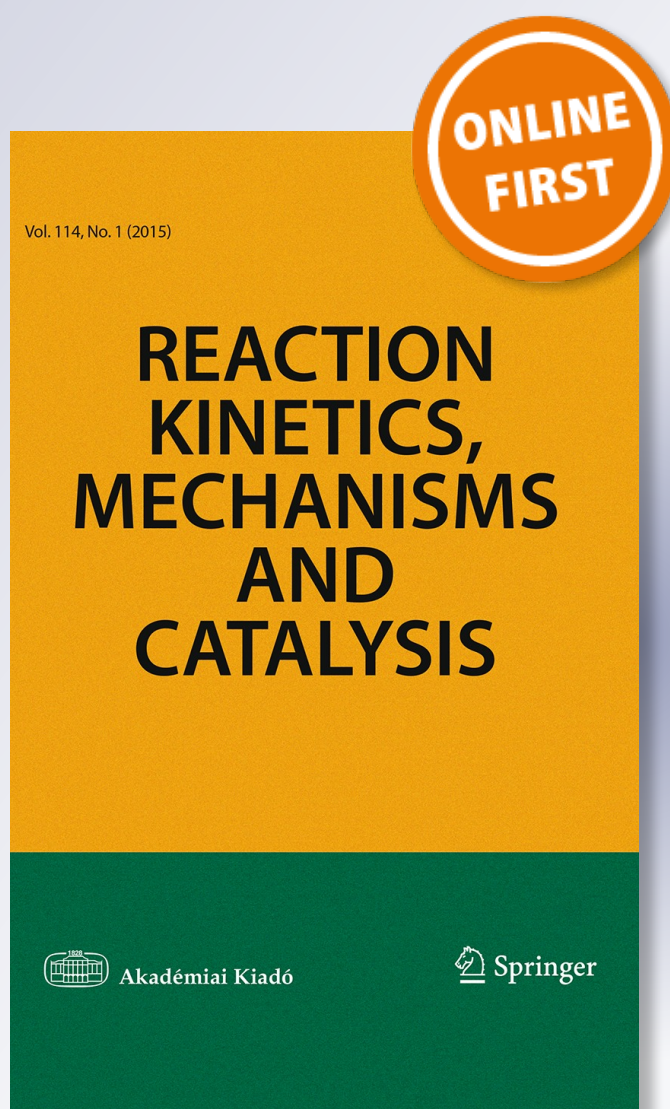
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Bimetallic Au–Ag/SiO₂ catalysts: comparison in glucose, benzyl alcohol and CO oxidation reactions

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Abstract SiO₂ supported Au–Ag nanoparticles prepared by the adsorption of bimetallic colloids of various Ag/Au molar ratio (0/100, 13/87, 23/77, 33/67, 51/49, 100/0) were characterized and studied in selective glucose oxidation reaction earlier (Benkó et al., *Applied Catalysis A* 479:103–111, 2014 [32]). The same catalysts of mean metal particle size between 3 and 5 nm were applied and compared in benzyl alcohol and CO oxidation after both calcination and successive reduction treatments. In temperature programmed CO oxidation tests of the Au-containing samples, different activity zones appeared with several conversion maxima, which were affected differently by the Au/Ag ratio and pretreatment conditions. CO oxidation results suggested the coexistence of several types of active sites in various population in the different samples. In all the three reactions, the sample with Ag/Au = 23/77 composition was the most active in calcined and also in reduced state, showing synergetic effect compared to the monometallic analogous. Upon H₂-treatment in benzyl alcohol oxidation, a significant, in glucose oxidation, a slight activity increase was observed for all the samples. In CO oxidation, the reduction treatment induced deactivation of sample with Ag/Au = 23/77 and 13/87 below 125 °C, while in the higher temperature region, all the samples were highly activated.

Introduction

Beside the outstanding low temperature CO oxidation and other total oxidation activity of nanodispersed gold catalysts supported typically on reducible oxides [1],

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its high potential was demonstrated also in key synthetic reactions [2–6] as a result of intense research activity in this field. Remarkably, a wide range of selective oxidative transformations performed by O_2 are promoted by gold at relatively low temperature and with very high selectivity. In these reactions, gold in very different size was reported to be efficient. Regarding the support effect, on the contrary to the CO oxidation reactions, where the reducible or semi-conductive oxide supported or promoted gold provide typically much higher activity compared to the so called inert SiO_2 , Al_2O_3 and carbon supported gold nanoparticles, in selective oxidation reactions, the latter catalysts may possess as high or even higher activity and selectivity [7]. Recently, highly active Au in CO oxidation could be prepared also on inert supports (SiO_2 [8–12] and Al_2O_3 [13]) with comparable activity to active oxide supported gold catalysts, when its small particle size was provided [14]. The origin of Au catalytic activity is still a topic of intense debate, the role of particle size, support, promoters, preparation, pre-treatments are investigated in the different catalytic processes.

The catalytic oxidation efficiency (activity and selectivity) of gold could be significantly improved or modified in different reactions combining it with a second metal as Pd, Pt, Ag, Cu and the occasionally studied Ni, Co, Rh, Ir. However, the reaction mechanisms, the reasons of the observed bimetallic effects are not well clarified, yet. Altered electronic state of the metals, O_2 activation ability introduced by the second metal, decrease of ensemble sites was related to the modified catalytic properties [15]. A lot of work was done on the investigation of Au–Ag co-operation in bimetallic oxidation catalysts. Synergetic activity increase of Au–Ag bimetallic system was reported in oxidation of CO [16–25], glucose [26–32] and alcohols [33–36].

Iizuka et al. experienced enhancing CO oxidation activity of Au powder containing Ag impurities in correlation with increasing surface concentration of Ag. The H_2 -treated samples were more active than the O_2 -treated ones [16]. The research group of Mou, in a series of publications, demonstrated the increased catalytic activity of aluminosilicate supported reduced AuAg alloy particles in CO oxidation that correlated with increased formation of O_2^- , superoxide, the favored electron transfer from the AuAg alloy to O_2 compared to monometallic catalysts. Despite the large particles (20–30 nm), exceptionally high activity was demonstrated for bimetallic catalysts, the best at Au/Ag = 3:1 composition with Au/Ag = 0.75:1 surface atomic ratio [17, 18]. With decreasing the Si/Al ratio, the AuAg particle size could be lowered and O_2^- concentration could be enhanced due to the defect sites of the support associated with Al^{3+} cations and even higher activity could be achieved [19]. In the case of 20–30 nm size AuAg particles, for the explanation of extra high activity, highly active AgO_x /Au formation was supposed as a result of phase segregation during the course of CO oxidation reaction [15]. Aluminosilicate supported 4–6 nm size AuAg alloyed particles produced by a two-step preparation on the functionalized support followed by calcination and reduction showed also synergetic activity increase, in the highest extent at Au/Ag = 8:1 [20]. According to the feasible mechanism suggested for CO oxidation on AuAg nanoparticles, the O_2 activation takes place on Ag sites forming O_2^- (superoxide) that reacts with CO adsorbed on neighboring Au sites. Qu and co-

workers observed clear synergetic CO oxidation activity increase of bimetallic AuAg/SBA-15 (d: 4–6 nm) after reduction preceded by calcination at Au/Ag = 5.4 bulk and Au/Ag = 2.3 surface molar ratio [22]. The synergetic effect of AuAg alloys in CO oxidation (and preferential CO oxidation in H₂) was reported also on TiO₂ [23] and CeO₂ [24] supported and unsupported nanoporous AuAg catalysts [25]. In the case of the TiO₂ supported system, it was suggested that TiO₂ was not much involved in the reaction, it must have taken place mainly on the bimetallic particles, since no additional activity increase was found compared to inert silica supported AuAg catalysts. DFT calculations of Chang et al. showed that Ag₂₅Ag₃₀ clusters provide larger co-adsorption energy of CO and O₂ compared to monometallic ones that may help CO oxidation through OOCO complex [37].

Unsupported PVP protected bimetallic AuAg nanoparticles with different relative concentration of the metals prepared in different ways (by the co-reduction of AuCl₄[−] and Ag⁺ precursor ions, by the reduction of Ag⁺ ions on the surface of preformed Au NPs [27, 28] and by physical mixing of Au and Ag monometallic NPs [30]) were studied and applied in glucose oxidation by Zhang and co-workers. The AuAg NPs of core–shell type arrangement with Au rich surface and Ag rich core of about 5 or 1.4 nm size presented synergetic activity increase, the largest at Au/Ag = 4 atomic ratio. Based on XPS and DFT calculation results it was explained by increased electron density on the metallic Au surface due to the charge transfer from the metallic Ag core and PVP stabilizer favoring O₂ activation [29].

In the aerobic oxidation of p-hydroxybenzyl alcohol to corresponding aldehyde in aqueous solution PVP stabilized AuAg alloy clusters of about 2 nm particle size with Ag content. <10 % gave higher turnover frequency than the monometallic analogous. This was attributed also to the partial anionic character of Au detected by XPS, caused by electron transfer from PVP, Ag (if its content was below 20 %) and water molecules [33]. Tsukuda et al. suggested too that negatively charged Au clusters were the active sites in oxidative dehydrogenation of alcohols [38]. P123 stabilized alloyed AuAg colloid of 3–4 nm particle size formed by simultaneous reduction of Au and Ag precursor ions by NaBH₄ presented increased activity especially at Au/Ag = 9 and 19 atomic ratio in benzyl alcohol oxidation without the addition of base [36], and in the reaction with added Na₂CO₃ [35], respectively. In the former case, first 100 % benzaldehyde selectivity was observed, then appearance of trace amount of benzoic acid caused deactivation due to its strong adsorption on the surface of metal particles. In the presence of Na₂CO₃, no such inhibition was observed, but the benzaldehyde selectivity dropped and benzoic acid was the main product besides benzylbenzoate. In the case of SiO₂ supported AuAg bimetallic (Au/Ag: 5.5, 3.2, 1.9) catalysts of 3–4 nm metal particle size prepared by consecutive reduction of AuCl₄[−] and Ag⁺ on functionalized silica followed by calcination and reduction, benzyl alcohol oxidation activity was lower than that of the corresponding Au catalyst, and decreased with increasing Ag content accompanied by diminishing selectivity of benzaldehyde [34].

Understanding the mechanism and the structure of active sites involved in the catalytic turnover of different substrates may help to predict what type of catalyst is appropriate for a target reaction. In the case of Au–Ag bimetallic catalysts, numerous valuable investigations proved the synergetic co-operation of the two

metals in different oxidation reaction as CO, alcohols and glucose oxidation. The structure of the differently prepared systems were studied and correlated with the catalytic performance in separate investigations for the various reactions. However, almost none of the powerful techniques may give direct information on the structure of the active sites. The deductions on them are based on the compromise of results partly from bulk, several surface atomic layer or indeed topmost surface sensitive methods. On the other hand, by most of the techniques except microscopies, one gets average type results, which do not say much about the heterogeneity of the system. Since all the details and aspects of the catalyst structure is hardly recognizable, the comparison of a system in different processes can be the most efficient by studying them on the same catalyst samples. This may add extra information for the exploration of mechanism of the single reactions.

In our earlier study [7] SiO₂, CeO₂ and TiO₂ supported Au catalysts derived from Au colloid of two different sizes were compared in CO oxidation and glucose oxidation reactions after calcination. The opposite activity order of these samples were found in the two reactions, Au/SiO₂ were more active in selective glucose oxidation and less in CO oxidation. This suggested differing activation of reactants, also O₂ in the two reactions. Next AuAg/SiO₂ with various Ag/Au atomic ratios were prepared also by adsorption of preformed bimetallic nanoparticles stabilized in aqueous sol. They were characterized by UV–Vis spectroscopy, high resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) and studied in glucose oxidation reaction both after calcination and following reduction treatments. According to these, Au and Ag were distributed on the surface of the dominantly homogeneously alloyed metallic particles (of size between 3 and 5 nm) with surface atomic ratio (determined by XPS) hardly dissimilar in the two states and close to the bulk ratio. The glucose oxidation activity of SiO₂ supported samples of Ag/Au: 13/87, 23/77 and 33/67 showed similar synergism as reported also for unsupported AuAg nanoparticles by other groups.

Table 1 Metal loading, bulk and surface Ag/Au ratio and metal particle size in the catalyst studied taken from Ref. [32]

Catalysts	Metal loading (mmol/g _{cat})	Ag/Au bulk (atomic ratio)	Ag/Au _{XPS} after calc. (atomic ratio)	Ag/Au _{XPS} after red. (atomic ratio)	d _{Metal} after calc. (nm)	d _{Metal} after red. (nm)
Au/SiO ₂	0.19	–	–	–	4.8 ± 2.4	4.0 ± 2.0
13Ag87Au/SiO ₂	0.11	0.15	0.18	0.17	3.5 ± 2.3	3.1 ± 1.6
23Ag77Au/SiO ₂	0.11	0.30	0.34	0.28	2.9 ± 1.2	3.5 ± 1.7
33Ag67Au/SiO ₂	0.10	0.43	1.14	1.00	3.4 ± 2.5	3.3 ± 1.2
51Ag49Au/SiO ₂	0.10	1.04	1.17	1.17	5.2 ± 2.2	n.a.
Ag/SiO ₂	0.09	–	–	–	4.8 ± 2.2	4.9 ± 3.6

These results were published in Ref. [32]. In this paper, the effect of Ag/Au ratio and pretreatments were studied using the same catalysts in two other reactions, benzyl alcohol and CO oxidation in liquid and gas phase, respectively.

Experimental

Catalyst preparation and characterization

Table 1 presents the SiO₂ supported bimetallic Au–Ag and monometallic Au and Ag samples studied. Their preparation and structural characterization were reported in our previous publication [32]. Aqueous Au–Ag sols of various Ag/Au molar ratio (0/100, 13/87, 23/77, 33/67, 51/49, 100/0) were fabricated by consecutive reduction of AgNO₃ and HAuCl₄ precursors by NaBH₄ and stabilized by polyvinyl alcohol (PVA) in aqueous sol. The monometallic sols were prepared similar way. The preformed nanoparticles were adsorbed on the surface of Aerosil A200 silica helped by addition of poly-(diallyldimethylammonium)chloride (PDDA). After adsorption had been completed the solid was filtered, washed and dried at 60 °C. To remove the organic residues from the samples, they were calcined at 400 °C for 1 h in synthetic air flow (heating ramp 10 °C/min), then to assure the metallic state of the active phase reduction treatment was applied at 350 °C for 30 min (heating rate 5 °C/min) in flowing hydrogen (both in heating up and cooling down). Before and after the H₂ treatment samples were purged with inert gas.

Several structural characteristics of the catalysts (metal concentrations, surface Ag/Au molar ratio determined by XPS, metal particle size in calcined and reduced state) selected from Ref. [32] are collected in Table 1, which are necessary for the discussion of the recent results. The relative molar percentage of Ag and Au are given in the designations XAgYAu/SiO₂, as X and Y, respectively. The metal loading varied between 3.7 and 1.0 wt%, while the molar metal concentration of bimetallic catalyst were about the same.

Catalytic studies

The samples were tested in CO and benzyl alcohol oxidation reactions both after calcination and the following reduction treatment. The results will be correlated with those of the glucose oxidation measurements on the same catalysts reported in Ref. [32].

The CO oxidation was measured in a plug flow reactor of 4 mm inside diameter at atmospheric pressure connected to a quadrupole mass spectrometer (Balzers QME 125-2). 40 mg of ex situ calcined catalysts were studied in two or more temperature programmed (TP) heating–cooling cycles with ramp rate of 5 °C/min up to 400 °C with 10 min isotherm period. Next, after in situ reduction treatment, further TP-CO oxidation cycles were carried out. 0.52 % CO+10.2 % O₂ in helium reaction mixture was used with a 10 mL/min flowing rate. The CO conversion was calculated both on the basis of the CO consumption (using m/e = 28 signal corrected with intensity of that fragment belonging to CO₂) and CO₂ production

(based on $m/e = 44$ signal). The two conversion curves fitted well confirming that the only transformation is the CO oxidation into CO_2 , except three cases. On $13\text{Ag}87\text{Au}/\text{SiO}_2$, $51\text{Ag}49\text{Au}/\text{SiO}_2$ and Ag/SiO_2 samples in the first heating of the ex situ calcined samples, a tiny amount of CO_2 evolved with a maximum rate at around 370°C that was not originated from CO conversion, but rather from some contamination of the catalysts. The first TP-CO oxidation cycle served for the conditioning of the catalysts and attaining quasi steady state of the system, the following TP-CO oxidation runs were applied for the characterization of the catalytic activity.

The initial reaction rates were calculated at several temperatures related to 1 mol of active metal for comparison with those of benzyl alcohol and glucose oxidation. For that pseudo-first order rate constants were determined using the integral reactor equation: $k_{\text{CO}} = -\ln(1 - x)F_0/W/C_M$, where x is the conversion at a given temperature, F_0 (mL s^{-1}) the volumetric reagent gas flow, W is the weight of the catalysts (g) and C_M molar concentration of active metal (Au+Ag) in the catalyst (mol/g).

The benzyl alcohol oxidation was performed in liquid phase in a thermostated glass reactor equipped with electronically controlled magnetic stirrer and a reflux condenser. In a typical reaction condition, 3 mL (29 mmol) alcohol substrate was added into 27 mL toluene, and the solution was heated to 80°C under stirring (1,350 rpm). O_2 was bubbled through the suspension with a flow rate of 150 mL/min (1 atm). After 20 min, the reaction was started by adding 40 mg of the catalyst calcined or calcined then reduced (the latter one with the shortest exposure with air) to the O_2 saturated solution. For analyzing the reaction mixture, ~ 0.2 mL sample was withdrawn with a syringe before addition of the catalyst, then during the reaction in 10 min intervals. After the filtration of the catalyst, the liquid was diluted with additional toluene, then analyzed by a CHROMPACK CP 9000 type gas chromatograph (GC) equipped with a FID detector using a CP-Sil-5-CB ($50.0 \text{ m} \times 0.32 \text{ mm} \times 0.1, 19 \mu\text{m}$) capillary column. For several cases, the analysis was confirmed by a GC-MS instrument (Shimadzu GCMS-QP2010 Ultra with a Shimadzu AOC-20i automatic injector) using a Phenomenex ZB-SemiVolatiles column ($30.0 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) scanning mass range 35–500 m/z . The only product detected was benzaldehyde with 100 % selectivity. The initial reaction rate was calculated from the first 3 points of the conversion curves (up to 30 min reaction time, conversion $< 2\%$, linear region). The reaction was in the kinetically controlled regime as confirmed by the constant specific reaction rates determined with different sample amount of the most active catalyst.

The conditions of glucose oxidation catalytic tests in short are the following (details in Ref. [32]). The reaction was performed in aqueous solution in a stirred thermostated glass reactor, O_2 was bubbled through the liquid. The reaction was started by addition of the catalyst. Using carbonate-bicarbonate (volume ratio: 2:3) buffer solution pH = 9.5 was provided during the reaction. Typical reaction parameters were: $m_{\text{catalyst}} = 30 \text{ mg}$, $c_{\text{glucose}} = 0.1 \text{ M}$ in 30 mL solution, O_2 flow = 100 mL/min (1 atm), $c_{\text{buffer}} = 0.1 \text{ M}$, $T = 35^\circ\text{C}$, stirring rate = 1,000 rpm. The reaction mixtures were analyzed by HPLC generally in 10 min intervals, no other product was

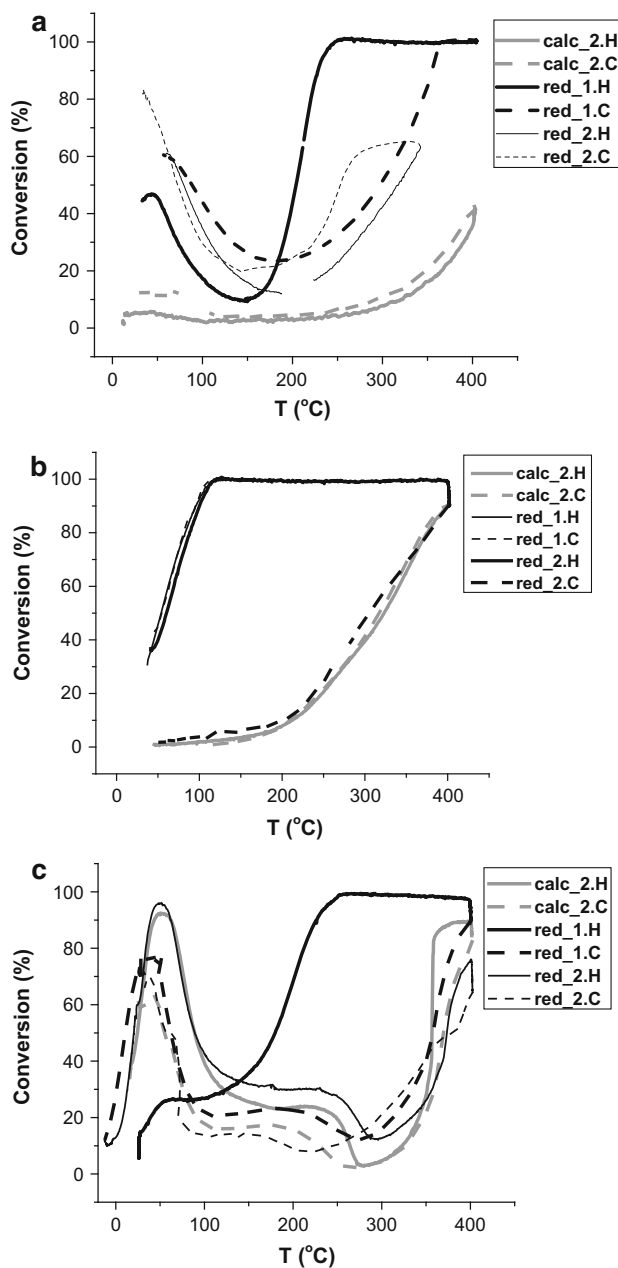


Fig. 1 Temperature programmed CO oxidation conversion curves of the calcined and reduced samples. **a** Au/SiO₂, **b** Ag/SiO₂, **c** 13Ag87Au/SiO₂, **d** 23Ag77Au/SiO₂, **e** 51Ag49Au/SiO₂. Reaction conditions: 40 mg catalyst, 0.52 % CO + 10.2 % O₂ in helium, 10 mL/min, 5 °C/min. (In legends “calc” and “red” refers to the calcination and reduction pretreatment before CO oxidation, respectively, “x.H” and “x.C” means xth-heating up and cooling down run, respectively after the pretreatment stated)

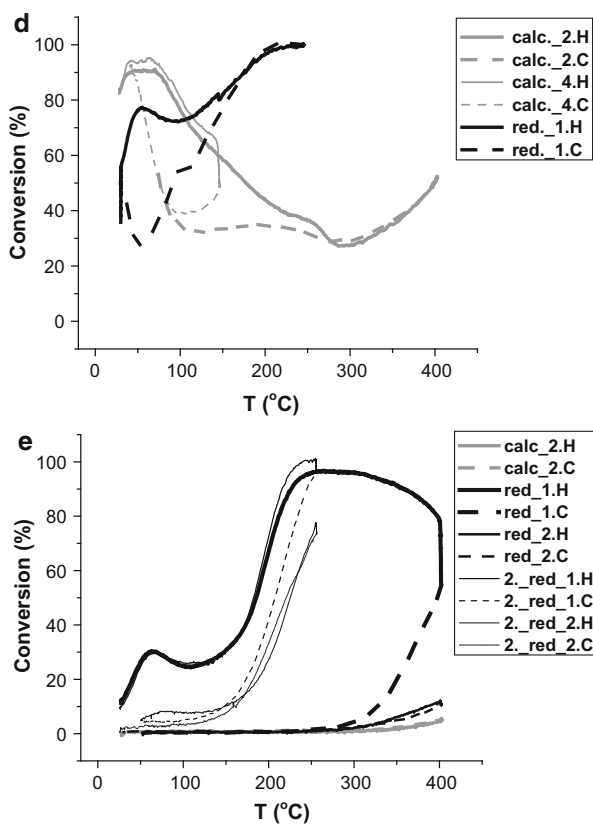


Fig. 1 continued

detected than gluconic acid. Initial reaction rates were determined based on the initial linear part of the conversion curves.

Results

CO oxidation

Figure 1 presents the temperature programmed CO oxidation conversion curves on the different monometallic and bimetallic Au–Ag samples after ex situ calcination and additional in situ reduction treatments. From the repeated TP cycles (heating–cooling runs), the first ones are not shown because in those the heating up period was somewhat different compared to the next runs and no CO converted below 200–250 °C on any of the samples. Afterwards, the curves in the cooling and the following TP cycles were similar. So we compare these curves of the different catalysts in the separate diagrams of Fig. 1. Designations indicate that in which heating or cooling runs of CO oxidation test were recorded the conversion curves in the calcined state or after reduction treatment (as e.g. *calc_2.H* and *red_1.C* mean

the second heating on calcined sample and first cooling after reduction, respectively).

First, let us discuss the behavior of the monometallic catalysts as a basis for the investigation of the effect of bimetallic compositions. In calcined state Au/SiO₂ (Fig. 1a) presented very low activity, much lower than Ag/SiO₂ (Fig. 1b) of similar metal particle size. On the contrary, the Au molar concentration is about two times higher than that of Ag. The maximum conversion at 400 °C was only 42 and 90 % reached by Au/SiO₂ and Ag/SiO₂, respectively. Between 100 °C and room temperature, some small strange activity evolved in the cooling period on Au/SiO₂, with maximum at around 50 °C. The in situ reductive pretreatment induced great activation of both monometallic samples, but both catalysts suffered deactivation during the high temperature reaction up to 400 °C possibly due to some re-oxidation and/or restructuring in the large excess of O₂. This can be seen in the first cooling and following second heating–cooling period on reduced Au/SiO₂ (Fig. 1a) and in the second cooling on reduced Ag/SiO₂ (Fig. 1b). When the reaction temperature was raised only up to 150 °C (in the first heating after reduction), the reduced Ag/SiO₂ was more stable in the next cooling and heating, their conversion curves are almost identical. The conversion curves of calcined and reduced Ag/SiO₂ (Fig. 1a) followed a normal scheme, with clear, continuously increasing conversion from about 200 °C and room temperature, respectively, providing on the reduced sample full conversion of CO from 100 to 400 °C. The picture in case of Au/SiO₂ (see Fig. 1a) is much more complex. The two activity zones detected already in the calcined state became more pronounced after reduction treatment. Both in a low temperature (LT, between RT and 150–200 °C) and a high temperature (HT, above 150–200 °C) activity region great activity increase could be seen in the first heating run after reduction. In the LT activity region 47 % maximum conversion at 45 °C was reached, then after interim decreasing of conversion in the HT region a normal CO conversion versus temperature feature can be observed attaining total conversion at around 250 °C and maintaining it up to 400 °C. The high temperature reaction resulted in lower conversion in the following cooling and next TP cycles only in the HT activity region as in case of Ag/SiO₂, but in the extraordinary LT activity region activation occurred.

Let us see how the CO oxidation behavior of Au–Ag bimetallic catalysts changed compared to the monometallic catalysts. Conversion curves of 13Ag87Au/SiO₂ with the lowest Ag-loading can be seen on Fig. 1c. In the second heating up of the calcined sample, three separate extraordinary activity zones (between RT–150, 150–270 and 270–400 °C) emerged, with local conversion maxima at 52 (92), 205–220 (24) and 400 °C (89 %), respectively. The cooling run shows similar features with some shift of the curve to higher temperature in the decreasing conversion regions and to lower temperatures in the increasing conversion zones. The 13Ag87Au/SiO₂ catalyst in calcined state was more active than Au/SiO₂ and Ag/SiO₂ over the entire RT–400 °C and RT–250 °C temperature range, respectively, especially if we take into account, that the molar metal concentration of Au/SiO₂ is almost two times higher than the catalysts. After the subsequent in situ H₂ treatment, the activity of the samples changed markedly. The extraordinary low

temperature activity (below 100 °C) decreased, while spectacular activation was indicated above 150 °C compared to the calcined state. The monotonous increasing conversion from about 100 °C up to 255 °C reaching 100 % conversion then maintaining up to 400 °C showed a regular character. This activity, however, deteriorated in the high temperature reaction and from the first cooling all conversion curves were similar to those of the calcined sample.

In Fig. 1d, TP-CO oxidation conversion curves of the higher Ag content 23Ag77Au/SiO₂ catalyst are shown. Similar features and trends were found as compared to those noticed for 13Ag87Au/SiO₂, but with further activation almost in the whole temperature range except above 350 °C. In the second TP cycle of the calcined sample, the two low temperature activity zones observed on 13Ag87Au/SiO₂ also emerged with conversion maxima at around the same temperatures (at 40–60 and 210–240 °C), but they were not as separated. There was similar type hysteresis (but larger below 300 °C) during the cooling as for 13Ag87Au/SiO₂. Reduction treatment caused activity increase for this catalyst, too, providing the highest activity between the Au-containing catalysts in the reduced state. 100 % conversion was reached at already 230 °C, but there was a local maximum of the conversion at 53 °C with 76 %. In this experiment, the temperature was not increased up to 400 °C, just to 250 °C, and in the following cooling down, there was no such great activity drop as in the case of the 13Ag87Au/SiO₂ and the monometallic samples. Only below 160 °C was the conversion lower than in the heating up run, it decreased monotonically until 55 °C, then started to increase again.

The calcined 51Ag49Au/SiO₂ was almost inactive (Fig. 1e). After reduction besides the light off curve above 110 to 260 °C approaching 100 % conversion before deactivation at higher temperatures, the low temperature activity zone (with 30 % maximum conversion at 65 °C) was also observed as on all of the gold-containing samples, but not on the Ag/SiO₂. In the cooling period, an even more sudden activity drop (no activity below 260 °C) happened than in the case of monometallic Ag/SiO₂. In a subsequent repeated reduction identical activity could be observed in the first heating as after the first reduction, and since the temperature was raised only up to 250 °C deactivation was smaller extent as indicated in the cooling and the next heating–cooling runs, where hardly any low temperature (at lower than 100 °C) activity remained.

Figure 2 helps to compare the five catalysts measured in CO oxidation in the second heating up run after ex situ calcination, and in the first heating up after reduction. In the calcined state (see Fig. 2a) the two lower Ag/Au content bimetallic catalysts were strikingly more active than other Au-containing samples and below about 250 °C also than Ag/SiO₂. In this latter range, there was spectacular synergetic effect in case of these two bimetallic samples. The highest conversion was 82 % for both at around 55 °C, between 55 and 350 °C 23Ag77Au/SiO₂, above 350 °C 13Ag87Au/SiO₂ was more active. The 51Ag49Au/SiO₂ were much less active than the monometallic analogous, practically inactive.

After H₂ treatment (see Fig. 2b), Ag/SiO₂ was definitely the best catalyst above about 75 °C. Around 230–250 °C all the samples reached 100 % conversion. Close to ambient temperature, 23Ag77Au/SiO₂ was the most active as a result of extraordinary LT activity zone, while Ag/SiO₂ was the second in a normal TP activity regime. Other

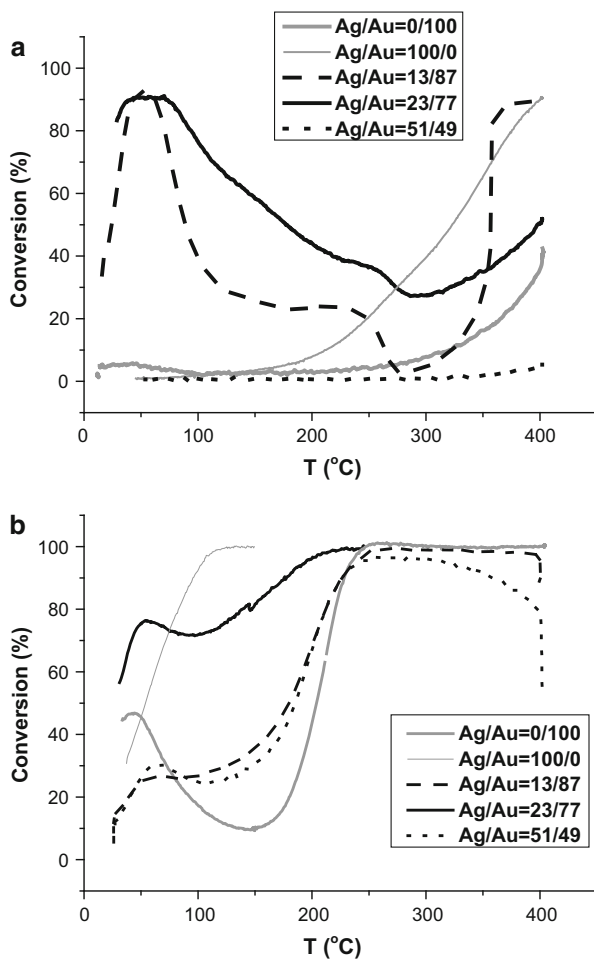


Fig. 2 Comparison of CO oxidation conversion curves of the calcined samples in the second temperature programmed heating up (a) and of the reduced samples in the first heating up (b). Reaction conditions: 40 mg catalyst, 0.52 % CO + 10.2 % O₂ in helium, 10 mL/min, 5 °C/min

Au containing samples also had the peculiar low temperature activity giving much lower conversion maxima (remember that in Au/SiO₂ the molar concentration of metal was 2 times higher than in other catalysts). It is worth mentioning that 51Ag49Au/SiO₂ (inactive in calcined state) showed almost identical conversion curve after reduction as 13Ag87Au/SiO₂. In the reduced state, a clear bimetallic synergetic effect could be observed only for 23Ag77Au/SiO₂ close to RT.

Benzyl alcohol and glucose oxidation

Figure 3a and b present the conversion curves of the calcined and reduced catalysts in benzyl alcohol and glucose oxidation reactions, respectively. The former reaction

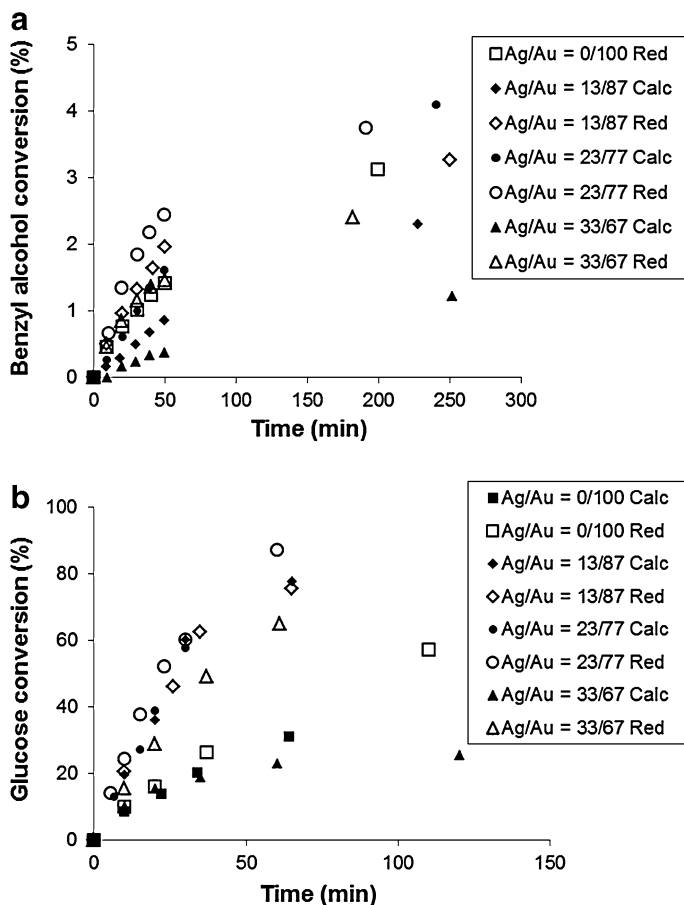


Fig. 3 Conversion curves of the different samples after calcination and reduction treatment in benzyl alcohol oxidation (a) and in glucose oxidation (b). (Ag/SiO₂ and 51Ag49Au/SiO₂ were not active neither in calcined nor in reduced state in any of these reactions. Calcined Au/SiO₂ was not active in benzyl alcohol oxidation.). Reaction conditions: (a) 40 mg catalyst, 30 mL 1.0 M benzyl alcohol/toluene solution, 150 mL/min O₂ (1 atm), 1,350 rpm stirring, 80 °C; (b) 30 mg catalyst, 30 mL 0.1 M glucose/water solution, 100 mL/min O₂ (1 atm), 1,000 rpm stirring, pH: 9.5 (carbonate-bicarbonate buffer), 35 °C

was performed in toluene solution of benzyl alcohol (1.0 M) at 80 °C, the latter, reported already in Ref. [31], in aqueous solution of glucose (0.1 M) at 35 °C. The Ag/SiO₂ and 51Ag49Au/SiO₂ catalysts were not active in any of these catalytic tests neither in calcined nor in reduced state. Also, the calcined Au/SiO₂ was inactive in the oxidation of benzyl alcohol between the applied conditions, but after reduction it became active.

In benzyl alcohol oxidation (Fig. 3a), the conversion curves were linear in the first 30–40 min, below 2.5 % conversion, then declined, and the conversion did not exceed 4.5 % after even 4 h. This refers to some kind of inhibition or deactivation effect that was reported also for Au/Al₂O₃ [39] in the reaction performed in toluene

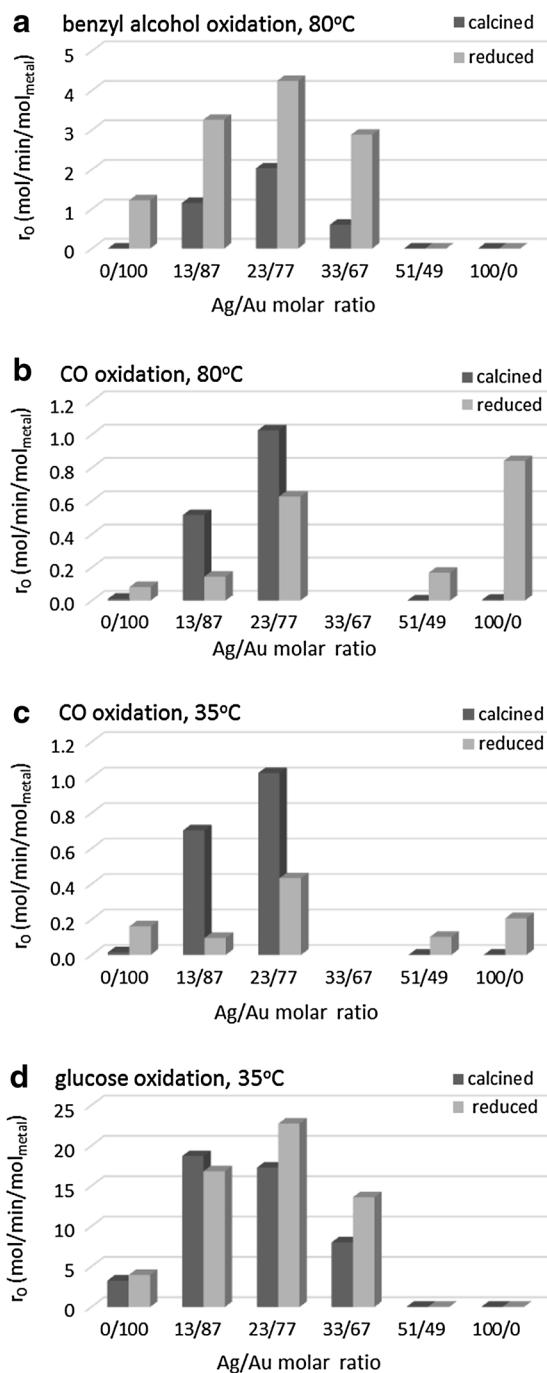
solution and in the case of colloidal AgAu in aqueous solution [36]. This inhibiting effect that could be weakened by addition of base was attributed to the strong adsorption of benzoic acid by-product. In our experiments, the benzoic acid concentration was below the detection limit, but regarding the high substrate/(Au+Ag) molar ratio (about 7,000 for bimetallic samples and 3,800 for monometallic gold) in the reaction mixture, low benzoic acid concentration may block relatively large part of surface Au atoms. On the most active reduced 23Ag77Au/SiO₂ the reaction rate decrease was somewhat stronger than on its calcined form, caused maybe by a slight re-oxidation of the catalyst. The initial reaction rates, nevertheless, characterize well the activity of the initial structure of the active sites.

In the glucose oxidation reaction (Fig. 3b), much higher conversions were reached during the same reaction time. However, the difference in the reaction rates are not as high regarding the ten times less initial concentration of glucose compared to benzyl alcohol (but do not forget, that the reaction temperature is lower in this case by 45 °C). In glucose oxidation, the conversion curves did not suggest any spectacular inhibition or deactivation during the course of reaction (expect in the case of the calcined 33Ag67Au/SiO₂).

The activity differences of the various samples after different treatments can be seen on the conversion curves, but comparison of the initial reaction rates related to 1 mol of the metals (Au+Ag) in the catalysts make the comparison more relevant (remember the different metal content of Au/SiO₂, on the other hand, the very similar metal particle sizes in all the samples) and easier as presented in the diagrams of Fig. 4a and d. In both selective partial oxidation reactions, bimetallic samples of Ag/Au ≤ 0.5 present synergetic activity increase compared to the monometallic ones. The activity order of the samples in the same state (calcined or reduced) is the same and even the relative activities especially in the case of the reduced samples are very similar. The highest activity of the samples with 13/87 and 23/77 Ag/Au ratio in glucose oxidation was explained by the compromised extent of advantageous Ag introduction for helping O₂ activation, but still providing large enough size of continuous Au ensembles for adsorption of glucose [32]. This may be valid for benzyl alcohol oxidation, too, since its size is similar to that of glucose. The pre-treatment effect, however, is significantly different in the two reactions. The reduction treatment at least doubled the benzyl alcohol oxidation activity of the calcined samples, more surprisingly, the largest increase was observed on Au/SiO₂, while in glucose oxidation hydrogen treatment caused significant activation only on 33Ag67Au/SiO₂ and in less extent on 23Ag77Au/SiO₂.

The initial reaction rates of the CO oxidation reaction over the same catalysts were also calculated (supposing pseudo-first order kinetics) for the temperatures of both benzyl alcohol and glucose oxidation tests, 80 and 35 °C, respectively, and shown in Fig. 4b and c. The CO oxidation activity order of the catalysts and even the reaction rates were quite similar at these two reaction temperatures except in the case of reduced Ag/SiO₂, which were much more active at 80 °C. The reaction rates are smaller than in the selective oxidation reactions (compare diagram *b* with *a*, and *c* with *d* in Fig. 4) again with the exception of reduced Ag/SiO₂ plus Ag51Au49/SiO₂, which were inactive in the selective oxidation reactions. The relative activities

Fig. 4 Initial reaction rates related to 1 mol metal content of the different calcined and reduced samples of various Ag/Au molar ratio in benzylalcohol oxidation at 80 °C (a), CO oxidation at 80 °C (b), CO oxidation at 35 °C (c) and glucose oxidation at 35 °C (d)



of the calcined samples of various Ag/Au ratio in CO oxidation were similar to those in selective oxidation reactions, but in reduced state those were different. After reduction 23Ag77Au/SiO₂ was the best and 13Ag87Au/SiO₂, 51Ag49Au/SiO₂ and at 35 °C Ag/SiO₂ had activity comparable with that of Au/SiO₂. The pretreatment effect was opposite in the selective oxidation of benzyl alcohol and glucose as compared to CO oxidation. In the former reactions, the treatment in hydrogen increased the activity, while in the latter reaction, the low temperature activity decreased on the effect of reduction treatment. However, it is worth noting that above 150 °C, the reduced samples were more active also in CO oxidation (see Fig. 2a, b).

Discussion

In benzyl alcohol oxidation, a synergetic activity increase of supported bimetallic AuAg nanoparticles free of organic stabilizers was observed. Earlier, such effect was reported only on polymer stabilized colloids [35, 36]. The activity order of the catalysts of various Ag/Au ratio was the same as observed in glucose oxidation reaction and similar to the published in case of AuAg colloids. The large activity difference in the two reactions (see reaction rates in Fig. 4a and d) originates possibly on one side from the different type transformations. Namely, in alcohol oxidation, a hydride transfer from the carbon bonded to the OH group takes place, while in glucose oxidation, an OH insertion on the carbonyl carbon atom forms an alkoxy intermediate of a geminal diol then the hydride transfer occurs from its carbon. On the other hand, the different solvents also must have affected the activities. Li and coworkers demonstrated by DFT calculations a water promoted oxidation mechanism on Au(111) surface [40]. By constructing a hydrogen bonding chain with H-containing reactants, water was found to notably facilitate hydrogen-transfer reactions, which lowered the formation barrier of OOH species that further dissociating to atomic oxygen and hydroxyl were highly reactive for the dehydrogenation of methanol.

After H₂ treatment, the increase of the activity was much larger in benzyl alcohol oxidation than in glucose oxidation, but the most striking was in CO oxidation concerning the opposite effect in case of low temperature activity of 13Ag87Au/SiO₂ and 23Ag77Au/SiO₂. Sensitive changes of the CO oxidation activity and the conversion curve features were observed depending on the pretreatments. This was in contrast with the results of structural characterization of the samples [32], which revealed no big difference between the calcined and reduced state by UV–Vis, XPS and TEM. The efficient activation of the calcined monometallic and 51Au49Ag/SiO₂ bimetallic catalysts and the more complex alteration of the other two, more active AgAu samples by reduction treatment described above cannot be attributed to particle size change, since it was small, as presented in Table 1. The hardly altered Au 4f and Ag 3d binding energies determined by XPS also did not give explanation [32]. Those suggested the metallic state of Au and Ag in the bimetallic and Au/SiO₂ samples both in calcined state and after reduction treatment. In case of Au/SiO₂ this was in accordance with several other publications [11, 41], but in Ref. [42] both Au⁰

and Au^+ was detected in an Au/SiO_2 catalyst after treatment in O_2 at 500°C , while reduction at 500°C completely reduced gold. However, in the latter case, SiO_2 supported $\text{Au}(\text{en})_2^{3+}$ was subjected to various pretreatments, while pre-formed metallic Au nanoparticles in our case. In AuAg bimetallic samples on inert supports, Ag–O bonds were found by others after calcination at 560 or 500°C on the surface of the bimetallic particles using EXAFS or XPS, and these samples were less active than the reduced ones or inactive [20, 21, 43]. After reduction, Ag was fully reduced and the catalyst activated. In these catalysts, Au(Ag) core@Ag shell type particles were calcined, where Ag-oxide formation was more favored, than in case of our alloyed bimetallic particles. Since the reduction of oxidized Au and Ag could not be fully disclosed under X-ray beam during our relatively long XPS measurements, the presence of some Ag-oxide (and less likely ionic Au) on the catalyst surface of our calcined bimetallic samples could not be fully ruled out. Nonetheless, the bulk of these particles were in metallic state as evidenced by UV–Vis spectra and HRTEM measurements (though the reduction of Ag-oxide by electron beam during TEM measurements could have been also possible). For the perception of different Au surface sites having different effective charge the CO adsorption followed by FTIR spectroscopy is a sensitive method, the investigation of our samples by that is planned.

The reductive and oxidative pretreatments influenced the Ag/Au surface atomic ratio. In the bimetallic particles, Ag enrichment was induced on the surface in oxidizing atmosphere as was observed also by others [15], in reducing conditions the alloying is favored [20, 21, 43]. However, the change of Ag/Au measured by XPS, as presented in Table 1, was quite small, likely because of the relatively short and moderate temperature reduction treatment ($350^\circ\text{C}/30\text{ min}/\text{H}_2$). This is the possible reason why the order of the catalytic activity of the bimetallic samples with different Ag/Au molar ratio did not change on the effect of reduction in the three reactions. Nevertheless, it has to be mentioned that the surface concentration determined by XPS can be significantly different from composition of the topmost atomic layer working in catalysis as was demonstrated on nanoporous Au–Ag system via comparison of XPS and low energy ion scattering (LEIS) results by Rousset and co-workers [25].

During the pretreatments, beside redox transformations and segregation effects, some further reconstruction may affect the catalytic properties, as altering the number of active low coordinated sites of gold [44]. For example the segregation of Ag on the AuAg surface was reported to be favored on these sites [25]. Activation was suggested in high temperature reduction treatment also via enhanced formation of O_2^- (superoxide) caused by O-vacancy generation in aluminosilicate support regarded generally inactive [9].

Temperature programmed CO oxidation test showed that the relatively short time reductive treatment ($350^\circ\text{C}/\text{H}_2/30\text{ min}$) and the oxidative effect of the reaction (temperature programmed heating up to 400°C in $0.5\% \text{CO} + 10\% \text{O}_2/\text{He}$) changed the conversion curve profile more or less reversible (Fig. 1b, c and e). This is typical rather for the redox changes of the active components. Thus, from the above listed possible structural reasons of the strong activating effect of reduction treatment in the higher reaction temperature region, the reduction of Ag-oxides,

undetected but likely present on the surface of bimetallic particles in the calcined samples, is thought to play a role.

The anomalous character of the temperature programmed CO oxidation conversion curves (see Fig. 1a and c–e) with emphasis on the decreasing activity versus increasing reaction temperature should be discussed. Such type of results were published on monometallic Au [9–11, 13, 41, 42, 45, 46] and also on bimetallic AuAg [17–19, 25] catalysts on different supports (SiO₂, MgO, ZnO). Date et al. revealed that H₂O by its involvement in activation of O₂ and decomposition of carbonates was a prerequisite for the activity at low temperatures [46]. They explained the activity decrease of a calcined Au/SiO₂ above about 50 °C by desorption of moisture. Qian et al. reported the stability of such peculiar CO conversion curves during 3 h time on stream, and interpreted the declining conversion by temperature-dependent formation of a CO oxidation surface intermediate and competition between its surface reaction and desorption [12]. Recently, Bogdanchikova and co-workers published a detailed work [42] concerning this phenomenon. Based on the comparison of structural results (XPS, UV–Vis, FTIR) and catalytic tests they distinguished various states of gold on Au/HMS, as Au³⁺ and Au⁺ ions, neutral and partly charged gold clusters and metal nanoparticles of different activity. Their presence was influenced by different pretreatments in O₂, He or H₂. The three activity regions they observed in temperature ranges 20–200, 200–400, >400 °C, where local conversion maxima were found they attributed to these different Au states. The lowest temperature activity was assigned to Au_n^{δ+} or/and Au⁺ ions (Au³⁺ were inactive), the 200–400 °C activity region to Au_n clusters, the high temperature activity to Au nanoparticles. As the reason of reversible deactivation/activation experienced in the course of temperature programmed reaction or on the effect of pretreatments, they advised the change in the oxidation states of gold. Oxidative treatment (O₂/500 °C) deactivated, reductive treatment (H₂/500 °C) activated the catalyst.

Our oxidized Au/SiO₂ was much less active than the reduced sample that showed two separate activity region during increasing temperature (Fig. 1a) similarly as for Au/SiO₂ of similar size and Au loading in Ref. [42]. In our sample, the size distribution of Au particles ranged between 2 and 6 nm, so highly active Au clusters smaller than 2–3 nm and less active larger particles co-existed both in calcined and reduced state. However, our results, namely the low temperature inactivity of the calcined state, and high activity around room temperature in reduced state with further increased LT activity and similar conversion profile in repeated temperature ramps (see Fig. 1a), could not be rationalized by the surface sites and their changes advised by Bogdanchikova. The promoting effect of water until its desorption according to Date may operate on our catalyst regarding the presence of water in low concentration in the reaction mixture.

Mou and co-workers studying reduced AuAg/MCM-41 and monometallic analogous of large particle sizes (>20 nm) found normal monotonically increasing conversion curves versus reaction temperatures for the monometallic samples, but for the bimetallic ones, two activity zones with lower activity in between [17–19]. A similar phenomenon, decreasing CO conversion with increasing temperature, was reported also in case of nanoporous Au–Ag catalysts [25]. These were suggested to

be caused by the desorption of O_2 from the Au–Ag alloy. A similar effect may be assumed also in case of our samples, but it should be noted that also our monometallic Au/SiO₂ presented such conversion curves.

According to our observations on the catalytic effect of the bimetallic AuAg/SiO₂ catalysts of various Au/Ag ratio, it can be stated that synergetic activity increase developed at low Ag/Au molar ratio in all three oxidation reactions in both calcined and reduced states. Although the mechanism of these catalytic reactions are different and the origin of the synergy is not clear enough based on our and literature results and interpretations, the synergy may be attributed to the cooperation of Ag and Au in the alloyed nanoparticles, enhancing the oxygen and substrate activation ability by Ag and Au, respectively, side by side. The outstanding Au/Ag = 23/77 molar ratio in case of glucose and benzyl alcohol substrates may be explained by providing the best compromise between the largest Ag concentration still providing the minimum ensemble size of continuous Au surface required by adsorption of these molecules of similar size. For CO oxidation, this explanation cannot be valid, because for CO chemisorption, much smaller Au sites are sufficient. Likely the Au/Ag = 23/77 composition may result in the optimal electronic interaction of the two metals. The effect of calcination and reduction treatment was different in the selective oxidation reactions compared to that in CO oxidation. Reduction induced activation of all the samples in glucose and benzyl alcohol oxidation, but decreasing activity of bimetallic catalyst with Au/Ag = 23/77 and 13/87 below 125 °C in CO oxidation, while in the higher temperature region, all the samples were highly activated. Ag/SiO₂, inactive in calcined state in CO oxidation below 125 °C and in both states in the other reactions, presented significant low temperature CO oxidation activity after reduction. To reveal the reasons of this dissimilar behavior needs further investigations. The mechanism of CO oxidation seems to differ more compared to that of the other two reactions. However, the CO oxidation reaction indicated intense modification of the catalysts surface as a result of calcination/reduction treatments, the presence of various active sites in altering populations that could not be identified, yet.

Conclusions

SiO₂ supported Au–Ag nanoparticles prepared by adsorption of bimetallic colloids of various Ag/Au molar ratio (0/100, 13/87, 23/77, 33/67, 51/49, 100/0) characterized and studied in selective glucose oxidation reaction earlier [32] were applied and compared also in benzyl alcohol and CO oxidation reaction both after calcination (400 °C/air/60 min) and successive reduction treatment (350 °C/H₂/30 min).

Temperature programmed CO oxidation conversion curves sensitively indicated the structural alterations in the different samples in different states. In the case of all gold containing samples, different activity zones, temperature ranges with local reaction rate maxima appeared, which were affected differently by the Au/Ag ratio and pretreatment conditions. All these changes point to the coexistence of various

active sites with various population after the different treatments. Nevertheless, the identification of these sites requires further investigations.

In all three reactions, the activity order of the Au-containing catalysts of different Ag/Au ratio was the same and the Ag/Au = 23/77 composition was the most active both in the calcined and reduced state with synergetic activity increase compared to the monometallic analogues.

On the effect of treatment in H₂ in benzyl alcohol oxidation significant, in glucose oxidation slight activity increase was observed for all the samples, while in CO oxidation large, more complex activity changes were induced. Reduction treatment induced deactivation of sample with Ag/Au = 23/77 and 13/87 below 125 °C, while in the higher temperature region all the samples were highly activated. The higher CO oxidation activity of the calcined AuAg bimetallic samples close to room temperature compared to that of the reduced ones was not reported in the literature before.

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References

1. Bond GC, Louis C, Thompson DT (2006) *Catalysis by Gold*. Imperial College Press, London
2. Corma A, Garcia H (2008) Supported gold nanoparticles as catalysts for organic reactions. *Chem Soc Rev* 37:2096–2126
3. Della Pina C, Falletta E, Prati L, Rossi M (2008) Selective oxidation using gold. *Chem Soc Rev* 37:2077–2095
4. Davis SE, Ide MS, Davis RJ (2013) Selective oxidation of alcohols and aldehydes over supported metal nanoparticles. *Green Chem* 15:17–45
5. Mallat T, Baiker A (2012) Potential of gold nanoparticles for oxidation in fine chemical synthesis. *Annu Rev Chem Biomol Eng* 3:11–28
6. Pina CD, Falletta E, Rossi M (2012) Update on selective oxidation using gold. *Chem Soc Rev* 41:350–369
7. Benkó T, Beck A, Geszti O, Katona R, Tungler A, Frey K, Guczi L, Schay Z (2010) Selective oxidation of glucose versus CO oxidation over supported gold catalysts. *Appl Catal A* 388:31–36
8. Chi Y-S, Lin H-P, Mou C-Y (2005) CO oxidation over gold nanocatalyst confined in mesoporous silica. *Appl Catal A* 284:199–206
9. Chiang C-W, Wang A, Mou C-Y (2006) CO oxidation catalyzed by gold nanoparticles confined in mesoporous aluminosilicate Al-SBA-15: pretreatment methods. *Catal Today* 117:220–227
10. Zhu H, Ma Z, Clark JC, Pan Z, Overbury SH, Dai S (2007) Low-temperature CO oxidation on Au/fumed SiO₂-based catalysts prepared from Au(en)₂Cl₃ precursor. *Appl Catal A* 326:89–99
11. Qian K, Luo L, Bao H, Hua Q, Jianga Z, Huang W (2013) Catalytically active structures of SiO₂-supported Au nanoparticles in low-temperature CO oxidation. *Catal Sci Technol* 3:679–687
12. Wu W, Pantaleo G, Venezia AM, Liotta LF (2013) Mesoporous silica based gold catalysts: novel synthesis and application in catalytic oxidation of CO and volatile organic compounds (VOCs). *Catalysts* 3:774–793
13. Comotti M, Li W-C, Spliethoff B, Schuth F (2006) Support effect in high activity gold catalysts for CO oxidation. *J Am Chem Soc* 128:917–924
14. Liu XY, Wang A, Zhang T, Mou CY (2013) Catalysis by gold: new insights into the support effect. *Nano Today* 8:403–416
15. Wang A, Liu XY, Mou C-Y, Zhang T (2013) Understanding the synergistic effects of gold bimetallic catalysts. *J Catal* 308:258–271

16. Iizuka Y, Kawamoto A, Akita K, Date M, Tsubota S, Okumura M, Haruta M (2004) Effect of impurity and pretreatment conditions on the catalytic activity of Au powder for CO oxidation. *Catal Lett* 97:203–208
17. Wang A-Q, Liu J-H, Lin S-D, Lin T-S, Mou C-Y (2005) A novel efficient Au–Ag alloy catalyst system: preparation, activity and characterization. *J Catal* 233:186–197
18. Liu J-H, Wang A-Q, Chi Y-S, Lin H-P, Mou C-Y (2005) Synergetic effect in Au–Ag alloy nanocatalyst: CO oxidation. *J Phys Chem B* 109:40–43
19. Wang A, Hsieh Y-P, Chen Y-F, Mou C-Y (2006) Au–Ag alloy nanoparticle as catalyst for CO oxidation: effect of Si/Al ratio of mesoporous support. *J Catal* 237:197–206
20. Yen C-W, Lin M-L, Wang A, Chen S-A, Chen J-M, Mou C-Y (2009) CO oxidation catalyzed by Au–Ag bimetallic nanoparticles supported in mesoporous silica. *J Phys Chem C* 113:17831–17839
21. Liu X, Wang A, Yang X, Zhang T, Mou C-Y, Su D-S, Li J (2009) Synthesis of thermally stable and highly active bimetallic Au–Ag nanoparticles on inert supports. *Chem Mater* 21:410–418
22. Qu Z, Ke G, Wang Y, Liu M, Jiang T, Gao J (2013) Investigation of factors influencing the catalytic performance of CO oxidation over Au–Ag/SBA-15 catalyst. *Appl Surf Sci* 277:293–301
23. Sandoval A, Aguilar A, Louis C, Traverse A, Zanella R (2011) Bimetallic Au–Ag/TiO₂ catalyst prepared by deposition–precipitation: high activity and stability in CO oxidation. *J Catal* 281:40–49
24. Sasikrekha N, Sangeeta P, Chen Y-W (2014) Bimetallic Au–Ag/CeO₂ catalysts for preferential oxidation of CO in hydrogen-rich stream: effect of calcination temperature. *J Phys Chem C* 118:15226–15233
25. Deronizier F, Morfin F, Lomello M, Rousset J-L (2014) Catalysis on nanoporous gold-silver systems: synergetic effects toward oxidation reactions and influence of the surface composition. *J Catal* 311:221–229
26. Zhang H, Okuni J, Toshima N (2011) One-pot synthesis of Ag–Au bimetallic nanoparticles with Au shell and their high catalytic activity for aerobic glucose oxidation. *J Colloid Interface Sci* 354:131–138
27. Tokonami S, Morita N, Takasaki K, Toshima N (2010) Novel synthesis, structure, and oxidation catalysis of Ag/Au bimetallic nanoparticles. *J Phys Chem C* 114:10336–10341
28. Zhang H, Toshima N (2012) Fabrication of catalytically active Ag/Au bimetallic nanoparticles by physical mixture of small Au clusters with Ag ions. *Appl Catal A* 447–448:81–88
29. Zhang H, Toshima N, Takasaki K, Okumura M (2014) Preparation of Agcore/Aushell bimetallic nanoparticles from physical mixtures of Au clusters and Ag ions under dark conditions and their catalytic activity for aerobic glucose oxidation. *J Alloys Compd* 586:462–468
30. Zhang H, Haba M, Okumura M, Akita T, Hashimoto S, Toshima N (2013) Novel formation of Ag/Au bimetallic nanoparticles by physical mixture of monometallic nanoparticles in dispersions and their application to catalysts for aerobic glucose oxidation. *Langmuir* 29:10330–10339
31. Zhang H, Toshima N (2013) Glucose oxidation using Au-containing bimetallic and trimetallic nanoparticles. *Catal Sci Technol* 3:268–278
32. Benkó T, Beck A, Frey K, Srankó DF, Gesztli O, Sáfrán G, Maróti B, Schay Z (2014) Bimetallic Ag–Au/SiO₂ catalysts: formation, structure and synergistic activity in glucose oxidation. *Appl Catal A* 479:103–111
33. Chaki NK, Tsunoyama H, Negishi Y, Sakurai H, Tsukuda T (2007) Effect of Ag-doping on the catalytic activity of polymer-stabilized Au clusters in aerobic oxidation of alcohol. *J Phys Chem C* 111:4885–4888
34. Li W, Wang A, Liu X, Zhang T (2012) Silica-supported Au–Cu alloy nanoparticles as an efficient catalyst for selective oxidation of alcohols. *Appl Catal A* 433–434:146–151
35. Huang X, Wang X, Tan M, Zou X, Ding W, Lu X (2013) Selective oxidation of alcohols on P123-stabilized Au–Ag alloy nanoparticles in aqueous solution with molecular oxygen. *Appl Catal A* 467:407–413
36. Huang X, Wang X, Wang X, Wang X, Tan M, Ding W, Lu X (2013) P123-stabilized Au–Ag alloy nanoparticles for kinetics of aerobic oxidation of benzyl alcohol in aqueous solution. *J Catal* 301:217–226
37. Chang CM, Cheng C, Wei CM (2008) CO oxidation on unsupported Au₅₅, Ag₅₅, and Au₂₅Ag₃₀ nanoclusters. *J Chem Phys* 128:124710
38. Tsunoyama H, Ichikuni N, Sakurai H, Tsukuda T (2009) Effect of electronic structures of Au clusters stabilized by poly(N-vinyl-2-pyrrolidone) on aerobic oxidation catalysis. *J Am Chem Soc* 131:7086–7093

39. Skupien E, Berger JB, Santos VP, Gascon J, Makkee M, Kreutzer MT, Kooyman PJ, Moulijn JA, Kapteijn F (2014) Inhibition of a gold-based catalyst in benzyl alcohol oxidation: understanding and remediation. *Catalysts* 4:89–115
40. Chang C-R, Xiao-Feng Yang X-F, Long B, Li J (2013) A water-promoted mechanism of alcohol oxidation on a Au(111) surface: understanding the catalytic behavior of bulk gold. *ACS Catal* 3:1693–1699
41. Rombi E, Cutrufello G, Cannas C, Casu M, Gazzoli D, Occhiuzzi M, Monaci R, Ferino I (2009) Modifications induced by pretreatments on Au/SBA-15 and their influence on low temperature CO oxidation. *Phys Chem Chem Phys* 11:593–602
42. Bogdanchikova N, Pestryakov A, Tuzovskaya I, Zepeda TA, Farias MH, Tiznado H, Martynyuk O (2013) Effect of redox treatments on activation and deactivation of gold nanospecies supported on mesoporous silica in CO oxidation. *Fuel* 110:40–47
43. Liu X, Wang A, Li L, Zhang T, Mou C-Y, Lee J-F (2013) Synthesis of Au–Ag alloy nanoparticles supported on silica gel via galvanic replacement reaction. *Prog Nat Sci* 23:317–325
44. Pászti Z, Hakkel O, Keszthelyi T, Berkó A, Balázs N, Bakó I, Guzzi L (2010) Interaction of carbon monoxide with Au(111) modified by ion bombardment: a surface spectroscopy study under elevated pressure. *Langmuir* 26:16312–16324
45. Margitfalvi JL, Fási A, Hegedűs M, Lónyi F, Göbölös S, Bogdanchikova N (2002) Au/MgO catalysts modified with ascorbic acid for low temperature CO oxidation. *Catal Today* 72:157–169
46. Date M, Okumura M, Tsubota S, Haruta M (2004) Vital role of moisture in the catalytic activity of supported gold nanoparticles. *Angew Chem Ed Int* 43:2129–2132