Silica-Supported Au Nanoparticles Decorated by CeO$_2$: Formation, Morphology, and CO Oxidation Activity

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ABSTRACT: SiO$_2$-supported Au nanoparticles derived from sol were promoted with 0.04–7.4 wt % CeO$_2$ using two methods. The addition of Ce precursor was done directly to the Au sols before sol immobilization step (method A) or to the suspension of parent Au/SiO$_2$ (method B). Both preparation routes resulted in CeO$_2$ decoration of 1–3 nm over Au nanoparticles, which induced high CO oxidation activity. However, above 0.6 wt % CeO$_2$ content, the activity did not change significantly, but it greatly exceeded that of pure Au/CeO$_2$ used for reference. High-resolution transmission microscopy (HRTEM) showed that up to this concentration ceria patches are attached onto gold surface, and the further increase in Ce-loading caused CeO$_2$ spread over the support surface as well. Strong interaction of Ce species with stabilizer ligands located around Au is suggested as the reason for CeO$_2$ localization on gold.

1. INTRODUCTION

Nowadays, one can witness an ever-increasing progress in material science. In the field of space technology, electronics, and semiconductor industry, there is a growing need for novel materials that possess unique mechanical, electronic, optical, and chemical properties. Therefore, investigation of nanosize materials is of great importance because particles built up from only a few hundreds of atoms have characteristics different from the bulk. As a result of their special electronic and morphological properties, these small particles can exhibit unique catalytic performance, but because of the high surface excess energy, they are very sensitive and in the absence of sufficient stabilization thermodynamical driving forces cause aggregation.

Since Haruta discovered the surprisingly high catalytic activity of nanosize gold, tremendous work has been done in the field of Au catalysis trying to expand the range of its applicability among others in selective oxidation reactions and explain the structure—activity relationship. It is widely accepted that in the most studied CO oxidation the activity depends on the particle size and oxidation state of Au and the type and structure of oxide support. Furthermore, the oxide–metal interface plays a crucial role in the CO oxidation mechanism proposed. CeO$_2$, TiO$_2$, Fe$_2$O$_3$, MgO, and so on are considered to be “active supports” because they provide good activity for Au, whereas SiO$_2$ and Al$_2$O$_3$ can be regarded as inactive or much less active supports. For inactive supports, the oxygen adsorption was suggested to happen on the defect sites of Au; that is why the activity shows stronger dependence on the dispersion. In the case of reducible, active oxides able to act as oxygen reservoir, the microstructure of oxide and the nature of metal—support interface are of key importance because the oxygen activated by the oxide active sites generated partially by the interaction with Au is suggested to react with CO adsorbed on gold in close vicinity of the gold-oxide perimeter. Ceria can provide reactive oxygen via forming surface and bulk vacancies through redox processes involving the Ce(III)/Ce(IV) couple. The interaction is more complicated when there is possibility of incorporation of cationic Au into the ceria lattice. Depending on the morphology (preparation method) of ceria, different catalytic activities can be obtained: Yi and coworkers experienced using Au/CeO$_2$ that the CO conversion depended on the shape (polyhedra, cube, or rod) viz. the crystal planes of CeO$_2$. The adsorption/desorption properties of CO and oxygen species were related to the nature of exposed crystal planes of ceria nanocrystals. The ceria rods with {100} and {110} dominant surfaces showed the best performance with higher concentrations of Au and Au$_3$.

The addition of ceria to other oxide supports usually induces strong effect on the reducibility of the other catalyst components, as proven by Idakiev and coworkers in the case of CeO$_2$-modified meso-macroporous TiO$_2$–ZrO$_2$-supported Au catalysts. The synergetic effect of the Au–CeO$_2$ interface can be investigated in a way when small amount of CeO$_2$ is used to modify the otherwise inactive support such as silica, and finally Au is deposited onto this CeO$_2$/SiO$_2$ support. However, if Au is introduced by the most frequently used deposition precipitation (DP) method onto the modified support having different

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Ce-loading, then the final Au particle size and oxidation state and thus the catalytic activity may be different because of the mechanism of DP method. Indeed, we must be very careful when assigning any catalytic behavior solely to the effect of oxide loading and structure if the Au particle size or oxidation state (concentration of Au\(^{3+}\) and Au\(^+\)) differs significantly in the catalyst samples investigated.\(^{12}\)

Qian and coworkers\(^{13}\) studied the effect of CeO\(_2\) microstructures present in Au/CeO\(_2\)/SiO\(_2\). They introduced 6% CeO\(_2\) loading by DP and impregnation method; then, Au was deposited by DP. They experienced that Au supported on CeO\(_2\)/SiO\(_2\) prepared by wet impregnation and calcined at only 200 °C was the most active sample where Au nanoparticles were dispersed on the CeO\(_2\) aggregates on SiO\(_2\) and the pure SiO\(_2\) surface as well. Au(1) species on CeO\(_2\) alone were not active, and it was concluded that metallic Au—CeO\(_2\) interaction is needed for high activity. The inhomogeneous distribution of Au on CeO\(_2\)-containing hexagonal mesoporous silica (HMS) support was seen by Castano and coworkers as well.\(^{14}\) Crystalline ceria domains were detected on the mesoporous silica by X-ray diffraction (XRD) and HRTEM with Au particles (introduced by DP) on their surfaces; however, many Au particles remained isolated from CeO\(_2\) particles of 4—10 nm size. When Ce modification of the mesoporous silica was done by direct synthesis or impregnation, the impregnated catalyst was better regarding the activity. Higher Au dispersion, highest content of Au, and larger degree of CeO\(_2\) coverage on HMS (more effective oxygen mobility, higher redox ability) were suggested as reasons.\(^{15}\)

Therefore, we can conclude that the preparation method and the pretreatment conditions are of vital importance when the effect of CeO\(_2\) loading on the properties of Au—CeO\(_2\) interface is to be studied using inactive (SiO\(_2\)) oxide support to provide high surface area against sintering. If there are Au particles not in contact with CeO\(_2\) but SiO\(_2\), then the overall activity measured will be the sum of activities originating from Au/SiO\(_2\) and Au/CeO\(_2\)—SiO\(_2\) areas present in the sample.

Supported Au nanoparticles for purposes of heterogeneous catalysis can be prepared by colloid chemical routes as well. Reduction of HAuCl\(_4\) precursor in water produces Au sol, in which several nanometer size Au particles are able to maintain their integrity only in the presence of stabilizers. The next adsorption step is a key point; the preformed metal particles of sol must be adsorbed onto solid oxide support provided that sufficient strong interaction prevails between the stabilized particles in water and the surface of oxide to obtain homogeneous distribution of Au. Stabilizers, however, must be eliminated before catalytic run by calcination treatment.

In our laboratory, Au sols for heterogeneous catalytic purposes have been studied and applied for the past few years.\(^{16–18}\) Gold supported on mixed oxide supports such as TiO\(_2\)—SiO\(_2\) and TiO\(_2\)—SBA-15 or CeO\(_2\)—SBA-15 was prepared with special regard to ensure intimate contact of the active oxide and Au on a high surface area SiO\(_2\). A unique approach, the so-called localized oxide promotion of gold, has been established and has developed producing Au/SiO\(_2\) catalysts that contain TiO\(_2\) moieties on Au particles due to the postmodification of preformed Au particles.\(^{19}\) This postmodification was done before or after the sol adsorption step. It was concluded that these “inverse catalysts” with even as low as 0.2 wt % TiO\(_2\) possess better CO oxidation activity than the parent Au/SiO\(_2\), whereas at 4 wt % TiO\(_2\) content they are more active than Au/TiO\(_2\), although the Au particle size for the latter sample was unfortunately higher (sintering on TiO\(_2\) could not be prevented). At low TiO\(_2\) concentration, transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) measurements proved the presence of TiO\(_2\) patches on Au particles, whereas at higher TiO\(_2\) loading Ti appeared on both Au and SiO\(_2\) support. The enhanced CO oxidation activity was interpreted as a result of large and especially active Au-TiO\(_2\) interface.

According to this novel, “inverse catalyst strategy,” we continued our research with the intention to produce CeO\(_2\) decoration selectively on Au nanoparticles because this approach may offer new and unknown possibilities in gold catalysis. Studies from the literature dealing with the inverse oxide/metal interface revealed that the oxide—metal interactions can alter the electronic states of the oxide producing unique chemical properties.\(^{20}\) The covering oxide nanoparticles are much easier to reduce than extended surfaces of, for example, bulk CeO\(_2\), and the strain caused by the mismatch between the lattices of the oxide and metal can facilitate the formation of O vacancies in, for example, ceria (CeO\(_2\) deposited on Rh(111)).\(^{21}\) Furthermore, it was found that CO molecules that do not adsorb on both titanium oxide and Au(111) surface separately held at a temperature of 200 K can easily be adsorbed on the formed titania/Au(111) system at the same temperature.\(^{22}\)

The work of Zhou and his coworkers\(^{23}\) is closely related to our results. They investigated the enhanced catalytic activity of inverse CeO\(_2\)/Au model structures produced by physical methods. The induced activation of the interface gold atoms with ceria nanoparticles (<5 nm) was independent of the grain size of the gold film, but it was proportional to the amount of CeO\(_2\). The other system investigated by Zhou and coworkers was the unique Au/CeO\(_2\) multilayer nanotowers,\(^{24}\) where Au and CeO\(_2\) interfaces were produced with layer thicknesses of 20 and 4.5 nm. The activity increased with the number of interfaces (length of the interface), but the difference in the activity of thick and thin layers indicated a size contribution as well (probably caused by the different degree of strains in the films).

The idea of postaddition of CeO\(_2\) modifier to Au catalyst was realized by Senanayake and coworkers\(^{25}\) as well; however, they investigated Au(111) model surfaces in water—gas shift reaction (WGS). Although the clean Au(111) was not catalytically active for the WGS, gold surfaces that were 20 to 30% covered by ceria nanoparticles had good activities, and they concluded that the moderate chemical activity of bulk gold was combined with that of a more reactive oxide in a synergetic way. The total encapsulation of Au by ceria was accomplished by using microemulsion method, but no activity was observed in water—gas shift reaction. The authors suggested that the activity depends rather on electronic aspects of metal—ceria interface instead of oxygen mobility of the ceria oxide shell.\(^{26}\)

The aim of the present work was to prepare Au/SiO\(_2\) powder catalysts modified by different amounts of CeO\(_2\) in a special way when nanosize Au is decorated with CeO\(_2\) patches. We wished to investigate the catalytically active Au—CeO\(_2\) interface when CeO\(_2\) is of nanosize and is present as thin slabs in intimate contact with gold.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. Aqueous solutions of HAuCl\(_4\), 3H\(_2\)O (Aldrich); poly(diallyldimethylammonium) chloride (PDDA), 20 wt % in water (Aldrich), Figure 1a; cerium(III) nitrate...
hexahydrate (Merck); tannic acid (Aldrich), Figure 1b; sodium-citrate (Aldrich); and commercial Aerosil 200 silica (Degussa) or ceria nanopowder (Aldrich) supports were used in the preparations.

The preparation of gold hydrosol with an average particle size of ∼6 nm is described elsewhere.18 In brief, HAuCl4 was reduced by a mixture of tannic acid and sodium citrate at 60 °C and left at that temperature for 30 min under stirring. The red color of the sol evidenced the reduction of Au3+ ions. Several batches were prepared, but the mean particle size was always checked and ranged between 5.7 and 6.5 nm.

The above Au sols were used in the next steps as “parent” sols. We used appropriate amounts of the sol to give 2 wt % Au in all supported samples, whereas the cerium content of the samples was planned to be varied between 0.5 and 7.5 wt % CeO2. The cerium precursor was introduced in two different ways.

In preparation method A, a calculated amount of aqueous solution of 20 mM Ce-nitrate was added to the Au sols at room temperature under stirring; then, the temperature was increased to 60 °C within 1 h and kept there for 4 h. Finally, the solution was cooled to room temperature. When the largest amount of Ce(III) nitrate was added to the Au sol, destabilization of the colloidal system happened and red precipitate with hardly observable tiny particles formed. Additional citrate seemed to dissolve this precipitate. Because of this experience, blank experiment (using all components without gold) was taken to elucidate whether the precipitate formed only in the presence of gold or the reaction media itself favors precipitate formation. Tannic acid-citrate solution at pH 8 was heated to 60 °C, where the tannic acid started to hydrolyze as during the usual sol preparation; then, HCl was added to set the pH 6.5 (the final pH of the parent gold sol). We added 20 mM Ce(III)-nitrate dropwise to the mixture at 60 °C, and white disperse precipitate was observed after the addition of 0.6 mL of Ce(III)-nitrate to 16 mL of blank solution. This white precipitate seemed to dissolve by the eye upon the addition of more Na-citrate (like in the case of Au−Ce composite sol described above). The next sample with less Ce content was prepared with more care, and thus the addition of Ce(III) nitrate solution to the Au sol was done drop-by-drop; finally, some additional citrate was added (half of the volume of actual Ce-nitrate added) and no change of color was observed this time, and the sol was stable on the following days as well.

The adsorption of Ce-containing Au sols (composite sol) onto Aerosil SiO2 was accomplished with the aid of PDDA polycation. Without this additive, the adsorption of the sols on silica could not be taken place. A certain amount of PDDA (depending on the actual sol, usually 1.5 to 1.7 mL of 0.08 wt % aqueous PDDA solution per 100 mg of SiO2) was preadsorbed on Aerosil under stirring at room temperature. Next, the pure Au or the composite sol was added to the silica suspension, and the white color of silica changed to red or reddish purple as a sign of the successful adsorption. In some cases, an additional amount of PDDA was necessary to complete the adsorption of the composite sol or to cause the flocculation of silica that facilitates filtration because Aerosil silica contains loose aggregates of individual SiO2 particles of 12 nm and so it is hard to filter. The suspension was vigorously stirred at room temperature for ∼1 h; then, the solid was separated by filtration, washed thoroughly with water, and dried for 2 days at 70 °C.

In preparation method B, the parent Au/SiO2 was further processed. The dried sample was mixed with the appropriate amount of cerium nitrate solution at 50 °C for 40 min; then, the temperature was raised to 60–65 °C, and the water was allowed to evaporate. (It usually took 4 to 5 h.) Finally, the Ce-loaded Au/SiO2 samples were dried for 2 days at 70 °C.

Therefore, catalysts with different CeO2 content were produced by methods A and B with more-or-less the same Au loading of ∼2 wt %. The samples prepared by method A are denoted, for instance, by ACe0.04, where the numbers at the end refer to CeO2 content in wt %. The samples produced by method B are labeled in the same way but with starting letter B. As references, ∼2 wt % Au/SiO2 and ∼2 wt % Au/CeO2 were prepared the same way without the addition of Ce precursor. However, in the case of CeO2 support, the sol adsorption step was done at pH 2 to 3 (to increase the positive surface charge of the support) without the addition of PDDA polycation.

2.2. Determination of Au and Ce Content. The Au and Ce content of the samples were first determined using a double-focusing inductively coupled plasma mass spectrometer (ICP-MS, ELEMENT2). All measurements were made using a Scott-type spray chamber operating at room temperature and a Meinhard concentric nebulizer. The dried catalyst sample was dissolved using 1 mL of HNO3 and 3 mL of HCl acid mixture and heated to 80 °C in water bath for 20 min and cooled to room temperature afterward. Further dilutions were made using 2% (w/w) HNO3/2% (w/w) HCl solution before the ICP-MS analysis using 1 ng g−1 Rh as internal standard.

The Ce content of three samples was determined using radioisotope-induced X-ray fluorescence spectrometry (XRF) method27 applying a very good correlation factor between ICP and XRF measurements. The Ce content of the samples of ∼50 mg was measured, and 241Am ring source with 3.65 GBq activity was used as an excitation source. The emitted X-rays were detected by a Canberra 30165 type Si(Li) X-ray detector. The detector signals were processed by standard NIM electronics and collected by a Canberra 33plus multichannel analyzer. Measurement time was 1800 s. The recorded spectra were evaluated by the AXIL software.28

CeO2 content of all samples was calculated from the Ce content obtained by the above techniques.

2.3. XRD Measurements. The phase composition of crystalline components of selected samples was investigated by X-ray
diffraction using a Philips Xpert powder diffractometer with Cu Kα radiation (λ = 0.15418 nm). The relative fraction of CeO2 and Au phases was characterized by the ratio of the integrated intensities of the strongest peaks of CeO2 and Au at 2θ = 28.7 and 38.3°, respectively. The crystallite size for each phase was determined from the full width at half-maximum of the first peak using the Scherrer equation.

2.4. XPS Measurements. XPS measurements were performed by a KRATOS XSAM 800 XPS machine equipped with an atmospheric reaction chamber. Al Kα excitation and 40 eV pass energy was used during data acquisition. The binding energies (BEs) were determined relative to C1s at 285 eV. The powdered samples were placed on the stainless-steel sample holder without any fixation and pumped down very slowly to avoid dusting. Spectra were taken in the as-received state and after 300 °C calcination in situ to get information about the surface concentration of gold and the oxidation state of cerium. Sensitivity factors given by the manufacturer were used for the quantification.

2.5. TEM Measurements. The distribution of Au and CeO2 and the size of gold particles was studied by a conventional Philips CM20 TEM operating at 200 kV equipped with energy dispersive spectrometer (EDS) for electron probe microanalysis. The TEM samples were prepared by dropping aqueous suspensions of the Au–CeO2/SiO2 samples on carbon-coated micro-grids. The gold particle size distribution was obtained by measuring the diameter of equiaxial metal particles. High-resolution transmission electron microscope (HRTEM) investigations were carried out by a JEOL 3010 microscope operating at 300 kV with point resolving power of 0.17 nm.

2.6. Catalytic Tests. CO oxidation was measured at atmospheric pressure in a plug flow reactor connected to a QMS-type Pfeiffer TSU 071 E. Catalyst (30 mg) was used, which was in situ calcined at 300 or 450 °C in 20% O2 in He mixture for 1 h (10 °C/min heating rate, 30 mL/min gas flow). Temperature-programmed reaction was performed with a gas flow of 0.54%

### Table 1. Metal Loading, Temperature of 50% CO Conversion, and Au Particle Size of the Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Au content (wt %)</th>
<th>CeO2 content (wt %)</th>
<th>T50% (°C)</th>
<th>Au particle size (nm)a</th>
<th>CO and 9.1% O2 in He at 55 mL/min with 4 °C/min ramp rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcCe0.04</td>
<td>2.0</td>
<td>0.04</td>
<td>300 °C</td>
<td>121</td>
<td>6.30 ± 1.45</td>
</tr>
<tr>
<td>AcCe0.08</td>
<td>1.8</td>
<td>0.08</td>
<td>450 °C</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>AcCe0.16</td>
<td>1.8</td>
<td>0.16</td>
<td>50</td>
<td>83</td>
<td>8.07 ± 3.44</td>
</tr>
<tr>
<td>BcCe0.06</td>
<td>2.0</td>
<td>0.06</td>
<td>40</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>BcCe0.11</td>
<td>2.0</td>
<td>0.11</td>
<td>50</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>BcCe0.60</td>
<td>2.0</td>
<td>0.60</td>
<td>50</td>
<td>48</td>
<td>5.73 ± 1.92</td>
</tr>
<tr>
<td>BcCe1.14</td>
<td>1.8</td>
<td>1.14</td>
<td>50</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>BcCe2.64</td>
<td>1.9</td>
<td>2.64</td>
<td>51</td>
<td>40</td>
<td>7.15 ± 1.75</td>
</tr>
<tr>
<td>BcCe7.40</td>
<td>1.7</td>
<td>7.40</td>
<td>40</td>
<td>40</td>
<td>6.57 ± 1.65</td>
</tr>
<tr>
<td>Au/SiO2</td>
<td>2.0</td>
<td>0</td>
<td>401</td>
<td>401</td>
<td>6.37 ± 3.78</td>
</tr>
<tr>
<td>AcCe0.08</td>
<td>2.0</td>
<td>0.08</td>
<td>40</td>
<td>74</td>
<td>8.00 ± 3.81</td>
</tr>
</tbody>
</table>

a Determined by TEM after calcination at 450 °C, followed by catalytic run and only for Au/CeO2 after calcination at 400 °C, followed by catalytic run. Nominal value.

**Figure 2.** Measured CeO2 content of samples prepared by method A versus intended CeO2 loadings.

CO and 9.1% O2 in He at 55 mL/min with 4 °C/min ramp rate. The conversion was calculated on the basis of the CO2 production.

### 3. RESULTS AND DISCUSSION

3.1. Formation of Au–CeO2 Nanostructures on Silica Support. Table 1 contains data of metal loading of the samples together with the particle size determined by TEM and catalytic data, which will be discussed later on. The Au contents of the samples agree reasonably with each other, and it is close to the nominal 2 wt %. We are certain that the undetermined Au loadings are ∼2 wt %, too, because the discoloration of liquid phase in the sol adsorption step showed that all Au nanoparticles in sol were attached to the silica.

It is certainly eye-catching that the final CeO2 content of samples prepared by method A is very low and more than 10 times less than the intended values (0.5, 2.5, and 7.5 wt %). Figure 2 shows that by method A the attachment of all Ce-containing components to the silica surface was very limited. Therefore, we prepared low-loaded samples by method B as well to be able to compare catalysts synthesized by the two methods at similar or the same Ce loadings. Of course, the success of Ce introduction by method B is obvious because it can be considered to be a kind of wet impregnation of Au/SiO2 by cerium nitrate; all Ce compounds remain on the surface of the sample after evaporation of water. In our previous work, the application of Ti–lactate complex allowed the attachment of Ti component with as high as 6.5 wt % TiO2 by method A. In this work, we used a simple Ce salt, cerium nitrate, as Ce precursor and this can make a difference.

Let us consider what happens at the addition of cerium nitrate to the parent Au sol, which has a pH 6.5 containing hydrolyzed tannin and citrate and all byproducts of reduction. For the preparation of crystalline CeO2 nanoparticles, the main synthesis methods are based on solution phase methods such as alcoholothermal,

hydrothermal, and thermolysis processes. In the hydrothermal route, the starting precursor can be Ce(III), which is usually oxidized to Ce(IV) by the presence of air or other oxidants. Because of the presence of base, provided at higher pH, Ce(OH)4 forms, then Ce(OH)4 nucleation and growth take place, and finally the Ce(OH)4 particles formed dehydrate into CeO2 during heat treatment.

Because Ce(IV) is more easily...
hydrolyzed than Ce(III), homogeneous precipitation can be initiated by H2O2 addition at low temperature that slowly oxidizes Ce(III). Therefore, precipitation can be induced by the change in the oxidation state of precursor cation and not by the pH; however, base is needed to complete the hydrolysis. Ce(III)-hydroxide is a definite compound, but Ce(IV)-hydroxide, which can be described as CeO2·2H2O, is considered to be a hydrous oxide that dehydrates progressively.33 The primary particle of hydrous ceria possesses at pH <7.2 a positive surface charge, and thus hydrous ceria is expected to adsorb anions.34

From the above references it is evident that the final oxidation state of hydroxide precipitates formed during hydrolysis is mostly Ce(IV). However, Kockrick and coworkers35 reported the formation of nanoscale Ce(OH)3 particles inside micelle structure of inverse microemulsion using cerium(III) nitrate and aqueous ammonia. Destabilization of microemulsion by acetone, filtering, washing, and drying at 100 °C resulted in Ce(OH)3 particles of 2 to 3 nm, as was detected by HRTEM. (Lattice spacing corresponded to Ce(III)-hydroxide.)

We should keep in mind that the presence of residual citrate and tannic acid or the hydrolyzed byproducts such as gallic acid may play a crucial role in determining the fate of Ce precursor. Both reducing/stabilizing agents present in the Au sol are able to complex metal ions such as Ce(III) or stabilize CeO2 or Ce-hydroxide particles as well.36–38 CeO2 nanoparticles from cerium salt were produced with citric acid as protective agent against particle growth. Cerium–citric acid complex formation was suggested to occur first, and after its hydrolysis cerium hydroxide sol formed, where the nanoparticles were covered with citric acid.39,40 Marcilly and coworkers also used citric acid during ceria preparation while increasing the pH to the basic region and applying fast evaporation of the solvent at 70 °C. The particles formed this way were amorphous and nanosize and contained mainly Ce(III), as was detected by XPS.41,42 Note that in the above literature data the pH of the liquid phase was basic during preparation and so Ce(III) hydrolysis certainly happened. We could ascertain the presence of cubic CeO2 and Au in both methods, the gold nanoparticles were located mainly on silica when Ce(III) nitrate was added. The samples were washed to remove the majority of organic and inorganic residues and dried at 60 °C before Ce addition; however, negatively charged residual-shell around the gold can be expected, which may localize a part of added Ce-nitrate.

In both methods, the final evolution of Au–CeO2 nanostructures takes place during calcination in air when all Ce species transform into CeO2.37

### 3.2. Structure of the Catalysts: Particle Size and Distribution of Ce Species

In whatever form Ce species are present after drying, calcination pretreatment to remove organic moieties transforms them into Ce-oxide. X-ray diffraction patterns of BCe7.40 and BCe6.40 shown in Figure 3 were taken after calcination at 450 °C to check the presence of crystalline CeO2 and Au phases. Highly dispersed CeO2 in samples of ~1 wt % CeO2 and lower cannot be detected by XRD. Crystallite sizes are listed in Table 2. We could ascertain the presence of cubic CeO2 fluorite structure with ~5 nm crystallite size in both samples. The intensity ratios of X-ray diffraction peaks for CeO2 and Au for samples BCe7.40 and BCe6.40 are also shown in Table 2. Because the scattering strengths are different for the various crystalline phases; therefore, these values do not give the volume or weight fractions of CeO2 and Au. It can be used only for comparison purpose between the two samples. Anyway, the four times larger intensity ratio for sample BCe7.40 revealed that a part of the CeO2 is not visible by XRD in BCe6.40, suggesting the presence of an X-ray amorphous part of CeO2.
Table 1 presents Au particle sizes determined by TEM and the standard deviations, which are characteristic of the particle size distribution. The nice, even distribution of individual Au particles is clearly seen in Figure 4 that depicts the TEM micrograph of Au/SiO₂ after calcination pretreatment at 450 °C and catalytic run. The particle sizes of all samples do not differ significantly; they range between 5.7 and 8.1 nm, which is not the interval of the usual sudden change in activity with Au dispersion (dₐu ≈ 0–5 nm). Accordingly, differences in catalytic behavior (see later) can be attributed rather to the characteristics of Au/CeO₂ interface than the Au particle size itself. Looking at the particle size distributions of Au/SiO₂ and Au/CeO₂ reference samples, it is clearly seen that ceria modification induces a kind of stabilization effect because the Au–CeO₂–SiO₂ systems are more monodisperse, except, no wonder, for ACe0.16, which was the sample obtained by the adsorption of previously destabilized Au/Ce composite sol.

We already know that XRD detected the crystalline CeO₂ phase. EDS measurements detected Ce and oxygen as well, and conventional TEM measurements (not shown here) gave us a hint on the existence of CeO₂ particles on silica surface of BCe7.40, but at lower Ce-content only Au particles could be distinguished by TEM.

HRTEM provided further information on the location, size, and structure of the promoting oxide in three samples prepared by method B and in the one with the lowest Ce content prepared by method A. The HRTEM micrographs of sample BCe7.40 are shown in Figure 5a,b. Figure 5a reveals the presence of nanosize CeO₂ particles, in contact with the Au nanocrystals surfaces. Two thin slabs with fringes can be observed partially covering the Au particles in the inset of the Figure. The fringe period (0.32 nm) corresponds to the (111) lattice spacing of cubic CeO₂. Far from the Au particles, the pure SiO₂ surface is also covered by thin CeO₂ particles of 5–15 nm size, as seen in Figure 5b by the lattice fringes characteristic to CeO₂ (111). Note that although most gold particles are decorated by fringes of CeO₂, we found Au particles with no sign of CeO₂. The absence of fringes does not definitely mean the absence of CeO₂. It may mean that the crystallographic alignment of a CeO₂ crystal is far from a suitable zone; that is, it does not favor lattice imaging. The sample BCe2.64 also contained CeO₂ particles both in contact with and separated from the Au, but the amount of separate CeO₂ was less because of the lower Ce content. Figure 6 shows the HRTEM and EELS elemental mapping results of BCe2.64.

Figure 4. TEM image of the sample Au/SiO₂ after calcination pretreatment at 450 °C, followed by a catalytic run. Even distribution of Au particles is seen that is characteristic to all investigated samples.

Figure 5. HRTEM of BCe7.40 with 7.4 wt % CeO₂. The 0.32 nm period lattice fringes represent CeO₂ crystals both attached to the Au particles (a) and located in large patches on the SiO₂ (b).
aim, a sample prepared by method A (0.04 wt % Ce) was also investigated. HRTEM and EELS found no trace of Ce-oxide on silica; however, it gave definite proof of CeO$_2$ associated with Au (the existence of Au–CeO$_2$ interface), as it is presented in Figure 8. Figure 8a–c shows the unfiltered HRTEM image, the EELS Ce-map, and the enlarged frame “c” from panel a, respectively. The bright contrast in the Ce map (b) indicates a distribution of Ce exclusively around/on the Au particles.

(See also the arrows.) No remarkable signal of Ce was detected apart from the Au crystals. Furthermore, in Figure 8c, a single Au particle is seen (enlarged frame from (a)), with the lattice fringes of CeO$_2$ nanoparticles on its surface.

We calculated the possible maximum coverage of CeO$_2$ exclusively on Au surface assuming 2 wt % Au and 0.0326 wt % Ce content and $d_{\text{Au}} = 6$ nm size particles. Using the work of Stanek and coworkers,$^{44}$ where the number of Ce atoms on CeO$_2$(111) surface is given as $2.31 \text{ Ce atoms}/a_0^2$ where $a_0 = 0.5412$ nm, and assuming monolayer coverage of CeO$_2$ on Au (which is not the case), we obtained that at such a low Ce content only 17% of the Au surface can be covered by CeO$_2$. If ceria is present in multiple layers, then this number is even smaller. Certainly, our calculation applies several assumptions; however, we get an approximate idea of how dispersed CeO$_2$ must be.

Considering all experimental results, XRD and HRTEM measurements proved the presence of crystalline CeO$_2$ particles/domains of different size (between $\sim$2 and 15 nm, depending on CeO$_2$ loading) in our samples. Depending on the Ce loading and preparation method, ceria can be found selectively on the Au nanoparticles or both on Au and on the bare silica surface. The localized oxide promotion of gold is greatly accomplished because it seems that independent of the preparation method, gold surface is somehow saturated by ceria first; then, the increase in Ce-loading causes Ce species spread over the support surface as well. Full coverage of a single Au particle by ceria, viz. core–shell structures, was not detected. Scheme 1 summarizes the main points and differences of the two preparation methods, depicting the assumed interactions and final catalyst structures.

### 3.3. Catalytic Properties.

CO oxidation was used as a highly sensitive tool to test the presence of Au–CeO$_2$ active interface. The catalytic measurements were conducted after calcination treatments at 300 or 450 °C. Carbonaceous deposits remaining on catalytic active sites were removed already at 300 °C in air; however, when applying 450 °C calcination treatment, the CO$_2$ peak centered at $\sim$300 °C had a negligible tailing above 300 °C,
which means that insignificant organic material may have been remained on the support after the lower temperature calcination.

Figure 9 summarizes the CO oxidation activity of the samples, viz. the temperatures where 50% CO conversion was achieved ($T_{50\%}$) as a function of ceria content. Data obtained after different calcination temperatures and different preparation methods are distinguished but surprisingly lay on the same line, which sharply increases at CeO$_2$ < 0.5 wt %, meaning the decline of activity. The numeric data are collected in Table 1. The dotted line at 74 °C in Figure 9 indicates the activity of the reference Au/CeO$_2$ sample. We can state that enhanced catalytic activity of CeO$_2$-modified samples was found compared with Au/CeO$_2$ reference sample at as low as 0.6 wt % of CeO$_2$-content on the other side makes ACe0.04 sample already a more efficient catalyst than the reference Au/SiO$_2$.

The difference between the activities of the samples is much more discernible in Figure 10, where a few representative conversion curves obtained after calcination pretreatment at 450 °C are plotted against temperature. The main issue is that after reaching 0.6 wt % CeO$_2$-content (by method B) there is only a minor difference between the catalysts. Furthermore, there is a slight difference in favor of method A because ACe0.04 sample exhibits better activity than BCe0.06 despite the higher Ce content of the latter. We tentatively suggest that when Ce precursor is added to the sol, the stabilizing sphere around Au is full and attracts more Ce species to be attached and complexed there than the one after washing off most of organic materials and drying (what applies for method B). It is still surprising (but is in accordance with the evolution of CO$_2$ in calcination resulting from the oxidation of organic residues) that washing leaves a sufficient part of negatively charged stabilizing sphere on the

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**Scheme 1. Main Steps of Preparation with the Suggested Structures and Interactions**

- **Method A**: starting with Au sol
  - Ce(NO$_3$)$_3$ + Au sol at 60°C/4h
  - PDDA preadsorbed on SiO$_2$
  - Filtering, washing, drying

- **Method B**: starting with dried Au/SiO$_2$
  - SiO$_2$ + Au/SiO$_2$ at 60-65°C until evaporation of water, drying

Negatively charged stabilizing sphere in solution: tanin/citrate + by-products of reduction

CeO$_2$ patches, decoration

Part of positively charged PDDA polycation

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**Figure 9.** CO oxidation activity of the samples prepared by methods A and B: the temperatures where 50% CO conversion was achieved ($T_{50\%}$) as a function of ceria content. 300 °C calcination/pretreatment temperature is shown with open symbols, and 450 °C calcination/pretreatment temperature is shown with solid symbols. The dotted line represents the activity of Au/CeO$_2$ after calcination at 300 °C. The small inset enlarges the range of 0 to 0.6 wt % CeO$_2$ content.
surface of Au, and so when Ce-nitrate added during preparation method B to the suspension it is bound first to the Au particles as HRTEM and catalytic studies proved. Otherwise, if 0.06 wt % CeO₂ was homogeneously dispersed on silica surface, then it would not provide a catalyst with T₅₀% = 140 °C. (Note that T₅₀% = 401 °C for Au/SiO₂.)

Considering the results of XRD and TEM, we are definite to say that nanosize, thin CeO₂ domains that are localized around Au particles play a crucial role in the reaction, and CeO₂ islands far from Au particles are not able to influence or enhance catalytic activity through the well-known oxygen storage and release capacity to a significant extent. The CeO₂ coverage on Au is somewhat limited because of the complexing capacity of stabilizing sphere; this is why at higher Ce-loading even more and more ceria is deposited on the bare silica and additional activity increase cannot be observed or it is only negligible.

Let us consider what the possible reasons of the very high activity of Au–CeO₂ interface can be. Gold particle size difference is not suggested to be the determining factor because dAu varies between 5.7 and 8.1 nm for all samples. The commercial ceria nanopowder, which is the support of the reference sample, consists of 6–50 nm size particles, whereas our ceria decoration over gold has a particle size of ∼2–5 nm. It is known from the literature that the structure and morphology of ceria can greatly influence catalytic activity. The morphology effects of nanoscale ceria possessing different shapes such as rod, polyhedra, or cube were investigated in Au/CeO₂ samples, and XRD, TEM, temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance Fourier transform infrared studies (DRIFTS) revealed that not the crystallite size but the surface structure, the exposed surface planes, are of high importance in achieving good redox ability and catalytic activity: the predominantly exposed {100}/[110]-dominated surface structures of ceria nanorods turned out to be the best supports for gold. The CeO₂ islands and slabs seemed to be very thin, but we could not find distinguished crystal planes in abundance by the characterization methods applied. However, because they formed by calcination treatment at a relatively low temperature from organic complexes or hydroxides arranged around Au particles in liquid phase, they must contain surface defect sites and many oxygen vacancies.

CO oxidation on Au/CeO₂ is suggested to take place via the reaction of CO adsorbed on low-coordinated Au sites and oxygen activated on the oxygen vacancies formed along the Au–CeO₂ interface (adsorption sites). There is a certain correlation observed between the presence of oxygen vacancies, the number of Ce(III) ions, and the increased catalytic activity, as the following studies reveal. The work of Widmann and coworkers using TAP technique (temporal analysis of products) proved that CO oxidation activity can be enhanced by the removal of ∼7% surface oxygen of ceria (reductive activation). Furthermore, model studies showed that the Ce(III) concentration is in line with the oxygen vacancy concentration, and the presence of a large number of oxygen vacancies in the oxide support influences the binding energy of small Au particles with d < 2 nm and the CO desorption temperature, but these effects disappear with an increase in Au size. According to Qian and coworkers, an increase in calcination temperature in air annihilates surface oxygen vacancies in CeO₂ (the Ce(III)/Ce(IV) ratio decreases measured by XPS), whereas Ce(III)/Ce(IV) increases when the support is loaded with Au, which means that the loading of Au facilitates the formation of surface oxygen vacancies. Escamilla-Perea and coworkers declared the promoting role of Ce(III) ions in CO oxidation because the decrease in their surface exposure led to a decrease in activity.

In our case, two parameters of ceria might be of high importance concerning the high activity observed, namely, the size (dimension) of ceria islands, and the preparation medium, which is reducing, with citric acid and gallic acid present. XPS, STEM, and IRAS techniques applied on gold deposited on CeO₂, thin films and CeO₂ nanoparticles revealed that 3+ is the dominating oxidation state of ceria in smaller particles in the nanosize CeO₂. XPS results suggested that ∼5 nm is the particle size below which ceria exhibits a significant degree of reduction. Tsunekawa and coworkers showed during investigation of ceria sols containing 6.7–2.1 nm particles that electron diffraction lattice parameter changes with size, meaning conversion of Ce(IV) near the surface to Ce(III). As for the reducing medium, Chen and coworkers found that ascorbic acid treatment of sol–gel derived Au/CeO₂ might have been the reason for the improvement of the Ce(III)-ion-related defect content of ceria and the higher ratio of ionic gold. Ceria that was prepared by Marcilly method in the presence of citric acid after only drying contains mainly Ce(III).

According to these literature references, it seemed reasonable to carry out XPS measurements on the samples to determine the Ce(III)/Ce(IV) ratio. Unfortunately, even at the highest CeO₂ content it did not make sense to fit the broad and unstructured peaks of the cerium region. The only definite result was that BCe7.4 sample does contain Ce(III) component beside Ce(IV) in as prepared state, which upon a 300 °C calcination treatment does not change significantly. This finding means that the Ce(III) component is highly stable. The determination of ~25% Ce(III) concentration is only approximate and was based on the ratio of the total Ce 3d area to the Ce(IV) satellite peak area at ∼917 eV BE. The Ce 3d intensity in the most interesting samples with low CeO₂ content was extremely low and could hardly be seen on the curved baseline. That is why we had to rely on the literature references of somewhat similar systems and keep in our mind that all reaction conditions (presence of reducing and
CeO$_2$ particles of 3 nm are assumed. Active sites are Au atoms within 1 nm range around the CeO$_2$ hemispheres; this is called perimeter.

Next, theoretical calculation was done to quantify the catalytic data at the extreme low CeO$_2$ contents. TOF values were calculated using the following model that we know includes several assumptions. Flat Au surface was supposed, which is covered by hemispherical CeO$_2$ particles of 3 nm, and TOF values were calculated related to one active Au site. The initial reaction rate was calculated at 30 °C when the CO conversion values were relatively low, below 15%. The results are summarized in Table 3. TOF values are in great accordance with the work of Zhou and coworkers, who did TOF calculation for a model type CeO$_2$/Au inverse system. The TOF of the sample of the three lowest CeO$_2$ contents does not differ significantly, suggesting that the increase in CeO$_2$ loading in this region results in an increasing number of similar active sites. The somewhat lower TOF calculated for BCe0.60 may reflect the appearance of some portion of CeO$_2$ on SiO$_2$ instead of Au.

We should consider finally the effect of 150 °C difference in the calcination temperatures applied as pretreatment. An increase in calcination temperature is expected to heat the oxygen vacancies to some extent and increase the crystallization of ceria. Our data, however, do not reflect any significant changes due to the increase in calcination temperature, meaning that the Au–CeO$_2$ interface formed is relatively stable under our reaction conditions. In the work of Beier and coworkers, liquid–phase oxidation of alcohols was studied on silver-based catalysts promoted by ceria in a simple way, viz. commercial CeO$_2$ was mixed and calcined at different temperatures with the 10 wt % Ag/Aerosil sample. The mixture that was calcined at 500 °C was highly active, and the calcination time had a great influence on activity and selectivity: a medium time (30 min) was the perfect choice, whereas the particle size determined by XRD did not change with an increase in calcination time. Other possible reasons were not discussed. In our case, BCe7.40 had an average of 6.42 nm Au particle size after 300 °C calcination (not included in Table 1), whereas that increased to 7.15 nm after 450 °C calcination. The difference in particle size is negligible; moreover, the sample calcined at 450 °C was more active than the other. This shows that Au particle size difference indeed is not the reason of the difference in catalytic activity between the samples. We can conclude that compared with the TiO$_2$–Au/SiO$_2$ system, where the activity reached the activity of the reference Au/TiO$_2$ sample only at 4 wt % TiO$_2$-loading, here in the case of CeO$_2$–Au/SiO$_2$ systems a small amount of Ce was enough to reach the activity of the Au/CeO$_2$ reference sample (0.16 wt % CeO$_2$).

4. CONCLUSIONS

In the present work, CeO$_2$–Au/SiO$_2$ inverse catalysts were produced and investigated. Au/SiO$_2$ catalysts were promoted by 0.04–7.4 wt % CeO$_2$ using two parallel methods based on the application of Au sols. In method A, Ce(III) nitrate was added to the Au sol, and after a heat treatment at 60 °C the adsorption step onto SiO$_2$ was accomplished using PDDA. In method B, the Ce precursor was added to the washed and dried Au/SiO$_2$ parent catalyst, producing a suspension that was also kept at 60 °C until the evaporation of water. By method A, the introduction of Ce was very limited; the maximum cerium content in the final samples corresponds to 0.16 wt % CeO$_2$.

XRD showed the presence of CeO$_2$ nanocrystals at 2.4 and 7.4 wt % CeO$_2$ content (above the detection limit of the technique). HRTEM measurements found thin CeO$_2$ moieties over gold already at 0.04 wt % CeO$_2$ in the calcined catalysts. This extreme low 0.04 wt % CeO$_2$ content decreased the temperature of 50% CO conversion by 280 °C compared with Au/SiO$_2$ reference, and 0.16 wt % CeO$_2$ was enough to closely approach the activity of the Au/CeO$_2$ reference sample. The increase in Ce-loading above 0.6 wt % CeO$_2$ content apparently did not increase the CeO$_2$ coverage on gold nanoparticles because the samples had almost the same activity up to 7.4 wt % CeO$_2$. HRTEM proved that the additional CeO$_2$ is located on the silica surface when this is the only possibility (method B) or removed by the filtration of liquid phase (method A).

The localization of Ce species around gold particles in the liquid phase must be provided and limited by the interaction with the organic stabilizing shell. This applies for method B as well.

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