Supported Ag Nanoparticles and Clusters for CO Oxidation: Size Effects and Influence of the Silver–Oxygen Interactions

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ABSTRACT: Supported Ag catalysts on silica and corundum have been synthesized applying an improved impregnation technique. The resulting Ag particle sizes can be divided into three categories concerning: (I) bulk-like, (II) nanoparticles of 1–6 nm, and (III) in situ created Ag clusters below 1 nm. Ag nanoparticles and bulk-like Ag are investigated concerning their pretreatment dependence for CO oxidation showing that harsher pretreatment conditions need to be applied for smaller particle sizes, based on their tendency to form Ag2CO3. A particle size effect for Ag in oxidation reactions is investigated using CO oxidation as a test reaction. The CO oxidation performance is increasing with decreasing particle size with Ag clusters showing the highest activity. A novel method based on the adsorption of ethylene (C2H4) as sensor molecule is further used to discriminate the silver–oxygen (Ag–O) interaction strength of bulk-like Ag, Ag nanoparticles, and Ag clusters, showing a distinct Ag–O chemistry for the three individual particle size regimes. By application of C2H4 breakthrough curve measurements, the available Ag surface area is determined which enables a correlation of Ag surface area and CO oxidation rate. Correlations of Ag–O interaction strength, Ag surface area, and CO oxidation activity are discussed within the scope of this work.

KEYWORDS: Ag nanoparticles/clusters, CO oxidation, Ag–oxygen interaction, apparent Ag surface area, size effect

INTRODUCTION

Supported Ag catalysts are used in several oxidation reactions such as of carbon monoxide1 and methanol2 or epoxidation of ethylene3 and propene.4 Since Ag is generally applied in a broad particle size (PS) regime, reliable studies on a Ag PS effect are rare. The investigation of PS effects in catalysis is significantly important since they can influence the catalyst’s activity and selectivity due to changes in chemical characteristics caused by quantum-confinement effects for very small particles of only a few nanometers.5–9 For the ethylene epoxidation reaction the influence of Ag PS in the regime of roughly 10–200 nm has already been well investigated with an overall consent that increasing Ag PS up to around 50–80 nm leads to more active but equally selective catalysts and that nanoparticles below 10 nm show a suppressed or decreased catalytic activity, following a volcano-type behavior.5–7,10–14 Only a limited number of studies were so far able to investigate the Ag PS regime of <10 nm concerning their catalytic activity in ethylene epoxidation,15 propylene epoxidation,16 carbon monoxide oxidation,17 or the interaction of Ag with oxygen18 and various oxide support surfaces.19,20 However, so far the results allow no clear conclusion whether Ag nanoparticles are more or less active in oxidation reactions when decreasing its size down to a few nanometers or cluster size. In addition, the debate is influenced by the complex and unique chemistry of Ag and oxygen.

The unique character of Ag compared to other metals is reasoned in the activation of oxygen on the surface and subsurface, while stable oxide phases at elevated temperatures and atmospheric pressure21–25 are absent. This intriguing surface and subsurface silver–oxygen (Ag–O) chemistry explains why, for example, for the ethylene epoxidation reaction exclusively supported Ag catalysts are used. Further, a large variety of oxygen species like atomic, molecular, strongly bound, ionic, covalent, surface, subsurface, near defects, bulk-dissolved, or surface-embedded oxygen have already been described and are...
still under debate. Nevertheless, most of these findings are made on single crystals, foils, or powders, since the synthesis and investigation of small and stabilized Ag nanoparticles are challenging.

The synthesis of well-defined small Ag nanoparticles with a narrow size distribution can be regarded as the first step to reliably facilitate PS effect investigations. Crucial parameters are the properties of the support material and the precursor material for Ag. For the suitability of the support, the specific surface area, structural stability, and number and nature of functional groups are important. Sticking to the partial oxidation reaction of ethylene, a feature of the desired product ethylene oxide is its high sensitivity to especially Lewis acidic groups on the support surface. This already limits the number of possible supports, with corundum (α-Al₂O₃) and silica (SiO₂) as most promising candidates. Besides, the low surface acidity of α-Al₂O₃ is based on the overall low number of functional groups due to its low specific surface area of usually <5 m²g⁻¹. For a successful synthesis and stabilization of nanoparticles, however, high surface area supports are needed. The necessary chemical inertness of the supports also limits the use of metal-support interactions, which is a common strategy for metal nanoparticle stabilization. Flame hydrolyzed silica exhibits a high concentration of surface OH-groups paired with a high hydrophilicity, a moderate surface acidity, and high structural as well as textural stability and is therefore identified as suitable support material for the synthesis of small nanoparticles and applied as support material in this work.

As precursor materials, among Ag carbonates, sulfates, acetates, oxalates, lactates, succinates, glycolates, and multiple amine systems, Ag nitrate (AgNO₃) offers the useful ability of melting at 210°C before its decomposition at 440°C. This enables a rather controlled development of Ag nanoparticles by thermal treatments. Additionally, AgNO₃ dissolves easily in water, thus being a suitable impregnation solution for hydrophilic silica. The OH-group rich surface of SiO₂ enables Ag⁺ ions to undergo ion exchange reactions, thereby being distributed and stabilized over the complete support surface area leading to metallic nanoparticles of <6 nm, which was, to the best of our knowledge, so far only achieved on very acidic and porous supports like zeolites. Furthermore, a partial calcination can be used to in situ create Ag clusters during the reaction conditions, which represents a novel approach in the course of the presented research.

In summary, the present work deals for the first time with the investigation of the Ag–O chemistry for a series of silica supported Ag catalysts with solely Ag nanoparticles of <6 nm down to cluster sized Ag. All samples were thoroughly analyzed by multiple techniques including powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA) coupled to evolved gas analysis (EGA), inductive coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy with energy dispersive X-ray detection (SEM/EDX), and transmission electron microscopy (TEM). We apply the oxidation of carbon monoxide as a text reaction for the activation of oxygen and a combination of microcalorimetry and ethylene adsorption (as probe molecule) for a qualitative and quantitative assessment of the Ag–O interaction. For comparison reasons, a conventional Ag/α-Al₂O₃ sample is analyzed.
N₂ physisorption was performed in a Quantochrome Autosorb-6-B-MP machine after degassing a specific amount (500 mg for α-Al₂O₃, 30 mg for SiO₂) of the sample at 150 °C for 15 h. The resulting isotherms were recorded at the temperature of liquid nitrogen. Calculation of the surface area was performed according to the equation of Brunauer, Emmet, and Teller ( BET equation).  

Thermogravimetric analysis/evolved gas analysis (TGA-EGA) was conducted using a STA 449 C Jupiter thermoanalyzer (Netzsch) under oxidative (21% O₂ in Ar) or inert (Ar) gas atmosphere with a total flow of 100 mL-min⁻¹. The sample was heated up with 2 °C-min⁻¹ to 500–600 °C without or with 1 h dwell time. The setup was connected to a quadrupole mass spectrometer (QMS200 Omnistar, Balzers) for evolved gas analysis via a quartz capillary heated to 40 °C. All data were analyzed using the Netzsch Proteus Thermal Analysis software package (version 6.10).

Scanning transmission electron microscopy (STEM) imaging was performed using a double Cs corrected JEM-ARM200CF (JEOL) operated at 200 kV and equipped with ADF (annular dark-field) and BF (bright-field) detectors. Samples were prepared by direct deposition of dry powder onto a Quantifoil Au holey grid. For the resulting histograms, the diameter of 1000 particles was measured for each sample.

Scanning electron microscopy (SEM) was performed on a Hitachi S4800 equipped with a field emission gun and YAG-BSE (back-scattered electrons) and energy dispersive X-ray (EDX) detectors. The system was operated at a working distance of 10 mm with 10 kV.

C₂H₄ adsorption measurements were performed using a temporal analysis of products approach at atmospheric pressure (atmTAP) at 40 °C using breakthrough curve measurements with a high-speed transient reactor. A plug-flow reactor was loaded with a catalyst sample with a mass of 100 mg. The sample was pretreated at 300 °C for 3 h under a constant flow of 21% oxygen in He, after which the reactor was cooled slowly to the desired temperature under the same gas flow. Before the C₂H₄ breakthrough curve was measured, the gas flow was first changed to pure He (100 mL·min⁻¹) to completely purge the gas-phase oxygen from the reactor. Then, the gas composition was instantly switched to 3.93 mbar of C₂H₄ in He. Besides C₂H₄, a small fraction of Ar was also present in the feed in order to determine the mean reactor residence time of a nonadsorbing reference species. C₂H₄ and Ar concentrations at the reactor exit were monitored using a mass spectrometer. For each sample the adsorption measurement was repeated three times. Between those measurements, C₂H₄ was thoroughly desorbed by ramping the temperature to 230 °C under 21% O₂ in He and subsequent cooling to 40 °C.

Microcalorimetry was performed in a HT1000 (RT to 1000 °C) and M570 (RT to 100 °C) Tian-Calvet calorimeter (SETARAM) combined with a custom-designed high vacuum (HV) and gas dosing apparatus. The sample was placed in a batch reactor. C₂H₄ adsorption experiments were performed after cleaning the samples at 300 °C for 3 h in synthetic air (200 mbar O₂) or additional reduction by CO oxidation feed (2% CO, 2% O₂) followed by stepwise dosing of around 0.01–4.00 mbar of C₂H₄ at 40 °C. Prior to readsorption of C₂H₄ the sample was treated at 10⁻⁸ mbar to desorb reversibly bound C₂H₄ and free C₂H₄ adsorption sites. Oxygen adsorption experiments were performed at 200 °C after (I) a pretreatment of 600 °C at 10⁻⁸ mbar for 1 h and (II) a proximate reduction at 400 °C for 1 h combined with 10 mbar H₂.

Inductive coupled plasma optical emission spectroscopy (ICP-OES) was used to determine the Ag loading of the catalysts. Therefore, the sample is solubilized using LiF, nitric acid, and water at 230 °C, diluted with water, and analyzed with a PerkinElmer ICP OES Optima 8300.

RESULTS AND DISCUSSION

Sample Preparation and Characterization. All samples were synthesized by impregnation following an incipient wetness approach, while the solvent capacity volume (SCV) was determined experimentally (for details see Experimental Section). For the impregnation, a modified vacuum evaporator was used. Benefits are the use of low vacuum (60 mbar), rotation of the flask, and controlled addition of impregnation solution, all occurring in a closed system. This enables a superior distribution of the impregnation solution compared to conventional impregnation techniques. An important criterion for Ag nanoparticles with a narrow PS distribution is the properly chosen surface area of the support. Figure 1 shows representative the ratio between the surface area, the PS of Ag, and the interparticle distance, which determines the sintering stability of the formed particles (near the Ag support interaction) for a support loaded with 5 wt % Ag. It reveals that for a good stabilization of nanoparticles <2 nm support surface areas of already a few hundred m²·g⁻¹ are necessary. For this reason hydrophilic flame hydrolyzed SiO₂ was selected since it offers a suitable BET surface area of 328 m²·g⁻¹. Thereby, it theoretically enables the synthesis and stabilization of nanoparticles consisting of less than 200 atoms down to even small clusters that consist of less than 50 Ag atoms.

In the following, the samples are named according to their Ag loading in wt % and the chosen support, i.e., 5 wt % Ag on silica as Ag/SiO₂. Calculation conditions are labeled as X/Y (X = temperature, T in °C, and Y = dwell time, t in h), i.e., Ag/SiO₂ 400/1 for a calcination at 400 °C with 1 h dwell time. Pretreatment conditions for catalytic or analytical tests are given with the same T/t notation. An overview of relevant samples and their corresponding characteristics is given in Table 1.

To identify proper calcination conditions, a AgNO₃/SiO₂ precursor was analyzed with TGA-EGA upon thermal treatment (Supporting Information, Figure S1A). After desorption of the physisorbed H₂O, a first NO release is detected at 160 °C with a NO evolution maximum at 220 °C, being in good agreement with reported 210 °C for the AgNO₃ melting point. It is assumed that AgNO₃ nanoslabs are formed, which are size determining for the final Ag particles and clusters. Upon further calcination, AgNO₃ decomposes to Ag⁺ which is again indicated by a strongly increased NO signal with an overall maximum at 390 °C. The detected mass loss of

Figure 1. Required support surface area per gram support versus Ag nanoparticle size for different interparticle distances x of 1, 2, 4, 6, and 8 nm. Calculations were performed for 5 wt % Ag loading, assuming no wetting.

The system was operated at a working distance of 10 mm with 10 kV.
3.33% during NO evolution \((m/z = 30, 150–500\,\degree C)\) is slightly higher than the theoretical weight loss of 2.87%, explained by additional \(\text{H}_2\text{O}\) evolution \((m/z = 18, 25–465\,\degree C)\).

On the basis of the TGA-EGA of differently calcined samples (Figure S1B), a remaining amount of 14% \(\text{AgNO}_3\) is calculated after a calcination temperature of 400 \(\degree C\) without dwelling (400/0) and 6% for 400 \(\degree C\) for 1 h dwelling (400/1). At calcination temperatures of 500 \(\degree C\) and higher no remaining NO evolution was detected. On the basis of these results (TGA-EGA, Figure S1), a set of samples with three different calcination temperatures (400, 500, and 600 \(\degree C\)) and two different dwell times (1 and 3 h) at each temperature was synthesized. The comparably mild calcination temperature of 400 \(\degree C\) (with 6% residual \(\text{AgNO}_3\)) is selected since any thermally induced sintering should be avoided.

Since all \(\text{Ag}_5/\text{SiO}_2\) samples are derived from the same precursor batch \(\text{AgNO}_3/\text{SiO}_2\) they are expected to have the same Ag loading. For an experimental analysis of the Ag loading ICP-OES was performed. The Ag loading for the \(\text{AgNO}_3/\text{SiO}_2\) precursor was determined to 4.3 wt %. This result is in very good agreement with the determined Ag loading for sample \(\text{Ag}_5/\text{SiO}_2\) calcined at conditions of 600/1 of 4.5 wt %. Both values are thereby very near the nominal loading of 5 wt % and show that the calcination does not influence the Ag loading.

For an overview of the resulting Ag PS after impregnation and calcination, STEM analysis was performed for the \(\text{AgNO}_3/\text{SiO}_2\) precursor dried at 110 \(\degree C\) for 12 h without calcination and additionally \(\text{Ag}_5/\text{SiO}_2\) samples calcined at conditions of 400/1 and 600/1. After drying, the \(\text{AgNO}_3/\text{SiO}_2\) already shows a uniform size distribution with Ag PS up to 4.6 nm and a median value of 1.8 nm (Figure 2A). Those nanoparticles show a d-spacing of the Ag 111 lattice plane of 2.40 Å (Figure S2), being in good agreement with the literature value of 2.36 Å.51 Besides, the inset of Figure 2A shows single Ag atoms that are well distributed over the whole support surface, which are likely atomically dispersed Ag\(^{+}\) species that formed after ion-exchange reactions on the silica support. The occurrence of Ag nanoparticles after drying at comparably mild 110 \(\degree C\) might be explained by the instability of nitrates which decompose already below 160 \(\degree C\) (see Figure 2A) as a function of 12 h dwell time. A representative STEM image for sample Ag/ \(\text{SiO}_2\) 400/1 is shown in Figure 2B with the corresponding PS distribution (histogram). The Ag particles are well distributed over the support without atomic species visible and a median PS of 2.0 nm (standard deviation SD = 0.71 nm). In comparison, the \(\text{Ag}_5/\text{SiO}_2\) 600/1 sample exhibits a median PS of 2.3 nm (SD = 0.72 nm; see Figure 6B). In addition, a very narrow size distribution is obtained without Ag particles larger than 5.8 nm. Comparable studies with \(\text{AgNO}_3\) impregnations on \(\text{SiO}_2\) led to increased Ag PS and broad size distributions, which emphasizes the advantage of the developed synthesis technique. As a direct result of the higher calcination temperature (from 400 to 600 \(\degree C\)), the amount of

Table 1. Overview of Investigated Ag (Pre-)Catalysts with Nominal (nom) and Experimentally (exp) Determined Ag Loading (ICP-OES and PXRD), BET Support Surface Area \((S_{\text{BET}})\), Median Ag Particle Size (STEM), Ag Domain Size (PXRD), and Internal FHI Number

| sample             | calc cond \([\degree C/h]\) | nom | exp       | support \(S_{\text{BET}}\) \([m^2\cdot g^{-1}]\) | median Ag particle size \([\text{nm}]\) | Ag domain size \([\text{nm}]\) | FHI no. |
|-------------------|-----------------------------|-----|-----------|-----------------------------------------------|----------------------------------------|-------------------------------|---------|
| \(\text{AgNO}_3/\text{SiO}_2\) | 400/1                      | 5   | 4.3\(^{a}\) | 328                                           | 1.8                                    | n/a                           | 27150   |
|                   | 400/3                      |     | n/a       |                                               |                                        | n/a                           | 27127   |
| \(\text{Ag}_5/\text{SiO}_2\) | 500/1                      | 5   | 2.4       | 328                                           | 2.0                                    | n/a                           | 27130   |
|                   | 500/3                      |     | n/a       |                                               |                                        | n/a                           | 27131   |
|                   | 600/1                      | 5   | 4.5\(^{a}\) | 328                                           | 2.3                                    | 6.1 ± 0.9                     | 27133   |
|                   | 600/3                      |     | n/a       |                                               |                                        | 6.3 ± 0.9                     | 27134   |
| \(\text{Ag}_{15}/\alpha-\text{Al}_2\text{O}_3\) | 280/0.2                    | 15.5| 12.4\(^{a}\) | ~1.0                                          | ~30 and ~200                     | 39.4                          | 26630   |

\(^{a}\)ICP-OES. \(^{b}\)PXRD full pattern fitting.
Ag clusters (<1 nm) is reduced from 6.4% to 1.7%. The impact of the calcination temperature on the Ag PS of >1 nm is insignificant, which underlines the high temperature stability of the synthesized Ag particles.

For all samples PXRD analysis was performed (Figure 3). PXRD provides integral information about the phase compositions, and no remaining AgNO₃ or Ag₂O as by-phase was detected. The broad diffuse signal between 16° and 40° 2Θ is assigned to amorphous SiO₂. For samples calcined at 400 °C the present Ag nanoparticles are X-ray amorphous, which is a result of the small Ag domains. With increasing calcination temperatures the Ag reflections start to appear and get well visible for applied 600 °C. For the samples Ag5/SiO₂ 600/1 and 600/3 also the volume-weighed mean domain sizes and lattice parameter can be extracted from full pattern analysis, with 6.1 ± 0.9 nm and 4.089 ± 0.012 Å for 600/1 and 6.3 ± 0.9 nm and 4.090 ± 0.009 Å for 600/3. Thereby, the domain sizes are in good agreement with the results from STEM analysis showing only particles of <5.8 nm for Ag5/SiO₂ 600/1. Within the uncertainty of the fitted results, all lattice parameters are in agreement with the reported reference of 4.086 Å for Ag₁₅/α-Al₂O₃.53 Besides, a diffuse signal at 37–39° 2Θ assigned to Ag₂CO₃ is visible. With a decreasing calcination temperature, the Ag₂CO₃ moieties are increasing; further, as a function of time (4.5 month, absence of light) the Ag₂CO₃ is continuously growing and crystallizing (Figure S3).

For this study a α-Al₂O₃ supported Ag reference sample was synthesized and labeled Ag₁₅/α-Al₂O₃. In contrast to the applied SiO₂ support, AgNO₃ based impregnation on α-Al₂O₃ (experimental details are described in the Supporting Information) led to the opposite effect resulting in large particles with a broad size distribution, ranging from nanoparticle of only a few nanometers up to particles of several micrometers (Figure S4 and Figure S5). Therefore, according to current patent literature,36 a Ag-oxalate source was used for the synthesis of a reference sample. This approach led to well dispersed Ag nanoparticles of 100–300 nm with a few particles being in the range of 20–40 nm (STEM analysis, Figure S6) but without particles of <20 nm. Therefore, the Ag-oxalate based Ag₁₅/α-Al₂O₃ sample can be applied as a reference for larger Ag particles,36 and, based on the Ag PS, can be circumscribed from Ag5/SiO₂ samples with Ag particles of <6 nm. The quantitative XRD analysis using the Rietveld method determined the Ag loading for Ag₁₅/α-Al₂O₃ to 14.0 wt %, being in good agreement with nominal loading of 15.5 wt % and the results from ICP-OES of 12.4 wt %.

Further, the crystalline domain size of Ag₁₅/α-Al₂O₃ was calculated to 39.4 nm (Figure S7) with a calculated lattice parameter of 4.086 03 ± 0.000 09 Å, being in very good agreement with the reference value.53 It seems reasonable that the present Ag particles of 100–300 nm detected by STEM analysis of Ag₁₅/α-Al₂O₃ therefore consist of multiple Ag domains, very likely formed by sintering of smaller Ag particles of around 40 nm as calculated from PXRD, probably during the calcination procedure. Furthermore, PXRD analysis revealed no or an insignificant (XRD amorphous) amount of Ag₂CO₃ even after 6 months. This might be interpreted as strong tendency of Ag nanoparticles to activate and stabilize oxygen since formally, the Ag₂CO₃ formation is based on the reaction of Ag₂O (here, rather Ag₂O₃) with CO₂. The stabilized oxygen species on Ag nanoparticles of <6 nm, in contrast to big or bulk-like Ag particles (>20 nm, smallest size detected via STEM analysis), might be of rather oxidic character (without forming any Ag₂O phase). This gives a first indication about the nature and reactivity of Ag nanoparticles and a pronounced size effect.

Catalytic Testing. Prior to testing the catalytic performance in the oxidation of CO to CO₂, it is indispensable to properly activate the catalysts. As observed by PXRD, Ag nanoparticles show a strong tendency to form Ag₂CO₃. During the activation phase, the surface of the active material is cleaned by the decomposition of unwanted species like carbonates and oxides, potentially blocking reaction sites. Due to the decomposition temperature of Ag₂CO₃ of 175–225 °C,34 and Ag₂O of around 200 °C,44 the lowest meaningful pretreatment temperature is 200 °C. All pretreatments were performed with 21% O₂ in He. For the following CO oxidation test a three-cycle run is applied, whereby the first cycle is used as additional pretreatment step for cleaning the Ag particle surface and to reduce remaining AgNO₃. The second and third cycles represent the actual CO oxidation performance test. In addition, the third cycle provides also information about the stability of the catalysts. We exclude poisoning effects by the product CO₂ since under reaction conditions Ag₂CO₃ formation is not favored. Besides, a dependence of the reaction rates from the ρ(CO) and O₂ indicates that the product desorption/poisoning has no impact on the rates (Figure S11).

To investigate the influence of the pretreatment conditions on the catalytic performance, the catalysts were activated at 200 °C for 12 h (200/12), 230 °C for 3 h (230/3), 300 °C for 3 h (300/3), or 300 °C for 12 h (300/12). For a direct comparison of the catalytic activity the temperatures reaching 10% CO conversions are identified (T_{10%}). With a stepwise increase of the temperature and dwell time, all catalysts tested were significantly increasing in their catalytic performance. Figure 4 shows the impact on the T_{10%} of the Ag₅/SiO₂ 400/1 and 600/1 catalysts for three different pretreatment conditions (all T_{10%} values are listed in Table 2). The 400/1 sample shows a huge dependency of the T_{10%} values upon different pretreatments. In particular, the first catalytic cycle deviates from the second and third cycles. This effect is more significant for the milder pretreatment conditions (230/3 ΔTₜ₁⁻₃ = 91 °C, 300/3 ΔTₜ₁⁻₃ = 27 °C), which is mostly likely explained by the transformation of the residual AgNO₃ (~6%) to catalytically active Ag⁶. The activity of the second and third cycles of
sample 400/1 is thereby much higher for all pretreatments (lower $T_{10\%}$ values) except for 300/12. Here, the pretreatment leads already to first deactivation and sintering events for the 400/1 sample which can be seen in the increased $T_{10\%}$ from cycle 1 to cycle 2. Luo et al. have already shown that for unsupported 2 nm sized Ag nanoparticles the corresponding Tammann temperature is below 100 °C, which makes sintering for the present silica supported nanoparticles in a comparable size range a likely deactivation mechanism. The 600/1 sample shows, upon cycling within a given pretreatment, stable $T_{10\%}$ values ($\Delta T_{c1-c3} = 1–3^\circ\text{C}$), supporting a complete calcination (no AgNO$_3$, Figure S1B). The higher activity with higher pretreatment temperatures can be ascribed to a more complete support of Ag$_0$ induced by the CO oxidation feed has a significant impact on the catalytic performance. In comparison to the thermolysis/calcination approach (>500 °C) the in situ creation of Ag nanoparticles is a rather mild and elegant method to create and stabilize even smaller particles or clusters, showing CO oxidation activity already at 30 °C (Figure S5). For the investigation of the emerging PS during the in situ autocatalytic conversion of residual AgNO$_3$ to Ag$^+$ induced by the CO oxidation feed has a significant impact on the catalyst performance.
the in situ reduction of AgNO₃ during CO oxidation, the Ag PS distributions of freshly synthesized Ag₅/SiO₂ samples 400/1 and 600/1 were compared to their spent counterparts after CO oxidation (Figure 6). The fraction of particles of >6 nm was determined to <1% for the samples before and after catalysis, thereby supporting their high sintering stability. The PS distributions of the 400/1 sample before and after three cycles of CO oxidation are presented in Figure 6A. The fresh sample exhibits a median PS of 2.0 nm with a fraction of 6.4% on Ag clusters of <1 nm (approximately <50 Ag atoms per particle). During the CO oxidation cycles the median PS is further decreased to 1.7 nm, also indicated by the increased moieties of Ag clusters to 14.2%. The higher fraction of Ag clusters is attributed to its in situ formation upon CO oxidation and conversion of residual AgNO₃. Figure 6B shows the PS distribution of the 600/1 catalyst. The fresh sample has a median PS of 2.3 nm, thereby being slightly larger compared to the fresh 400/1 sample. Also the fraction of Ag clusters of <1 nm, determined to 1.7%, is smaller. After CO oxidation the median of the present PS (2.4 nm) and the fraction of Ag clusters (1.6%) are almost unchanged compared to the fresh sample, which is in very good agreement with the stable catalytic activity and Tₐ₀% values (see insets of Figure 6). The 400/1 catalyst shows, in contrast, a significant increase in CO oxidation activity upon cycling (Tₐ₀% decreased by 27 °C). This is in direct correlation to the in situ formation of Ag clusters, strongly indicating its huge impact on catalysis.

These findings are not consistent with the results of Lim et al.¹⁸ claiming that Ag particles of <3 nm are no good catalysts for CO oxidation and of Qu et al.¹⁷ reporting that catalysts with Ag PS of 6−8 nm are the most active for CO oxidation. Those results are indicating a structure sensitivity with inferior catalytic activity for nanoparticles of <3 nm and are in contrast to our work. This discrepancy is likely explained by an inappropriate pretreatment and the low reaction temperatures applied in their studies.

To exclude different reaction mechanisms for samples Ag₅/SiO₂, the reaction order at 100 °C for selected catalysts was calculated after 300/3 pretreatment and performing one CO oxidation cycle to 250 °C for a final AgNO₃ removal and Ag cluster formation (Figures S11 and S12). In general, for all samples the reaction order is below 1 and higher for CO than for O₂, which indicates a higher dependence on the ρ(CO) than on ρ(O₂). Values for catalysts 500/1, 600/1, and 600/3 range between n(O₂) = 0.30−0.32 and n(CO) = 0.63−0.68. This indicates a higher coverage with oxygen in comparison to CO as general feature. For sample Ag₅/SiO₂ 400/1 the reaction orders are lower with n(O₂) = 0.09 and n(CO) = 0.41. This implies that the reaction rates are almost independent of the ρ(O₂) and that the activation of O₂ is facile. Since Ag tends to form also subsurface oxygen species, the particle and/or cluster size might serve as descriptor for this behavior and vice
versa; small clusters stabilize oxygen rather near the surface. This discrepancy between sample 400/1 and the samples calcined at higher temperatures is interpreted as a result of the highly active Ag clusters. They are in situ created during the first CO oxidation cycle for the 400/1 sample, and their distinctness is also visible in the different kinetic parameters (reaction orders).

Evaluation of the Silver–Oxygen Interaction. To investigate the ability of Ag catalyst systems to activate $\text{O}_2$, microcalorimetry experiments were conducted (Figure 7). The

![](image)

Figure 7. Microcalorimetric oxygen adsorption on Ag15/$\alpha$-Al2O3 and Ag5/SiO2 calcined at 600/1. O2 adsorption was performed at 200 °C after pretreatment at 600 °C in UHV and after 400 °C with H2. On the right the corresponding adsorption sites are shown based on DFT calculations.

Ag15/$\alpha$-Al2O3 sample and the AgNO3/SiO2 precursor were both in situ calcined at 600 °C for 1 h prior to the O2 dosing at 200 °C. The integral heat of adsorption ($Q_{\text{ads}}$) of the Ag15/$\alpha$-Al2O3 sample is in the range of 120 kJ·mol$^{-1}$ and decreases upon titrating to a plateau at ~70 kJ·mol$^{-1}$ and finally reaches values below 30 kJ·mol$^{-1}$. On the basis of DFT calculation for the adsorption energy ($E_{\text{ads}}$) of oxygen on various Ag surfaces (for details see Supporting Information), the experimental results are interpreted as dissociatively activated oxygen species, with heats of adsorption in the range of 120–70 kJ·mol$^{-1}$, followed by molecular oxygen adsorbed on defects and grain boundaries ($Q_{\text{ads}}$ in the range of 60–20 kJ·mol$^{-1}$). The SiO2 supported Ag nanoparticles show no interaction with the dosed O2 at 200 °C. This is explained by the already stable oxygen saturated state forming Ag$^{\text{sp}}$O4 species during in situ calcination (mainly from AgNO3) that are consequently unable to further activate molecular oxygen. Subsequently, to remove oxygen species in and on Ag, both samples were pretreated in hydrogen at 400 °C. Temperature-programmed reduction (TPR) experiments under 0.25% H2 atmosphere were already performed to monitor the consumption of different kind of oxygen species by H2 under the formation of water (Figure S13), showing that 400 °C is a reasonable temperature for a complete reduction of Ag. H2O events at higher temperatures are related to support effects. Titrating the reduced samples again with O2 led qualitatively to comparable results for both samples, with $Q_{\text{ads}}$ values in the range of 30–40 kJ·mol$^{-1}$. The Ag nanoparticles offer more adsorption sites for oxygen, which are according to DFT calculations for both samples in the regime of molecular oxygen on different surfaces. These results show that the oxygen species were successfully removed by the reducing treatment (also the stabilized oxygen on Ag nanoparticles). Besides, it is clearly shown that for a dissociative activation of oxygen, oxygen species in and on Ag (not too ionic and stable) have to be already present. If not, oxygen is only molecularly adsorbed, since the oxygen-free Ag$^0$ particles have a closed d-band and are inactive. After the microcalorimetry experiments a median PS of 2.5 nm (99.9% < 7.2 nm, Figure S14) is found via STEM analysis, confirming that the in situ created sample is comparable to Ag5/SiO2 600/1 and representative for the series of Ag nanoparticles stabilized on SiO2. However, the results obtained by the integral microcalorimetry offer valuable insights in the nature of the Ag–O interaction, but a surface quantification of Ag (or an identification of the number of reaction sites on Ag) due to the subsurface contributions is very difficult.

To further evaluate the strength of the Ag–O interaction on the surface, we have to introduce a probe molecule, which interacts with the partially oxidized Ag$^{\text{sp}}$O4 and is unable to develop a Ag subsurface chemistry. For this purpose, ethylene ($\text{C}_2\text{H}_4$) is identified since the Ag$^{\text{sp}}$O4 surface behaves like a selective “chromatographic column” and C2H4 adsorbs easily. Besides, it is well-known that metallic Ag is not able to interact with C2H4 since its electronic configuration of s1d10 does not allow transferring electrons to the Ag d-band.22,57,58 This fact was confirmed for a Ag5/SiO2 600/1 sample reduced at 400 °C in 5% H2, resulting in a metallic supported Ag catalyst. This sample showed no heat evolution upon C2H4 dosing via microcalorimetry and therefore no interaction with C2H4. For the partially oxidized Ag$^+$, electron density from the Agd$^0$ d-band is removed which enables the donation of $\pi$-electrons. This interaction allows C2H4 to be a suitable sensor for the titration of all kinds of Ag$^+$ sites from Ag2O, AgNO3, and Ag$^+$ sites from partially oxidized Ag$^{\text{sp}}$O4. Furthermore, the C2H4 interaction strength with Ag$^{\text{sp}}$O4 is also an indirect measurement for the strength of Ag–O interaction, since the binding strength of C2H4 depends on the strength of interaction of oxygen with Ag and the corresponding acceptance of $\pi$-electrons. However, for a correct comparison of the adsorption on Ag some important criteria have to be fulfilled: (I) The Ag surface sites have to be available for C2H4 to adsorb. This implies a proper pretreatment sequence. (II) Any interaction of the support materials and C2H4 has to be ruled out. Therefore, a pure SiO2 sample that was equally treated additionally in situ reduced using CO as reduction agent, was con…

Figure 8 illustrates the results of the microcalorimetric C2H4 adsorption experiments and the corresponding integral heat evolutions. At first, the AgNO3/SiO2 precursor was in situ activated at 300/3, and subsequently C2H4 was dosed. The $Q_{\text{ads}}$ is in the range of 85–90 kJ·mol$^{-1}$ and decreases gradually upon dosing. The adsorption of the C2H4 molecules was reversible (qualitatively and quantitatively under vacuum treatment, 90 μmol·g$^{-1}$) and for this sample very likely related to Ag$^{\text{sp}}$O4 from Ag nanoparticles and Ag$^+$ adsorption centers from residual AgNO3. For a possible discrimination between the nature of the Ag–O interaction of Ag clusters (<1 nm) and Ag nanoparticles (1–6 nm) the precursor AgNO3/SiO2 was additionally in situ reduced using CO as reduction agent, comparable to one CO oxidation cycle as demonstrated in Figure S5. As shown before, the reductive CO atmosphere in situ reduces the Ag$^+$ species of the residual AgNO3 under the formation of Ag nanoparticles and clusters. The resulting C2H4 adsorption led to $Q_{\text{ads}}$ in the range of 100 kJ·mol$^{-1}$, which is a
This implies that the in situ created Ag clusters exhibit Ag upon C2H4 titration also. The ex situ calcined 600/1 sample without Ag clusters showed the amount of Ag clusters of the 400/1 samples after CO oxidation. Again, the sample with the irreversible adsorption sites from the microcalorimetry study was investigated via STEM for a PS analysis. Figure 8B shows the corresponding histogram of the PS distribution being in very good agreement with the PS distribution of the 400/1 sample (see also Figure 6). This strongly indicates a direct correlation between the number of Ag clusters and the number of irreversible adsorption sites. These adsorption sites, binding the oxygen species stronger (more oxidic), might also be responsible for the lowered reaction orders and the higher ability in activating oxygen within a catalytic cycle. Finally, an inverse trend for the strength of the Ag–O interaction and the corresponding PS and ionicity is manifested by complementary techniques (PXRD, STEM, and microcalorimetry): bulk-like (20–300 nm) < Ag nanoparticles (1–6 nm) < Ag clusters (<1 nm).

**Correlation of Ag Surface Area and Catalytic Activity.** For a better comparison and investigation of catalytic relations it is necessary to determine the specific surface area of a catalyst. Conventional analysis of Ag surface areas is done by oxygen involving methods59–61 which are from our point of view very challenging. Due to the complex Ag–O chemistry, oxygen might be located on the surface or in the subsurface/bulk of Ag, since the low oxophilicity enables diffusion processes. So any techniques involving oxygen species (direct titration or consumption of prestored) is ruled out. Determining the geometric Ag surface by TEM analysis would also give a meaningless number, not correlating with the relevant sites. Therefore, we used the already introduced concept of partially oxidized Ag samples to interact with C2H4 as probe molecule of choice as for the microcalorimetric study. In comparison to the microcalorimetric setup (static and semiquantitative), we combined this idea with a temporal analysis of products approach at atmospheric pressure (atmTAP50). The C2H4 is dosed at 40 °C into a high-speed transient fixed bed operating under plug flow conditions as described in the Experimental Section. By use of this setup, the calculated C2H4 adsorption capacities are determined under conditions comparable to standard catalytic test reactors creating highly reliably correlations.

Figure 8B illustrates the principle of measurement. By comparison of the reactor residence time of C2H4 with the nonadsorbing reference Ar, the amount of adsorbed C2H4 can be calculated from the mass balance. Let the signal for C2H4 as a function of time t be denoted by S(t) and the total volumetric flow rate by FV. From the mass balance it follows that the number of moles of adsorbed molecules Ncat per gram catalyst is given by

\[ N_{cat} = \frac{c_{C2H4}}{F_v} \int_0^\infty \left( 1 - \frac{S(t)}{S(\infty)} \right) dt \]

where \( c_{C2H4} \) is the molar concentration of C2H4 and \( S(\infty) \) is the steady-state signal reached after the mean breakthrough time. Since C2H4 is very low, indeed <0.5%, we can neglect the change of \( F_v \) due to adsorption and consider it a constant. The resulting amounts of adsorbed C2H4 are presented in Figure 9A showing the average over three measurements for each sample. All measurements were performed on Ag5/SiO2 samples pretreated at 300/3. Samples without remaining AgNO3 like 500/1, 500/3, 600/1, and 600/3 are all in the same range with an average C2H4 adsorption capacity of 28.3 \( \mu mol \cdot g_{cat}^{-1} \), 25.9 \( \mu mol \cdot g_{cat}^{-1} \), 30.8 \( \mu mol \cdot g_{cat}^{-1} \), and 31.5 \( \mu mol \cdot g_{cat}^{-1} \), respectively. These results indicate that samples calcined

![Figure 8](image-url)
pronounced for sample 400/1, with only a weak decrease from 51.9 μmol·gcat⁻¹ to 50.6 μmol·gcat⁻¹ and 50.4 μmol·gcat⁻¹, whereas the difference of measurement 2 to 3 is within the measurement error of the setup of approximately ±0.3 μmol·gcat⁻¹. Furthermore, samples 400/1 and 400/3 are resulting in the same adsorption capacities, indicating that for sample 400/1 no remaining AgNO₃ was present for the second and third analyses.

On the basis of the adsorption measurements, an apparent Ag surface is estimated. Under the assumption of a full oxygen coverage of the Ag surface, it is assumed that one C₂H₄ molecule binds to one Ag₂O site, consequently meaning that one C₂H₄ titrates two Ag atoms. Thereby, we can estimate the number of Ag atoms present on the surface. Using a covalent radius for Ag of 144 pm, the following Ag surface areas are calculated based on the number of Ag atoms. The determined adsorption capacities as well as the calculated apparent Ag surface areas are presented in Table 3.

Table 3. C₂H₄ Adsorption Capacities Determined by atmTAP, Corresponding Apparent Ag Surface Areas, and CO Oxidation Rates at 100 °C

| sample       | C₂H₄ adsorption capacity [μmol·g⁻¹] | Ag surface area [m²·g⁻¹] | rateₜₐₚ CO oxidation, cycle 3 [μmol·g⁻¹·C⁻¹] |
|--------------|-------------------------------------|--------------------------|-------------------------------------------|
| Ag5/SiO₂ 400/1 | 50.9                                 | 4.00                      | 158.3                                     |
| Ag5/SiO₂ 400/3 | 51.2                                 | 4.02                      | 154.9                                     |
| Ag5/SiO₂ 500/1 | 28.3                                 | 2.22                      | 59.3                                      |
| Ag5/SiO₂ 500/3 | 25.9                                 | 2.03                      | 61.6                                      |
| Ag5/SiO₂ 600/1 | 30.8                                 | 2.42                      | 77.0                                      |
| Ag5/SiO₂ 600/3 | 31.5                                 | 2.59                      | 67.9                                      |
| Ag15/α-Al₂O₃ 400/1 | 21.7                                | 0.17                      | 2.9                                       |

* Determined by microcalorimetric C₂H₄ adsorption.

The Ag15/α-Al₂O₃ reference was measured using surface titration experiments via microcalorimetry, since the surface area values are too small for the atmTAP approach. The C₂H₄ adsorption (Figure S18) is determined to 2.17 μmol·gcat⁻¹ and is further compared to the catalytic CO oxidation performances (see values in Table 2).

As presented in Figure 9B, the calculated C₂H₄ adsorption capacities are related to the rate in CO oxidation at 100 °C for cycle 3 after a 300/3 pretreatment (identical to the atmTAP measurements). A linear correlation can be drawn for samples up to adsorption capacities of 31 μmol·g⁻¹ taking nearby various Ag5/SiO₂ samples, also pure SiO₂ support and the reference Ag15/α-Al₂O₃ sample into account. As discussed above, these samples are free of Ag clusters and therefore have a different Ag–O interaction. By comparison of the high Ag surface area catalysts of around 50 μmol·g⁻¹, the linear correlation does not fit. The calculated rate is about 35 μmol·g⁻¹·s⁻¹ higher than extrapolated by the linear correlation. Since these samples are prone to form Ag clusters, the discrepancy is explained by the nature of the Ag clusters and also indicated by the irreversible sites for C₂H₄ adsorption (Figure 8). Since CO oxidation is only possible upon activation of oxygen by the catalyst, the Ag–O interaction strength is also relevant for CO oxidation. Therefore, it is reasonable that the linear correlation does not include the Ag clusters dominating the catalysis. This is also visible by a change of reaction orders and finally resulting in a Ag particle/cluster size effect for the CO oxidation reaction.
**CONCLUSION**

We report on an improved synthesis approach for a set of SiO₂ supported Ag nanoparticles with a narrow PS distribution and median PS of ∼2 nm based on an advanced incipient wetness impregnation technique. Ag nanoparticles show a high tendency to form Ag₂CO₃, as demonstrated by PXRD, which was absent for bulk-like Ag particles of a Ag15/α-Al₂O₃ reference sample. Catalysts Ag5/SiO₂, exhibiting solely Ag nanoparticles and clusters, were highly active in CO oxidation, after a dedicated pretreatment which is related to the Ag₂CO₃ formation. Performing detailed investigations concerning the pretreatment conditions, we were able to demonstrate that Ag nanoparticles need a significantly harsher pretreatment compared to bulk-like Ag particles (higher temperature and/or longer dwell times). This pretreatment dependence might also be the reason for differentiated findings in literature concerning Ag nanoparticles and their catalytic performance. Further, Ag clusters were in situ created and showed a significantly higher activity in CO oxidation.

Investigations on the correlation of Ag PS and the strength of the Ag–O interaction were performed. The formation of high temperature stable oxygen species with a strong Ag–O interaction on Ag nanoparticles and clusters was confirmed by microcalorimetric oxygen and C₂H₄ adsorption experiments. The strength of the Ag–O interaction was attributed to the higher ionicity of the Ag⁺O⁻ species directly correlating with the tendency of carbonate formation. Especially, the Ag clusters, also responsible for different reaction orders upon comparison to Ag nanoparticles, showed, using C₂H₄ titration, an in parts irreversible adsorption behavior. This finding supports a PS effect for Ag clusters in CO oxidation.

A newly introduced method for estimating the available reactive surface area was applied based on the C₂H₄ adsorption capacity. Thereby, a linear correlation of the CO oxidation rate with the C₂H₄ adsorption capacity of bulk-like Ag and Ag nanoparticles was demonstrated. Ag clusters exhibited a superior CO oxidation activity compared to nanoparticles and bulk Ag particles and deviate from the linear correlation, which can be directly attributed to the discussed Ag–O interaction and a distinct cluster size effect for Ag of <1 nm in size.

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