Supported Gold Nanoparticles from Quantum Dot to Mesoscopic Size Scale: Effect of Electronic and Structural Properties on Catalytic Hydrogenation of Conjugated Functional Groups

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Abstract: Titania- and zirconia-supported gold particles of 1–5 nm size, prepared by various routes of synthesis, were employed in the partial hydrogenation of acrolein. In-depth characterization of their structural and electronic properties by electron microscopy, electron paramagnetic resonance, and optical absorption spectroscopy aimed at disclosing the nature of the active sites controlling the hydrogenation of C=O vs C=C bonds. The structural characteristics of the catalysts, as mean particle size, size distribution, and dispersion, distinctly depend on the synthesis applied and the oxide support used whereby the highest gold dispersion (DAu ≈ 0.78, Au/TiO2) results from a modified sol–gel technique. For extremely small gold particles on titania and zirconia (1.1 and 1.4 nm mean size), conduction electron spin resonance of the metal and paramagnetic F-centers (trapped electrons in oxygen vacancies) of the support were observed. Besides the influence of the surface geometry on the adsorption mode of the α,β-unsaturated aldehyde, the marked structure sensitivity of the catalytic properties with decreasing particle size is attributed to the electron-donating character of paramagnetic F-centers forming electron-rich gold particles as active sites. The effect of structural and electronic properties due to the quantum size effect of sufficiently small gold particles on the partial hydrogenation is demonstrated.

Introduction

The preferred hydrogenation of the carbonyl group of α,β-unsaturated aldehydes to yield allylic alcohols is an important step in the industrial synthesis of fine chemicals by selective catalytic hydrogenation of conjugated functional groups and has been attracting much interest for fundamental research in catalysis. The fundamental problem is that because of the stronger negative free reaction enthalpy of ~35 kJ mol⁻¹, thermodynamics favors hydrogenation of the C=O over the C≡O group. Furthermore, for kinetic reasons, the olefinic double bond is more reactive than the C≡O group. Thus, as expected, conventional hydrogenation catalysts mainly provide saturated bonds. The structural properties of the catalysts, as mean particle size, size distribution, and dispersion, distinctly depend on the synthesis applied and the oxide support used whereby the highest gold dispersion (DAu ≈ 0.78, Au/TiO2) results from a modified sol–gel technique. For extremely small gold particles on titania and zirconia (1.1 and 1.4 nm mean size), conduction electron spin resonance of the metal and paramagnetic F-centers (trapped electrons in oxygen vacancies) of the support were observed. Besides the influence of the surface geometry on the adsorption mode of the α,β-unsaturated aldehyde, the marked structure sensitivity of the catalytic properties with decreasing particle size is attributed to the electron-donating character of paramagnetic F-centers forming electron-rich gold particles as active sites. The effect of structural and electronic properties due to the quantum size effect of sufficiently small gold particles on the partial hydrogenation is demonstrated.

Supporting Information Available

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(1)

where \( E_F \) is the Fermi energy of electrons, \( N \) is the number of conduction electrons, and \( d \) is the particle diameter. According to Kawabata, d is small enough to show QSE if the conditions \( hv\delta \gg 1 \) and \( h\tau\delta \gg 1 \) are fulfilled, where \( h \) is the Planck constant, \( \nu \) is the microwave frequency, and \( \tau \) is the spin relaxation time. Then the peak-to-peak line width \( \Delta H_{pp} \) of CESR signals may be described by eq 2, where \( \nu_p \) is the Fermi velocity.

\[ \Delta H_{pp} = \nu_p (\Delta g_{\omega})^2 \hbar \nu_c \delta^{-1} d^{-1} \approx d^2 \]  

(2)

electrons, \( \Delta g_{\omega} \) is the g-shift for the bulk metal (\( \Delta g_{\omega} = g(\text{metal}) - g(\text{free electron}) \)), and \( \nu_c \) is the electron magnetograyc ratio. By applying eqs 1 and 2, we estimated the diameter of Ag-on-titania particles which fairly well agreed with the transmission electron microscopy (TEM) size evaluation.

For nanosized gold particles, only a few markedly different results with respect to CESR signals are published. While no CESR line was detected for Au particles (1.6–2.5 nm) dispersed in a lithium fluoride matrix, a signal of 20-mT line width and 0.22–0.27 g-shift was observed for Au clusters of 3-nm mean diameter. In contrast, a narrow CESR signal (line width 0.6–0.9 mT, \( g = 2.0024 \)) at room temperature has been assigned to Au particles (2–8 nm) deposited on quartz. With too small metal particles, discrimination between them and the support material by electron microscopy becomes difficult. Then, EPR is a sensitive technique for very small metal particles and clusters.

In the following, we will report in detail on the preparation and in-depth characterization of titania- and zirconia-supported gold nanoparticles by TEM/HREM, EPR, and UV/VIS-DRS measurements and their influence on activity and selectivity in the gas-phase hydrogenation of acrolein. The combination of these methods together with reaction experiments is a useful strategy to achieve a more detailed understanding of the influence of structural properties of very small gold nanoparticles on hydrogenation reactions. Since variations of the catalytic properties are expected in the 1–3-nm size range, we tried to determine whether there is a possible selectivity switching between hydrogenation of the C≡C and C=O functional group and at which particle size this will occur.

Experimental Section

Supported Gold Catalysts. Three different gold-on-titania catalysts were prepared by the following methods: deposition—precipitation (DP), impregnation (I), and sol–gel techniques (SG). The support used for the DP and I methods was Degussa P25 titania (phase composition 65% anatase and 35% rutile, specific surface area 50 m²/g). The gold precursors for the DP and I methods were HAuCl₄ (Strem) and AuCl₄ (Aldrich), respectively. For the deposition—precipitation of Au(OH)₃ onto TiO₂, we started with the preparation of a suspension of 4.9 g of titania in 75 mL of distilled water followed by addition of ammonia (0.31 mL of a 4.98 N solution). Then, the gold precursor solution was prepared by dissolving 99 mg of HAuCl₄ in 10 mL of distilled water. Thereafter, the latter was added dropwise under vigorous stirring to the aqueous suspension of titania followed by addition of 4 mL of

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ammonia. After stirring for 6 h and aging for 3 h, the slurry was filtered and washed with distilled water until it was chloride-free (proved by addition of silver nitrate). Drying (373 K, 12 h), calcination in flowing and washed with distilled water until it was chloride-free (proved by 

| Table 1. Designation and Texture Properties of the Titania- and Zirconia-Supported Gold Catalysts Used in This Study |
|-----------------|-----------------|-----------------|-----------------|
| catalyst        | preparation     | gold content    | surface area   | pore vol        |
| designation     | method           | (wt %)          | (m²/g)          | (mL/g)          |
| Au/TiO₂-DP      | deposition–      | 1.7             | 42              | 0.35            |
| Au/TiO₂-I       | impregnation     | 2.9             | 42              | 0.38            |
| Au/TiO₂-SG      | sol–gel         | 4.8             | 117             | 0.17            |
| Au/ZrO₂-F       | coprecipitation  | 1.0             | 151             | 0.37            |

Crystallinity and crystal structure of the samples were evaluated from selected area electron diffraction (SAED) patterns as well as by high-resolution electron microscopy (HREM) done at a JEM 4000EX operating at 400 kV. For electron microscopy examination, the catalyst samples were dissolved in 2-propanol, dispersed carefully in an ultrasonic bath, and then deposited on carbon coated copper grids. Image processing for, for example, contrast enhancement and image evaluation, was done at digitized electron micrographs by means of the programs Digital Micrograph (Gatan) and NIH Image.²⁵

**Electron Paramagnetic Resonance (EPR).** EPR spectra of samples Au/TiO₂-SG, Au/TiO₂-DP, Au/TiO₂-I, Au/ZrO₂-F, and TiO₂ were recorded with the cw spectrometer Elexys 500-10/12 (Bruker) in X-band (ν = 9.151 GHz) at 77 and 293 K using a finger dewar. The magnetic field was measured with reference to a standard of 2,2'-diphenyl-1-picrylhydrazyl hydrate (DPPH). Reduction of the catalysts was performed in flowing hydrogen (45 mL min⁻¹) at 723 K (samples Au/TiO₂-SG and TiO₂) and 573 (sample Au/ZrO₂), respectively, with an EPR flow cell consisting of two coaxial tubes similar to that described by Mesaros and Dybowski.²⁶ EPR spectra were recorded after treatment in H₂ without contact to ambient atmosphere.

**UV/VIS-DRS.** UV/VIS-DRS measurements were performed by a Cary 400 spectrometer (Varian) equipped with a praying mantis diffuse reflectance accessory (Harrick). All samples were diluted with BaSO₄ white standard (Merck) in 1:50 ratio.

**Selective Hydrogenation of Acrolein.** Gas-phase hydrogenation of acrolein (AC, purchased from Aldrich) was carried out in a computer controlled fixed-bed microreactor system which has been described in detail elsewhere.²⁷ This equipment allows the performance of high-pressure gas-phase hydrogenations of unsaturated organic compounds, which are usually liquids with low vapor pressures at standard conditions (STP). The reactor effluents were on-line analyzed by an HP 5890 gas chromatograph, equipped with a flame ionization detector and a 30-m J&W DB-WAX capillary column. The gold catalysts were reduced in situ at the conditions described above. The reaction conditions of the acrolein hydrogenation were as follows: temperature range 453 K ≤ T ≤ 593 K, total pressure p = 2 MPa, molar ratio H₂/AC = 20, reciprocal space time W/Fₐ = 15.3 g mol⁻¹ h⁻¹, where W is the weight of catalyst (0.23 g; particle size 0.2–0.5 mm) and F is the molar flow of acrolein. Temperatures in the range of 513–553 K were required for zirconia-supported gold catalysts to be active, and conversion data up to 10% were obtained. Using Au/TiO₂ catalysts, acrolein hydrogenation to allyl alcohol and propanal started at lower temperatures around 473 K. For the purpose of comparison, the catalytic data are reported at 513 K, which is close to a common reaction temperature for all catalytic runs. Over the titania-based catalysts, increased formation of 1-propanol due to consecutive hydrogenation of propanal and allyl alcohol was observed above 553 K. Moreover, the extent of C₂ and C₃ hydrocarbon formation also increased at higher temperatures because of the increased extent of side reactions (decarboxylation of acrolein and propenal, dehydration of allyl alcohol). All the gold catalysts exhibited good activity maintenance during the time on stream (catalytic runs over 3 h). Minimal activity loss was only observed during the first 10 min in the case of Au/TiO₂ catalysts. This could be due to the formation of acrylic acid and formyldihydropyran, which were detected as byproducts. At 553 K, they were formed with a maximum selectivity of 8%. In contrast to that, acrolein hydrogenation at temperatures between 513 and 553 K over Au/ZrO₂ catalysts gave allyl alcohol and propanal as main products beside traces of 1-propanol and hydrocarbons. Note, that all given catalytic data (specific activities, selectivities) are based on steady-state behavior of the catalysts. The selectivities of reaction products were calculated from moles of product formed per moles of acrolein converted, and the catalyst activities were expressed as specific activities (on a gram of gold basis).

organic compounds as stabilizers (e.g., surfactants, polymers, ligands). Moreover, this size distribution is much narrower as compared to other routes of synthesis of supported nanosized gold clusters as, for example, through inverse micelle/sol–gel synthesis and Au–phosphine clusters. Due to the sol–gel synthesis, most of the gold particles of the Au/TiO$_2$-SG sample are embedded in the TiO$_2$ network, which makes electron microscopy characterization somewhat difficult because of their small sizes and the contrast features (eigen contrast) of this highly nonplanar and nonuniform support material.

Au/TiO$_2$-I exhibits a broader size distribution and a larger mean size, $d_{Au} = 2.0 \pm 0.4$ nm (Figure 2). Nevertheless, a certain amount of particles smaller than $\sim 1$ nm, being “invisible” for electron microscopy, may be present and change slightly the actual mean size in this and all other samples. As revealed by dark-field imaging, the gold particles are situated at the surfaces of TiO$_2$ grains. HREM revealed that the smallest gold particles were mostly single crystalline, but the larger ones partly exhibited some defect structures. Gold particles of Au/TiO$_2$-DP (Figure 3) are the largest among the titania-supported ones, $d_{Au} = 5.3 \pm 0.3$ nm. They showed mostly octahedral facets and also distinct single crystalline electron diffraction patterns (SAED). Mean particle sizes smaller than 5 nm are usually achieved during deposition—precipitation by pH above 6 where the main gold species in solution is transformed from AuCl$_4$ to Au(OH)$_2$Cl$_4-n$ (n = 1–3) as shown for calcined Au/TiO$_2$ catalysts. The gold particle size of the catalyst Au/ZrO$_2$-F (Figure 4) is found to be $d_{Au} = 1.4 \pm 0.3$ nm, which is similar to the 1.1 $\pm 0.2$ nm size of the sol–gel-derived gold-on-titania catalyst. These gold particles are in good approximation spherical and have a larger amount of lattice defects. The results presented above show that, besides depending on synthesis and processing, the size and morphology of Au nanoparticles distinctly are governed by the choice of a suitable oxide support.

Quantum Size Effects. The EPR spectrum of sample Au/TiO$_2$-SG recorded before reduction in hydrogen flow (Figure...
contains a hyperfine quartet ($A = 4.5$ mT) which may be due to the $g_{||}$ part of Au$^{2+}$ ions ($^{197}$Au: $I = 5/2$, 100% natural abundance). This is in agreement with data measured for Au$^{2+}$ ions in gold fluoride. The quartet is superimposed on a narrow singlet close to the free electron $g$-value. Upon reduction in hydrogen at 723 K, the hyperfine quartet vanishes since Au$^{2+}$ ions are reduced to elementary gold (Figure 5b). Simultaneously, a strong signal at $g = 1.936$ assigned to Ti$^{3+}$ appears that indicates a marked reduction of the support. When the reduced sample is stored in ambient atmosphere, the Ti$^{3+}$ signal vanishes.

again with time due to reoxidation; however, the narrow singlet at $g = 2.0053$ is still present (Figure 5c,d). While the latter can also be detected at room temperature, the Ti$_{3}^{3+}$ signal can only be seen at 77 K due to the short relaxation time. In the case of samples Au/TiO$_2$-I and Au/TiO$_2$-DP (not shown here), no signal is visible in the room-temperature spectra. The only EPR signal detectable in the spectra of these samples is that of Ti$_{3}^{3+}$ at 77 K after reduction.

Now the question arises whether the singlet at $g = 2.0053$ in Figure 5a–d is due to CESR of small Au particles as assigned by Monot et al.$^{21}$ According to Kawabata, the $g$-shift of a CESR signal is determined by $\Delta g = \Delta g_{\infty} - h/2\pi \delta \tau$. For particles small enough to exhibit QSE, the last term tends to zero since $\delta \gg \hbar$ and $\delta \gg h/\tau$. Hence, $\Delta g = \Delta g_{\infty}$ should be observed. On the other hand, the magnitude of $\Delta g_{\infty}$ increases with the spin–orbit interaction.$^{16}$ This contribution becomes important for the heavier metals so that the $g$-shift of QSE particles increases too. For silver particles, $\Delta g$-values of 0.0077, 0.0317,$^{34}$ and 0.0117$^{17}$ have been observed. The $g$-shift of gold particles is expected to be at least in the same order of magnitude or even larger. Thus, it is rather unlikely, that the signal at $g = 2.0053$ in Figure 5 and also the signal observed by Monot et al.$^{21}$ are due to CESR of nanosized Au particles.

To facilitate reliable assignment of the signals, the sol–gel-derived TiO$_2$ support prepared by the same procedure but without addition of gold has been studied by EPR in the same way (Figure 6). The spectra at 77 K indicate a redox behavior of the titanium ions similar to that observed in sample Au/TiO$_2$-SG. After reduction, a strong singlet is seen at 293 K, the line width and $g$-value of which are almost equal to those occurring in sample Au/TiO$_2$-SG (Figure 5a–d). That means position and shape of this line are characteristic for paramagnetic defects, namely, F-centers (single electrons trapped in anion vacancies).$^{35}$ This assignment is supported by the fact that the TiO$_2$ sample is black after reduction. It is well known that F-centers in ionic crystals give rise to deep colors. For example, ZrO$_2$ nanopowder with a high concentration of F-centers was found to be brown.$^{35}$ During exposure to air, the color of reduced TiO$_2$ turns to white again, the defect signal at 293 K decreases markedly, and the characteristic signal for $O_2^-$ radicals appears at 77 K (Figure 6c,f), the formation of which can be explained by reaction of molecular oxygen with the F-centers. On comparing the EPR results of Au/TiO$_2$-SG and pure TiO$_2$, it is quite evident that the signal at $g' = 2.0053$ in the former is due to F-centers formed by reduction of the TiO$_2$ support and does not originate from CESR of small Au particles.

The EPR spectrum of Au/ZrO$_2$-F contains a similar narrow singlet near the free electron $g$-value (Figure 5e) although its intensity is markedly lower than in Au/TiO$_2$-SG. It is assigned to F-centers in ZrO$_2$.$^{35}$ Additionally, signals at $g' = 1.974$ for Zr$^{3+}$ and at $g' = 2.0636$ occur. The latter vanishes almost completely after repeated treatment in flowing hydrogen at 673 K for 3 h (Figure 7b), while the F-center signal as it was observed also vanishes after reduction of TiO$_2$. As in TiO$_2$, upon exposure to air, the concentration of F-centers decreases while...
the line at $g' = 2.0636$ reappears (Figure 7c). The large $g$-shift suggests an assignment of this signal to CESR of small Au particles.

As mentioned above, the diameter of QSE particles is related to the peak-to-peak line width of the respective CESR signal, using eqs 1 and 2. With the density of gold ($\rho_{Au} = 197.2$ g mol$^{-1}$) and assuming a spherical particle shape, eq 1 yields $\delta = 3.82 \times 10^{-37}$ d$^{-3}$. Inserting this value in eq 2 and taking $v_p = 10^6$ m s$^{-1}$, $\gamma_e = 1.76 \times 10^{11}$ s$^{-1}$ T$^{-1}$, $E_F = 8.8 \times 10^{-19}$ J, and $h\nu = 6.3 \times 10^{-24}$ J, the relation between the particle diameter and the peak-to-peak line width becomes

$$d^2[m] = 1.066 \times 10^{-18} \frac{\Delta H_{pp}(T)}{(\Delta g)}^{-2}$$ (3)

With the experimental values of sample Au/ZrO$_2$-F ($\Delta g = 0.0613$, $\Delta H_{pp} = 6.9$ mT), a particle diameter of $d_{Au} = 1.4$ nm is calculated, which is exactly the value obtained by TEM measurements (see Table 2). This result, too, indicates that the assignment of the signal to CESR of Au particles is reliable.

From Figure 8 it can be seen that the peak-to-peak line width increases rapidly with the particle diameter. Using $\Delta g = 0.0613$, a line width of 38.4 mT would result for Au/TiO$_2$-I (TEM-derived $d_{Au} = 2.0$ nm) and of 118.6 mT for Au/TiO$_2$-DP ($d_{Au} = 5.3$ nm). Both values are far beyond detection of low-intensity signals. The line broadening would be even more pronounced for higher $g$-shifts when approaching the bulk metal value of $\Delta g_{Au} = 0.11$ (Figure 8). Thus, it is easily understood why no CESR signals are observed in the spectra of the two latter samples. In the case of Au/TiO$_2$-SG ($d_{Au} = 1.1$ nm) for which such a signal should be expected, dipolar interaction of the Au particles with the F-centers in the support may broaden the line and prevent detection. In fact, such a process is observed, too, for the CESR signal of sample Au/ZrO$_2$-F after reduction when the F-center concentration is high (Figure 7b). Interestingly, it was shown that already calcined ZrO$_2$ has two types of similar EPR signals which may be assigned to bulk Zr$^{3+}$ ions and surface-related F-centers$^{35}$ comparable to that in Figure 7a.

Because of the distinct surface plasmon resonances of small noble metal particles, optical absorption spectroscopy is well suited to complete the in-depth structural characterization of our metal/oxide nanoparticulate composites. The relative ease of recording such spectra must be faced with the difficulties of interpreting the rather complex results. In the UV/visible spectra of Au/TiO$_2$-SG, Au/TiO$_2$-DP, and Au/ZrO$_2$-F (Figure 9), the typical plasmon band of small Au particles between 500 and 600 nm is evident.$^{37,38}$ For the titania-supported gold catalysts prepared by deposition–precipitation and sol–gel technique, the spectra in Figure 9 reveal the expected trend that the bandwidth decreases from full with at half-maximum ($fwhm$) = 136 nm (curve b) to $fwhm = 115$ nm (curve a) with the particle size increasing from $d_{Au} = 1.1$ nm to $d_{Au} = 5.3$ nm, i.e., $d_{Au(TiO_2-SG)} < d_{Au(TiO_2-DP)}$. The mean particle diameter is related to the peak position and full width at half-height of the plasmon band.$^{39}$ This relation, however, is not only influenced by the width and shape of the particle size distribution but also by the dielectric function of the supporting or surrounding medium as well as possible particle interactions deviating from the single-particle assumption of Mie’s theory.$^{40}$ A careful interpretation of the spectra obtained would require extensive calculations according to appropriate models, which is beyond the scope of the present paper. In the context of these considerations, it may be understood that Au/ZrO$_2$-F exhibits a greater $fwhm$ (163 nm) than Au/TiO$_2$-SG although the latter is characterized by the highest degree of gold dispersion (Table 2). The described nanoparticle characteristics, however, are thought to play an important role in determining the catalytic behavior of the gold catalysts that will be treated in the following section.

Particle-Mediated Hydrogenation of Acrolein over Nano-sized Gold on TiO$_2$ and ZrO$_2$. As shown in Figure 10, the hydrogenation of acrolein over the titania-supported catalysts Au/TiO$_2$-DP and Au/TiO$_2$-I at 453 K and 2 MPa gave, at acrolein conversion of <10%, the desired allyl alcohol with a selectivity of 41 and 43%, respectively, as a consequence of the hydrogenation of the C=O group. Note, that this steady-state level of selectivity is up to 1 order of magnitude higher than in the case of supported group 8–10 metals used for the hydrogenation of acrolein.$^{34,41}$ The competitive hydrogenation of the C=C bond of acrolein to give propenal mainly accounts for the difference to 100% selectivity, whereas the formation of further possible reaction products (propanol by consecutive hydrogenation, hydrocarbons by decarbonylation of aldehydes, acrylic acid by oxygen transfer from the support, formyldihydropyran by acrolein dimerization) contributes only to a much

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less extent to the product composition. Moreover, keeping in mind the size of the gold particles in both catalysts, Au/TiO$_2$-DP ($d_{Au} = 5.3$ nm) and Au/TiO$_2$-I ($d_{Au} = 2$ nm), it is obvious, that the selectivity is nearly independent of the particle size. Thus, the hydrogenation of acrolein over Au/TiO$_2$ catalysts appears to be structure-insensitive for sizes above 2 nm, although a particular catalytic system can exhibit structure sensitivity in only a small range of the particle size.$^{42}$ It is noteworthy to mention that at 453 K the other two gold catalysts of the present study, Au/TiO$_2$-SG and Au/ZrO$_2$-F, showed no activity so that higher temperatures (513–593 K) had to be applied. Therefore, in Table 3, the catalytic properties in terms of activity, apparent activation energy, and selectivity data of all catalysts are compared at 513 K. Note that, within the whole temperature range, the selectivity to the reaction products was independent of acrolein conversion for Au/TiO$_2$-SG and Au/ZrO$_2$-F whereas with the catalysts Au/TiO$_2$-DP and Au/TiO$_2$-I the selectivity to allyl alcohol was somewhat lower due to secondary reactions (formation of propanol and hydrocarbons). However, again the selectivity (25%), catalyst activity, and also the apparent activation energy did not depend on the gold particle size (see Table 3). Interestingly, with further lowering of the gold particle size to 1.4 (Au/ZrO$_2$-F) and 1.1 nm (Au/TiO$_2$-SG), a drastic decrease of the catalytic activity was observed by up to 2 orders of magnitude (Table 3). Likewise, the apparent activation energy and the selectivity to allyl alcohol were diminished: With the 1.4-nm Au particles of the catalyst Au/ZrO$_2$-F, the lowest apparent activation energy was found. In line with the antipathetic structure sensitivity are the findings for a zirconia-supported gold catalyst prepared by the deposition–precipitation technique$^{45}$ (Au/ZrO$_2$-DP; see Table 3): Although a comparison is somewhat difficult because of its bimodal particle size distribution, it is obvious that gold particles above 2 nm in size yielded a considerably higher selectivity to allyl alcohol (42%). However, the low activity of the sol–gel-derived catalyst could also be due to particles, either surrounded by titania or partially buried within the support framework, leading to a reduction of the accessible gold surface area. There may be also contributions from covering the gold by residual organic material or even by modification of the electronic properties of metal particles through their coordination to titania.

**Discussion**

In a first approximation, the pronounced change of the catalytic behavior of TiO$_2$- and ZrO$_2$-supported gold particles with changes of the particle size can be satisfactorily accounted for by steric constraints on the metal surface: If hydrogenation of the C=O group of the $\alpha$-$\beta$-unsaturated aldehyde is favored by face atoms, most likely the increased fraction of dense (111) planes of the larger gold particles will give higher formation rates of the allylic alcohol than low-coordinated atoms of smaller sized particles. In terms of reaction mechanism, this means that the C=O group is preferentially activated on the closed-packed structure of the (111) surface whereas sites of low coordination, mostly present on small particles as corners and edges, strongly favor the activation of the C=C group. Interestingly, this unusual catalytic behavior of gold catalysts is comparable with the structure sensitivity observed in our studies over titania-supported nanosized silver particles used for the selective hydrogenation of crotonaldehyde, where the ultradispersed 1.4-nm Ag particles gave both a lower activity and selectivity to the unsaturated alcohol than the 2.8-nm Ag particles. Evidence for the antipathetic structure sensitivity emerges also from studies with platinum catalysts where a marked increase of selectivity toward the unsaturated alcohol with increasing fraction of Pt(111) surfaces has been observed in the hydrogenation of crotonaldehyde.$^{44}$

However, in sufficiently small particles, changes of the surface coordination are linked to changes in electronic properties. Hence, in addition to the influence of the surface geometry determining the adsorption mode of the $\alpha$-$\beta$-unsaturated aldehyde,$^{43–45}$ unusual electronic properties of nanosized gold should be taken into consideration to understand the significant changes of the hydrogenation behavior observed by downsizing the particles, i.e., when particle sizes of $<2$ nm gave 1–2 orders of magnitude lower catalytic activities and hydrogenate preferably the olefinic double bond instead of the carbonyl group. It is likely that a marked change in the electronic character of nanosized gold particles in the 1–2-nm range may indicate a transition to the nonmetallic phase and that the structure sensitivity originates from a quantum-size effect. On the other hand, gold particles larger than 2–3 nm are certainly metallic in character and activate the C=O group to produce allyl alcohol with significantly higher selectivity at increased activity. Indeed, as shown by Valden et al.,$^{12}$ who prepared Au/TiO$_2$ model catalysts by vapor deposition on single crystalline titania TiO$_2$ surfaces, a metal-to-nonmetal transition occurs as the gold cluster size decreased below 300 atoms per cluster (i.e., 3.5 nm in diameter and 1.0 nm in height) giving rise to a structure sensitivity of the oxidation of carbon monoxide.

Concerning the nature of active sites, the above-described in-depth characterization showed EPR signals for F-centers in Au/ZrO$_2$-F and Au/TiO$_2$-SG together with CESR signals of small gold particles in the former, whereas in the latter, dipolar interaction of the Au particles with the F-centers of the support gave rise to a line broadening that probably prevented CESR signal detection. Paramagnetic F-centers, i.e., electrons trapped as shown by Valden et al.,$^{12}$ who prepared Au/TiO$_2$ model catalysts by vapor deposition on single crystalline titania TiO$_2$ surfaces, a metal-to-nonmetal transition occurs as the gold cluster size decreased below 300 atoms per cluster (i.e., 3.5 nm in diameter and 1.0 nm in height) giving rise to a structure sensitivity of the oxidation of carbon monoxide.

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surface of small three-dimensional particles. By an electron transfer due to the interaction of nanosized gold particles and F-centers, gold is expected to become enriched in valence electron density, thereby altering the interaction of the active sites with the functional group and facilitating a partial transfer of electron density to the \( \pi^* \) orbital of the unsaturated bond. A similar situation is encountered, e.g., for the adsorption of the olefinic double bond of ethene on electron-rich silver. For the hydrogenation of \( \alpha,\beta \)-unsaturated aldehydes, an increase of the specific reaction rate of the \( \mathrm{C=C} \) double bond with increasing occupation of the \( \mathrm{d} \)-orbitals of the metal and, hence, with increasing polarity of the metal—hydrogen was observed so that the reaction of atomically chemisorbed hydrogen with the olefinic group was claimed to proceed as nucleophilic ligand addition. For the reaction of atomically chemisorbed hydrogen with the olefinic double bond via an increase of the repulsive four-electron interaction and favors the back-bonding interaction with the \( \pi^* \) CO orbital to a larger extent than with \( \pi^* \) CC orbital, so that the hydrogenation of the \( \mathrm{C=O} \) group should be favored over that of the \( \mathrm{C=C} \) group. In terms of the frontier orbital (HOMO—LUMO) model, the Fermi energy is increased by such an electron transfer. However, if quantum size effects occur, a decreasing density of occupied states within the HOMO (in terms of the band model: narrowing of the valence band, d band) induces a decreasing repulsion because of lowering the probability of interaction between orbitals \( \psi \) of the surface and the discrete adsorbed molecules according to

\[
E_{\text{repulsion}} \approx \sum_{ij} (|\Psi_i^{\text{metal}}|\Psi_j^{\text{ads}}|^2)
\]

This should lead to an overall decrease of repulsion enabling preferred hydrogenation of the \( \mathrm{C=C} \) group on quantum-sized systems (Au/\( \mathrm{ZrO}_2 \)-F, Au/\( \mathrm{TiO}_2 \)-SG). Furthermore, a lower density of states in the HOMO should induce a lower probability of back-donation, resulting in a decrease of \( \mathrm{C=O} \) adsorption and, thus, in a lower selectivity to the unsaturated alcohol. On the other hand, for larger gold particles (Au/\( \mathrm{TiO}_2 \)-DP, Au/\( \mathrm{TiO}_2 \)-I), the \( \mathrm{C=O} \) hydrogenation is markedly enhanced, as described in detail above.

Note, that besides the \( \eta^2-(\mathrm{C=C}) \) and \( \eta^2-(\mathrm{C=O}) \) adsorption geometries according to the classical Horiiuti—Polanyi mechanism, acrolein could also be activated through a competing \( \eta^3-(\mathrm{C,C,O}) \) mode which gave \( \pi \)-allylic and oxo-\( \pi \)-allylic inter-


| catalyst          | \( \bar{d}_{\text{Au}} \) (nm) | activity (mmol \( g_{\text{Au}}^{-1} \) s\(^{-1} \)) | \( E^*_\mathrm{A} \) (kJ mol\(^{-1} \)) | \begin{tabular}{c|c|c|c|c|c|c|c} \hline \text{selectivity} (%) \hline \text{AyOH} & PA & PrOH & HC & OP & ref \hline \hline Au/\( \mathrm{TiO}_2 \)-DP & 5.3 & 513 & 58 & 23 & 58 & 5 & 5 & 9 & d \\
Au/\( \mathrm{TiO}_2 \)-I & 2.0 & 400 & 60 & 26 & 47 & 11 & 10 & 6 & d \\
Au/\( \mathrm{TiO}_2 \)-SG & 1.1 & 2 & 34 & 19 & 79 & 2 & d & & \\
Au/\( \mathrm{ZrO}_2 \)-F & 3.8 & 54 & & 19 & 78 & 3 & d & & \\
Au/\( \mathrm{ZrO}_2 \)-DP & & & & 43 & 56 & 1 & 39 & & \\
\hline \end{tabular} |

\( ^{(a)} \) Overall activity at \( T = 513 \text{ K} \), \( \rho_{\text{total}} = 2 \text{ MPa} \), \( \mathrm{H}_2/\mathrm{acrolein} = 20 \), and \( W/\beta_{\text{Au}} = 15.3 \text{ g mol}^{-1} \). \( ^{(b)} \) Selectivity to \( \text{AyOH} \) (allyl alcohol), \( \text{PA} \) (propenal), \( \text{PrOH} \) (1-propanol), \( \text{HC} \) (hydrocarbons: ethane, ethylene, propane, propene), and \( \text{OP} \) (other products: acrylic acid, formylidihydropyran).

\( ^{(c)} \) Apparent activation energy. \( ^{(d)} \) This work. \( ^{(e)} \) Bimodal particle size distribution (2.1 and 7.4 nm).
catalytic activity of supported gold catalysts. The better activity of Au/TiO$_2$ in this oxidation reaction was explained by the number of low-coordinated gold sites being higher on TiO$_2$ than on ZrO$_2$ due to different support interactions causing different particle shapes. However, similar changes of the shape of gold particles could not be detected with TEM/HREM in the samples of the present study.

**Conclusions**

Nanostructural and catalytic properties in partial hydrogenation of acrolein have been studied for gold particles in the diameter range of 1–5 nm deposited on titania and zirconia. Catalyst activity and selectivity to the desired allyl alcohol are increased with increasing gold particle size. We conclude that adsorption of the C=O group of the $\alpha$, $\beta$-unsaturated aldehyde is favored by face atoms, so that most likely the increased fraction of dense (111) planes of the larger gold particles will give higher formation rates of allyl alcohol than low-coordinated atoms of smaller sized gold particles. However, from structural analysis by TEM/HREM and in-depth characterization with EPR, we conclude that the influence of small gold particles on the intramolecular selectivity of the hydrogenation of conjugated functional groups originates from active sites comprising paramagnetic F-centers of strong one-electron donating character and electron-rich gold particles. The origin of the antiphatetic structure sensitivity of the hydrogenation of the C=O vs C=C group may be attributed to quantum size effects which alter the electronic properties of sufficiently small gold particles. Thus, nanosized gold particles on oxide support prepared by appropriate methods open new prospects to adjust within wide limits material properties for the design of heterogeneous catalysts.

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