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Very Low Temperature CO Oxidation over Colloidally Deposited Gold Nanoparticles on $Mg(OH)_2$ and MgO

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Gold nanoparticles supported on metal oxides are being used as catalysts for a number of reactions, among which the low temperature CO oxidation has attracted the highest interest and is the most extensively studied one.[1−5] Highly dispersed gold catalysts with particle sizes of 2−5 nm supported on reducible metal oxides, in particular on TiO_2,[6−9] Fe_2O_3,[10] CeO_2,[11,12] Co_3O_4,[1] are well-known for their high activity for CO oxidation at low temperatures. However, at ultralow temperatures below −70 °C, only gold clusters with sizes below 1 nm supported on $Mg(OH)_2$ were reported to be active for this reaction.[13−15] Once the particle size of the gold increased to 3−5 nm after calcining the $Au/Mg(OH)_2$ catalyst at 300 °C, the activity for CO oxidation at −70 °C was completely lost.[14] Based on DFA and EXAFS studies, Cunningham et al. claimed that the active state of gold in a $Au/Mg(OH)_2$ catalyst is in the form of icosahedral metal clusters smaller than 1 nm.[14] Along similar lines, also Hutchings et al.[10] attributed the high activity of gold supported on iron oxide to very small units of only a few gold atoms. Up to now, supported gold nanoparticles with sizes above 1 nm, which are highly active for ultralow temperature CO oxidation, have not been reported.

Among various preparation methods for the synthesis of highly dispersed supported gold catalysts, the colloidal deposition method is an attractive alternative, since it allows decoupling of gold particle synthesis and deposition on the support.[16] Using this method, small gold nanoparticles in the size range 1−5 nm can be prepared.[16,17] The high reproducibility of both the preparation and the catalytic activities of the resulting catalysts has been proven in our previous studies.[16,18] In this contribution we used the colloidal deposition method to prepare $Au/Mg(OH)_2$ catalysts (0.7 wt % gold loading) with gold particle sizes from 1.5 to 5 nm which exhibited unprecedented activity for CO oxidation even at −89 °C. Similar catalytic performance is also found for the Au/MgO catalyst prepared through the calcination of the corresponding $Au/Mg(OH)_2$ at 375 °C for 3 h. These results show that the presence of very small gold entities with sizes below 1 nm is not mandatory for the synthesis of extremely active gold catalysts, which could open up new routes in the search for highly active systems.

The $Au/Mg(OH)_2$ (0.7 wt % gold loading) catalyst was prepared by the colloidal deposition method; the detailed preparation procedure is given in the Supporting Information. One should note that mesoporous MgO (see Figure S1) was used as the starting support, while the resulting catalyst is $Au/Mg(OH)_2$, which is attributed to the hydrolysis of MgO in aqueous solution during the gold particle deposition process. The XRD pattern (Figure S2) confirms the high phase purity of the catalyst as hexagonal $Mg(OH)_2$. The supported gold is difficult to detect by XRD due to its low loading amount. Also HR-TEM analysis is difficult due to the high energy of the electrons at an acceleration voltage of 200 kV which induces dehydration of $Mg(OH)_2$. In spite of numerous attempts, no good contrast images could be obtained on the Hitachi HF 2000 instrument. Therefore, HR-SEM (Hitachi S 5500) working at a low acceleration voltage of 30 kV was employed to characterize the particle size and dispersion of the gold particles supported on $Mg(OH)_2$. With this instrument, no problems were encountered in both the SEM and the STEM mode. Figure 1a−c show typical HR-SEM (a) images and the corresponding bright (b) and dark field (c) STEM images, additional images are shown in Figure S3. As can clearly be seen the size of gold particles mainly ranges from 1.5 to 5 nm (Figure 1d), and the average value is ca. 3 nm. No indication of smaller gold clusters with sizes below 1 nm were found (these would be detectable in the STEM mode), which is consistent with the results of the HR-TEM investigation (Figure S4) on the pure gold colloid before deposition which has a very similar particle size distribution as given in Figure 1d. The presence of very small gold entities with sizes far below 1 nm cannot fully be excluded. However, even if very small gold species existed, their amount would be very low, since the gold detected as larger particles roughly corresponds to the loading.

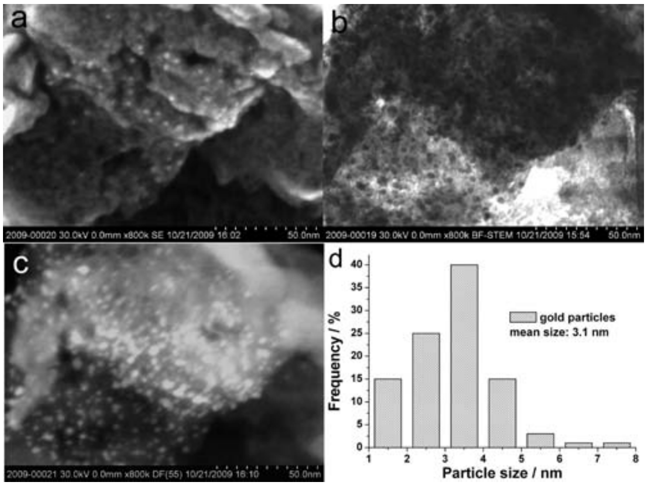

Figure 1. HR-SEM image (a), Bright (b) and dark field (c) STEM images, and gold particle size distribution graphic (d) of the $Au/Mg(OH)_2$ catalyst.

The catalytic activity of the catalysts for CO oxidation was measured in a plug flow reactor using 1% CO in air (20% O_2 and rest N_2) (details in Supporting Information). Previously described supported gold catalysts, such as Au/TiO_2[6−9,14] and Au/Mn_2O_3,[19] have typical conversion curves which show increasing conversion with increasing temperature. In contrast to this the $Au/Mg(OH)_2$ catalyst exhibited quite different catalytic behavior: Figure 2 shows the temperature dependence of the CO conversion for the $Au/Mg(OH)_2$ catalyst measured with a temperature ramp from −85 to 275 °C at a heating rate of 2 $°C \cdot min^{-1}$. At space velocities (SV) $= 80\,000\ mL \cdot h^{-1} \cdot g_{cat}^{-1}$, the temperature dependent activity curve shows a "U" shape with the lowest conversion at ca. 90 °C (CO

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conversion = 73%). At both ultralow (from −85 to 20 °C) and high temperatures (>230 °C), the catalyst is very active with full CO conversion, while, at temperatures from approximately 20 to 230 °C, the activity first decreases and then increases again with the increase of the temperature. It should be noted that −85 °C is below the sublimation point of CO_2 at atmospheric pressure (−78 °C). However, the maximum partial pressure of CO_2 is only 1000 Pa, and thus no condensation is expected. Nevertheless, occasionally some CO_2 condensation in colder parts of the system outside of the catalytic zone was observed, which could easily be detected by an incomplete carbon balance (both CO and CO_2 were analyzed on line).

To analyze this catalytic behavior in more detail, the space velocity was increased to 400 000 $mL \cdot h^{-1} \cdot g_{cat}^{-1}$. Now at temperatures from −85 to −30 °C, the activity for CO oxidation increased with increasing temperature; however, the rest of the curve showed essentially the same features as those for lower space velocity, i.e. a decrease, followed by an increase in conversion in the temperature range between approximately −30 and 275 °C. The light-off curves for the first and second run are almost identical, indicating the reproducibility of this effect. Identical conversion curves were also found reproducibly for separately synthesized batches of catalysts.

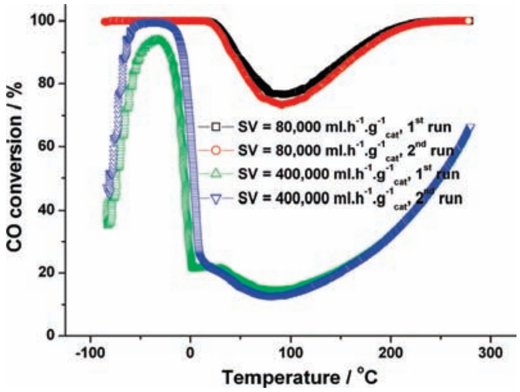

Figure 2. Temperature dependence of the activity for CO oxidation for the $Au/Mg(OH)_2$ catalyst at a space velocity of 80 000 $mL \cdot h^{-1} \cdot g_{cat}^{-1}$ (catalyst: 50 mg, reaction gas flow rate: 67 $mL \cdot min^{-1}$) and 400 000 $mL \cdot h^{-1} \cdot g_{cat}^{-1}$ (catalyst: 10 mg $Au/Mg(OH)_2$ diluted with 90 mg quartz, reaction gas flow rate: 67 $mL \cdot min^{-1}$).

Light-off curves measured under transient conditions may give misleading results concerning catalytic activity, if steady states are reached only slowly. Therefore activity tests under stationary conditions were performed at different temperatures, also with the aim to detect possible deactivation of the catalysts. The stability of the $Au/Mg(OH)_2$ catalysts was tested at −89, −50, and 90 °C, since these temperatures correspond to typical points of the conversion curves, i.e. in the low temperature branch where rate increases with temperature, close to the maximum low temperature rate, and close to the lowest conversion at intermediate temperatures. The $Au/Mg(OH)_2$ catalysts are extremely active and quite stable for CO oxidation at low temperatures (see Figure 3). At −89 °C, the $Au/Mg(OH)_2$ catalyst deactivated slightly and the CO conversion only decreased by 28% over more than 6 h. At −50 °C, no deactivation was visible over 400 min, but one should note that a possible deactivation could not be picked up at 100% conversion. It should be noted that, even at −89 °C, the specific rate during the whole experiment exceeded 3.7 $mol_{CO} \cdot h^{-1} \cdot g_{Au}^{-1}$ which is almost 20 times higher than that observed for the reported gold clusters (<1 nm) supported on $Mg(OH)_2$ at −70 °C.[12,15] Turnover frequency at −70 °C can be estimated to ∼2 s^{-1}, more than 2 orders of magnitude higher than previously reported. At 90 °C, the catalyst deactivated severely, and CO conversion decreased from 80% to 43% within 400 min. Overall, the results of the steady state analysis are consistent with those of the light-off activity tests.

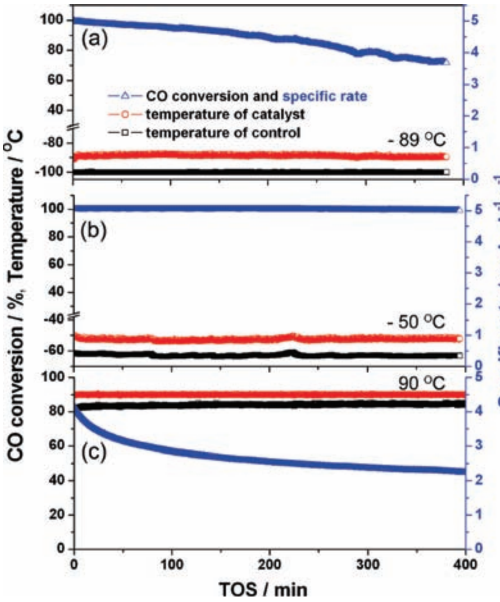

Figure 3. Performance of the $Au/Mg(OH)_2$ catalyst at different temperatures at constant temperature of (a) −89 °C for 380 min, (b) −50 °C and (c) 90 °C for 400 min. (catalyst: 50 mg, reaction gas flow rate: 67 $mL \cdot min^{-1}$, SV = 80,000 $mL \cdot h^{-1} \cdot g_{cat}^{-1}$).

A negative apparent activation energy for CO oxidation over gold catalysts had been reported before by Cunningham et al.,[15] but no fully convincing explanation was given. Generally, negative apparent activation energies in heterogeneous catalysis are not unusual, since the apparent activation energy is a composite of the activation energy of the surface reaction and adsorption enthalpies which can lead to negative apparent energies over certain temperature ranges. In this case, the unusual temperature curve could be caused by an interplay between such effects and participation of the support in the reaction. It is often suggested that gold catalysts supported on reducible transition metal oxides exhibit high activity for CO oxidation due to the support's ability to provide reactive oxygen.[20,21] The unusual temperature dependence of the activity of the $Au/Mg(OH)_2$ catalyst for CO oxidation may be attributed to differences in the ability for providing reactive oxygen at different temperatures, although $Mg(OH)_2$ is normally not considered as a reducible material. We used a CO titration technique to investigate the possible participation of the support in the reactive oxygen supply at different temperatures. For comparison, CO titration experiments were also performed on Au/TiO_2 (1 wt % Au loading, kindly provided by AuTEK) which is the most intensively studied gold catalyst for CO oxidation. For this reference catalyst, at low temperatures (= −50 °C), the ability to provide reactive oxygen is very weak, since a preoxidized catalyst gives a very low amount of CO_2 after exposure to CO. However, it is strongly enhanced with an increase in temperature of the titration, which corresponds to the temperature dependence of the activity (see Figure S5).

This is markedly different for the $Mg(OH)_2$ supported gold catalyst. Figure 4 shows the transient response of CO_2 and CO evolution over the $Au/Mg(OH)_2$ catalyst at different temperatures. At −50 °C, a strong CO_2 evolution is observed with a peak (CO_2 concentration = 0.98%) at 150 s when also the CO breakthrough occurs. The initial sharp CO_2 response is expected for a fast reaction, which proceeds by the direct adsorption of CO and reaction between CO and reactive oxygen at the metal surface.[20] It is noticed that CO_2 is detected earlier (after 72 s) than the CO response, indicating that initially all CO is oxidized by the reactive oxygen supplied by the catalyst. At 105 °C, the CO_2 signal emerged simultaneously with the CO. The concentration (= 0.84%) of the CO_2 response peak at 107 s is lower than that at −50 °C. At high temperature (at 215 °C), CO_2 was first detected at 77 s and its peak (CO_2 concentration = 0.92%) appeared at 123 s simultaneously with the detection of CO. So the time interval between the CO_2 and CO responses is 46 s, shorter than the 72 s observed at −50 °C. Summarizing the above results, the activity of the $Mg(OH)_2$ support to supply oxygen is substantially higher at −50 °C than at 105 and 215 °C. So compared to the reference Au/TiO_2 catalyst, the $Au/Mg(OH)_2$ exhibits quite different behavior in the reactive oxygen supply during the CO titration. Integrating the CO_2 response curves gives an indication of the amount of reactive oxygen available, and from comparison of this with the available gold surface area in the catalyst, the vast majority of this oxygen must be located on the support.

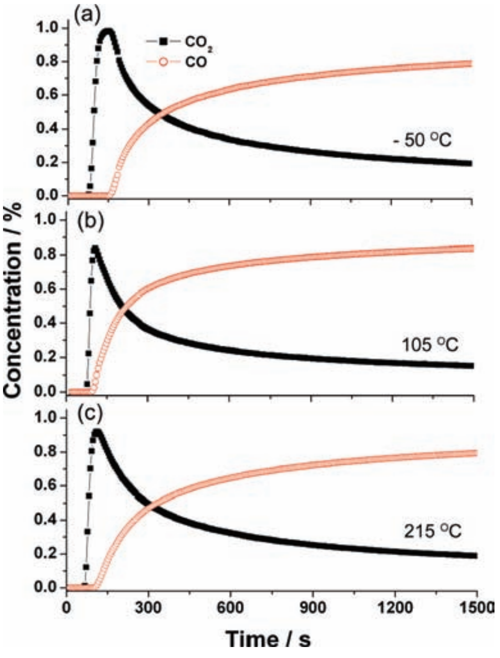

Figure 4. CO_2 response in CO titration experiments of the preoxidized $Au/Mg(OH)_2$ catalyst at different temperatures: (a) −50, (b) 105, and (c) 215 °C (catalyst: 100 mg; 1% CO in N_2; flow rate: 67 mL·min^{-1}).

The depletion of active oxygen with increasing temperature is suggested to be responsible for the negative apparent activation energy at intermediate temperatures. We propose the high activity of the support to supply reactive oxygen as the origin of the remarkable activity of $Au/Mg(OH)_2$ for CO oxidation at low temperatures. Further studies to elucidate the details of this effect are in progress in our group.

Recently, there have also been many reports of gold supported on MgO as catalyst for CO oxidation,[20,22−25] but reports on Au/MgO catalysts with high activity at ultralow temperatures are not available. Therefore, also Au/MgO catalysts were prepared by calcining the as-prepared $Au/Mg(OH)_2$ at 375 °C for 3 h (see Figure S6). In spite of this high temperature process, no obvious growth of the gold particles was observed, as shown in Figure S7. It is interesting to note that the Au/MgO catalyst resulting from $Au/Mg(OH)_2$ is also very active for CO oxidation even at a low temperature of −89 °C. It exhibits very similar temperature dependent catalytic performance as in the case of $Au/Mg(OH)_2$ (see Figures S8 and S9).

Interestingly, only the catalysts prepared with mesoporous MgO as starting material are active. Using directly $Mg(OH)_2$ as a support for the colloidal deposition (labeled $Au/Mg(OH)_2$-II), highly active catalysts could not be synthesized (Figure S10). Thus, the selection of the support precursor is crucial in the synthesis of Au supported catalysts, even if very similar materials are used.

In summary, we have synthesized gold supported on $Mg(OH)_2$ and MgO as catalysts for CO oxidation which show CO oxidation activities at least 2 orders of magnitude higher than the previously described system, in spite of the fact that gold particles are bigger than 1 nm. Both $Au/Mg(OH)_2$ and Au/MgO catalysts exhibit high activity for low temperature CO oxidation even at −89 °C. The high activity of the support to supply reactive oxygen is suggested as the origin of this high activity, and the depletion of these oxygen species with increasing temperature causes the negative apparent activation energy at intermediate temperatures. However, the exact nature of the oxygen species remains still elusive, and further experiments are in progress.

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Supporting Information Available: Details of experiments and additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

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