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Journal of Catalysis 240 (2006) 108–113

JOURNAL OF CATALYSIS

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Relation between nanoscale Au particle structure and activity for CO oxidation on supported gold catalysts

Ton V.W. Janssens *, Anna Carlsson, Anna Puig-Molina, Bjerne S. Clausen

Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

Received 31 January 2006; revised 17 March 2006; accepted 17 March 2006

Abstract

The CO oxidation activity of Au/TiO_2, $Au/MgAl_2O_4$, and Au/Al_2O_3 catalysts, all containing approximately 4 wt% Au, was compared with the detailed size and shape of the gold particles in these supported catalysts. Based on the indications that CO oxidation on Au catalysts requires low-coordinated Au atoms, the turnover frequency per Au atom located at the corners of the Au particles was calculated. A value of approximately 0.8 s^{-1} for both the Au/TiO_2 and the $Au/MgAl_2O_4$ catalyst was found. This represents an example in which the difference in catalytic activity of a Au catalyst with a reducible and irreducible support can be explained by a difference in Au particle geometry only, without the need to invoke other support-induced effects. The turnover frequency per corner Au atom in the Au/Al_2O_3 catalyst is approximately 4 times lower, indicating that other support-induced effects not related to the reducibility may play a role in this case.

Keywords: Gold catalysts; Support effect; CO oxidation activity; Particle geometry; Particle size; Scanning transmission electron microscopy

1. Introduction

Gold has traditionally been known as a catalytically inactive material. However, it has been shown that small supported Au particles can be effective catalysts for CO oxidation, particularly at low temperatures [1–6]. Although several explanations for the catalytic activity of small Au particles have been advanced, a final consensus on this issue has not yet been reached. It has been shown that the gold particle size and activity of gold catalysts depend critically on the support material, the synthesis method, and the activation procedure [7–14]. To date, explanations for the catalytic activity of small gold particles have mainly focused on the size of the Au particles [5,6,15–19] and the nature of the support material [20–22], and include electronic quantum-size effects, strain, oxygen diffusion via the support, and the oxidation state of the gold particles [13,23–27].

A more fundamental approach to understanding the catalytic activity of small gold particles is to determine how the properties of these particles differ from the inert bulk gold. Density functional theory (DFT) calculations on various gold configurations show that the interaction between CO and O_2 molecules depends on the coordination number of the gold atoms [18,28–30]. The interaction between molecular CO and O_2 and gold atoms with a high coordination number (>8), which are present in the dense (100) and (111) surfaces of gold, is repulsive, and thus these atoms are expected to not be catalytically active. However, on Au atoms with lower coordination numbers, CO and O_2 adsorption is feasible [18,28], indicating that the presence of such low-coordinated Au atoms is required in an active catalyst. In fact, the catalytic activity may change by several orders of magnitude due to the effect of the Au–Au coordination number, which makes this effect dominant and crucial for catalysis by Au [18]. Other effects, including strain, support-induced effects, electronic effects, and charging of the Au atoms, may also contribute to the catalytic activity of the Au particles, but their influence is significantly smaller. Several infrared studies have provided strong experimental evidence of the calculated relationship between Au coordination number and CO or oxygen interaction by demonstrating that CO adsorbs on edge and corner sites of Au particles, independent of the size or thickness of the Au particles [31–33].

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* Corresponding author.
E-mail address: tvj@topsoe.dk (T.V.W. Janssens).

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doi:10.1016/j.jcat.2006.03.008

In supported gold catalysts, the gold atoms at the edges and corners of the nanoparticles have a coordination number <8, and thus the active sites in gold catalysts very likely contain one or more of these atoms. Consequently, the overall activity of a supported Au catalyst should be determined mainly by the total number of atoms located at the corners and edges of the Au nanoparticles in the supported catalyst. The challenge is to determine how many gold atoms are located in those positions in a given supported catalyst. This can be achieved through a recently developed method in which the size and volume of the individual Au particles measured by scanning transmission electron microscopy (STEM) is combined with the Au–Au coordination number determined by extended X-ray absorption fine structure (EXAFS) analysis [34]. On the basis of these data, a geometric model for the Au particles in a supported catalyst is constructed in which the local environment of every gold atom is known.

From the geometric models, the number of Au atoms in specific positions in the supported catalysts (e.g., edge, corners, or interface) can be estimated. In this way, the catalytic activity of a supported catalyst can be correlated with atomic-scale information that can be addressed by DFT calculations or model studies. In the present article, the CO oxidation activity at 0 °C over Au/TiO_2, Au/$MgAl_2O_4$, and Au/Al_2O_3 catalysts was measured. The measured activities were correlated with the atomic-scale geometry of the Au nanoparticles derived from STEM measurements of the same supported catalysts as used in the activity measurements. Combining the activity data is combined with the structural information obtained from the geometric models allows calculation of the turnover frequency per corner, edge, and surface Au atom. By comparing these site-specific turnover frequencies for the Au/TiO_2, Au/$MgAl_2O_4$, and Au/Al_2O_3 catalysts, a new insight in the catalytic activity of Au based catalysts is obtained.

2. Experimental

The Au/TiO_2, Au/$MgAl_2O_4$, and Au/Al_2O_3 catalysts used in this study were prepared by homogeneous deposition precipitation of 1.145 g of $Au(NH_3)_4(NO_3)_3$ [35] with 0.344 g of urea in 1200 mL of water at 90 °C, to which 10 g of the respective support material was added. The catalysts were washed with warm water and dried overnight at 110 °C. The Au content found in chemical analysis of the final product was 4.41 wt% for the Au/TiO_2, 4.08 wt% for the Au/$MgAl_2O_4$ catalyst, and 3.99 wt% for the Au/Al_2O_3 catalyst.

The activity measurements were performed in a quartz U-tube reactor with an inner diameter of 2 mm. The samples consisted of catalyst powder with a particle size in the range of 125–300 µm; the amounts were 21.4 mg of Au/TiO_2, 20.5 mg of Au/$MgAl_2O_4$, and 20.1 mg of Au/Al_2O_3. Before the activity measurement, all catalysts were activated in situ by heating at 400 °C for 1 h in a gas mixture containing 1% CO and 21% O_2 in Ar at a flow of 42 NmL/min. Note that this activation procedure was not optimized to obtain maximum activity; we chose a uniform activation procedure for all three catalysts that results in measurable CO oxidation activity. Immediately after this heat treatment, the activity of the gold catalysts at 0 °C was measured by immersing the same quartz U-tube reactor in an ice bath to maintain a temperature of 0 °C. The same reactor feed gas and flow (42 NmL/min) was used, except for the Au/TiO_2 catalyst where the flow was increased to 214.4 NmL/min, to reduce the period with 100% conversion after cooling the reactor to 0 °C. The composition of the gas leaving the reactor was continuously monitored with a calibrated mass spectrometer (Balzers GAM 400), from which the catalytic activity was derived.

Immediately after the activity measurements, a small sample of the catalyst was taken out of the reactor and transferred to an electron microscope for STEM analysis. To avoid uncontrolled changes in the gold particle structure, the time between the activity measurement and STEM analysis was kept as short as possible, typically about 1 h. The STEM analysis was performed with a Philips CM200 FEG electron microscope with a primary electron energy of 200 keV. In the STEM measurements, the electron beam was focused to a spot size of about 5 Å, which is sufficiently small to measure Au particles as small as 7 Å. For each catalyst, a series of images was recorded, showing a total of 1500–2000 Au particles, which was used as input for the construction of the geometric models.

To obtain the overall Au–Au coordination number, separate in-situ EXAFS measurements with the same catalysts were performed at the X1-beamline at Hasylab. A sample of the catalysts was loaded in a reactor cell and exposed to the reaction gas mixture containing 1% CO, 21% O_2, and 78% Ar and heated to 400 °C for 1 h, then cooled to room temperature. The EXAFS spectra at the Au–L_3 edge (11921.2 eV) were recorded at room temperature with the samples kept in the reaction gas atmosphere. None of the catalysts demonstrated an increase in coordination number after the samples were maintained at room temperature for several hours.

3. Results

The CO oxidation activities of the Au/TiO_2, Au/$MgAl_2O_4$, and Au/Al_2O_3 catalysts were determined by following the CO, CO_2, O_2, and Ar concentrations at the reactor outlet for about 15 h at a reactor temperature of 0 °C, using a feed of 1% CO, 21% O_2, and 78% Ar. The time, $t = 0$, was set at the point at which the temperature reached 0 °C after the heat treatment. The reaction rate was computed from the data under the assumption that the reactor was operating under plug flow conditions and that the CO oxidation reaction was pseudo-first order in CO ($r = kp_{CO}$). With these assumptions, the rate constant for the reaction is given by

$$k = -\frac{F \cdot \ln(1 - X)}{W}, \tag{1}$$

where k is the rate constant (mol/(g_{cat} s)), W is the catalyst weight (g), F is the total flow (mol/s), and X is the conversion of CO. To correct for the differences in flow and sample amount, the CO oxidation rate at $X = 0$ was used as a measure of the catalytic activity; this was found by multiplying the rate constant by 0.01, the molar fraction of CO in the feed.

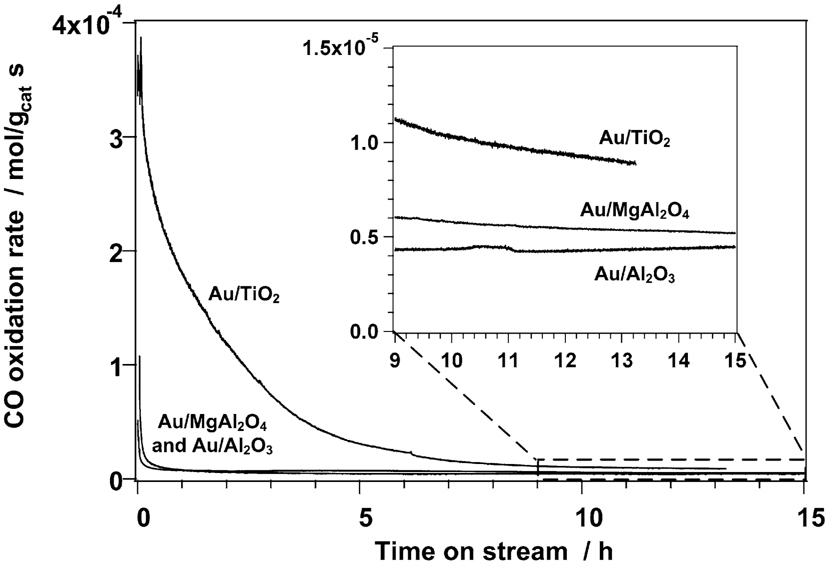

Fig. 1. CO oxidation activity of Au/TiO$_2$, Au/MgAl$_2$O$_4$, and Au/Al$_2$O$_3$ catalysts at 0 °C during the first 10–15 h of operation. Inset: enlargement of the final part, showing that the Au/TiO$_2$ catalyst is about twice as active as the Au/MgAl$_2$O$_4$ and Au/Al$_2$O$_3$ catalysts after 10–15 h of operation.

Fig. 1 displays the CO oxidation activity at 0 °C as a function of time on stream for the Au/TiO$_2$, Au/MgAl$_2$O$_4$, and Au/Al$_2$O$_3$ catalysts. Initially, the Au/TiO$_2$ catalyst was very active, but the activity gradually dropped to only a few percent of its initial value within the first hours on stream and reached a more or less stable level after 10–15 h on stream. In contrast, the Au/MgAl$_2$O$_4$ and Au/Al$_2$O$_3$ catalysts reached a stable level within the first hour on stream. The difference in behavior indicates that the initial deactivation and stabilization of the Au/TiO$_2$ catalyst differed from that of the Au/MgAl$_2$O$_4$ and Au/Al$_2$O$_3$ catalysts, reflecting the different natures of the three catalysts in terms of interaction of Au and the support and interaction of the Au particles and support with the reaction gas. Because long-term activity is of the greatest relevance for technical applications, we used the stabilized activity measured after 10–15 h on stream as a measure of the activity (see the inset in Fig. 1). Clearly, after 10–15 h on stream, the Au/TiO$_2$ was about twice as active (on a weight basis) as either the Au/MgAl$_2$O$_4$ or the Au/Al$_2$O$_3$ catalyst. At the point at which the catalysts were transferred to the electron microscope for the STEM analysis, the activities were 8.8 $\mu\text{mol}_{\text{CO}}/(g_{\text{cat}}\,\text{s})$ for Au/TiO$_2$, 4.8 $\mu\text{mol}_{\text{CO}}/(g_{\text{cat}}\,\text{s})$ for Au/MgAl$_2$O$_4$, and 4.2 $\mu\text{mol}_{\text{CO}}/(g_{\text{cat}}\,\text{s})$ for Au/Al$_2$O$_3$.

To relate CO oxidation activity to the atomic-scale geometry of the Au particles, a geometric model for the Au particles in the three catalysts was constructed, based on STEM measurements and the overall Au–Au coordination number derived from EXAFS. The method applied and the derivation and exact description of the geometric models for the Au/TiO$_2$, Au/MgAl$_2$O$_4$, and Au/Al$_2$O$_3$ catalysts used here has been described in detail elsewhere [34]. The basic geometry of the Au particles used in the geometric models is a top slice of a truncated octahedron, in which the variations in diameter and thickness of the Au particles are described by the number of atoms in an edge of the octahedron (m, edge length) and the number of layers (l). The sizes and shapes of the Au particles in the three catalysts differ significantly; Fig. 2 displays some typical gold particles resulting from the geometry analysis for the three catalysts [34]. Clearly, the Au particles in the Au/Al$_2$O$_3$ catalyst are small. In addition, the Au particles in the Au/TiO$_2$ catalyst appear somewhat rounder than those in the Au/MgAl$_2$O$_4$ catalyst.

From the geometric models, the number of Au atoms in specific locations in the gold particles can be estimated. Table 1 summarizes estimates for the number of Au atoms in some locations, including surface, edge, particle perimeter, and corners. According to the requirement of a low Au–Au coordination number at the active site for the CO oxidation [18, 28–30], the Au atoms located at the edges and corners of the Au particles are the possible active sites; therefore, Table 1 also lists the turnover frequency per surface, edge, and corner Au atom.

The estimated turnover frequencies per exposed surface atom, per edge atom, and per corner atom did not scale with the measured activities. This indicates that the observed activities for the Au/TiO$_2$, Au/MgAl$_2$O$_4$, and Au/Al$_2$O$_3$ catalysts cannot be explained by a single geometric requirement only. However, results from DFT calculations [18,28–30] and IR measurements [31–33] indicate that low-coordinated Au atoms are crucial to the catalytic activity of Au catalysts. Moreover, it seems to be the only parameter that can explain changes in catalytic activity by several orders of magnitude [18]. Therefore, the gold atoms located at the corners of the Au particles are expected to contribute the most to the overall activity.

Considering the turnover frequency per corner Au atom on the Au/TiO$_2$ and Au/MgAl$_2$O$_4$ catalyst, we find approximately the same value of about 0.8 s^{-1} for both catalysts, even though the Au particle shapes differ in these catalysts (see Fig. 2). The turnover frequency becomes 2.4 s^{-1} if it is assumed that the reaction occurs at the corners in contact with the support, or 1.1 s^{-1} if only the corner Au atoms not in contact with the support are counted (see Table 1).

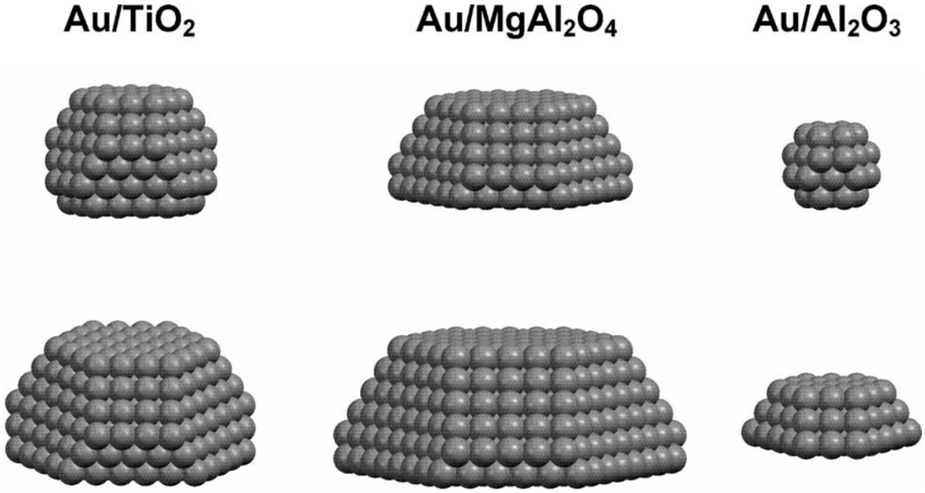

Fig. 2. Examples of common gold model particles for the Au/TiO_2 (left), Au/$MgAl_2O_4$ (center), and Au/Al_2O_3 (right) catalysts, see Ref. [34] for more details. The particles in the Au/TiO_2 catalyst are somewhat rounder than in the Au/$MgAl_2O_4$ catalyst; the Au/Al_2O_3 catalyst contains many small Au particles. The edge length (m, in number of Au atoms) and number of layers (l) in the particles shown are: Au/TiO_2: $m = 3$, $l = 6$ (top) and $m = 4$, $l = 6$ (bottom); Au/$MgAl_2O_4$: $m = 4$, $l = 5$ (top) and $m = 5$, $l = 6$ (bottom); Au/Al_2O_3: $m = 2$, $l = 4$ and $m = 3$, $l = 3$.

Table 1
Geometric properties and count of Au atoms located at specific sites, obtained from the geometric models for the Au/TiO_2, Au/$MgAl_2O_4$, and Au/Al_2O_3 catalysts, as derived in Ref. [34]

Property	Au/TiO_2	Au/$MgAl_2O_4$	Au/Al_2O_3
Au content (wt%)	4.40	4.10	3.99
Average diameter (nm)	2.10	3.60	1.60
Total Au atoms ($\mu mol/g_{cat}$)	223.90	207.14	202.57
Number of Au particles (g_{cat}^{-1})	3.49×10^{17}	2.07×10^{17}	9.67×10^{17}
Not in contact with support			
Corner atoms ($\mu mol/g_{cat}$)	7.93	4.06	14.08
Edge atoms ($\mu mol/g_{cat}$)	16.07	12.40	20.38
Surface atoms ($\mu mol/g_{cat}$)	48.89	43.32	46.48
In contact with support			
Corner atoms ($\mu mol/g_{cat}$)	3.47	2.06	9.37
Edge atoms ($\mu mol/g_{cat}$)	9.74	8.31	20.22
Atoms contact perimeter ($\mu mol/g_{cat}$)	13.21	10.37	29.59
Dispersion	38%	34%	55%
Au–Au coordination number from EXAFS	10.0	10.2	8.7
CO oxidation activity at 0 °C ($\mu mol/(g_{cat}\,s)$)	8.8	4.8	4.2
TOF per exposed Au atom (s^{-1})	0.10	0.07	0.04
TOF per edge atom (s^{-1})	0.34	0.23	0.10
TOF per corner atom (s^{-1})	0.77	0.79	0.18
TOF per corner atom in contact with support	2.54	2.33	0.45
TOF per corner atom not in contact with support (s^{-1})	1.11	1.18	0.30
TOF per corner atom in a concave site (s^{-1})[a]	4.33	4.12	1.30

[a] See Refs. [40–43] for a detailed description of a concave site.

This means that the requirement for low-coordinated Au atoms alone is sufficient to account for the different overall activity for the Au/TiO_2 and Au/$MgAl_2O_4$ catalysts. This provides an example of different catalytic activities of Au catalysts on a reducible (TiO_2) and irreducible ($MgAl_2O_4$) support that can be explained by a difference in Au particle geometry only.

The turnover frequency per Au corner atom in the Au/Al_2O_3 catalyst is ca. 0.2 s^{-1} per corner atom (or 0.3 s^{-1} per corner Au atom not in contact with the support or 0.45 s^{-1} per corner Au atom in contact with the support), which is 4–5 times lower than that for the Au/TiO_2 and Au/$MgAl_2O_4$ catalysts. This illustrates that the support can still have an impact on the catalytic activity of the Au particles that is not directly related to the number of low-coordinated gold atoms. The lower turnover frequency for the Al_2O_3-supported catalyst agrees well with an earlier conclusion that support effects not related to the number of low-coordinated Au atoms can be significant, but typically do not change the catalytic activity by orders of magnitude [18].

4. Discussion

By comparing the catalytic activity of a Au/TiO_2, Au/$MgAl_2O_4$, and Au/Al_2O_3 catalyst with the atomic-scale models of the Au nanoparticles in these catalysts, it is possible to relate the catalytic activity to the estimated amount of Au atoms in specific locations. Such an analysis results in a turnover frequency per Au corner atom that is practically the same for both the Au/TiO_2 and the Au/$MgAl_2O_4$ catalysts even when the corner atoms in contact or not in contact with the support are counted separately. The fact that the turnover frequency per Au corner atom is the same for the Au/TiO_2 and Au/$MgAl_2O_4$ catalysts indicates that the catalytic activity is not determined by the reducibility of the support in these cases. The role of the support is limited to determining the final Au particle shape through the interface energy [36]. Other support-related effects, such as the previously proposed support-mediated oxygen transport [20,21], seem to be insignificant for these catalyst systems.

Nevertheless, reducible supports can be advantageous, because they often contain oxygen vacancies that can serve as Au anchor sites [36–38]. For a Au/TiO_2 catalyst, the Au–support interaction becomes more attractive with increasing oxygen vacancy density [36], and thus the number of low-coordinated atoms can be expected to increase with increasing oxygen vacancy density in the support, which undoubtedly affects the catalytic activity of the Au/TiO_2 catalyst. According to this argument, the interface energy is a crucial parameter. But the final particle size is determined not only by the interface energy, but also by the density of nucleation sites, and consequently we cannot expect a straightforward correlation between interface energy and catalytic activity. A high density of nucleation sites may result in a high dispersion of the Au or in smaller Au particles despite low interface energy, and thus result in a different overall catalytic activity.

In our calculation of the turnover frequency over a given site, it is implicitly assumed that the overall activity is completely determined by the reaction rate at that particular site. In principle, the overall catalytic activity of the Au nanoparticles is not necessarily determined by a single atom configuration, but rather is the sum of different contributions of all atom configurations present. The contribution of a single configuration is then the turnover frequency at that particular site weighted by the amount available in the catalyst. The turnover frequency at a given site can even depend on the way in which the molecules are adsorbed [39]. As a result, the overall catalytic activity may depend on the particle structure in a complex manner. The similar turnover frequency per corner Au atom for CO oxidation over the Au/TiO_2 and Au/$MgAl_2O_4$ catalysts, however, suggests that the reaction rate on these catalysts is determined by a single contribution that involves the Au corner site with no significant influence from the support.

Another way to obtain different contributions to the overall activity is by multiple reaction pathways occurring simultaneously. Each pathway will have its own turnover frequency, and the measured overall activity will be a weighted average of these turnover frequencies. In fact, Remediakis et al. proposed two different reaction pathways for CO oxidation on Au nanoparticles: a "gold only" pathway and a "metalloxide boundary" pathway. In both scenarios, the function of the low-coordinated Au atoms is to bind the CO molecules [29,30]. The difference between these pathways lies in how the oxygen is adsorbed on the catalyst. In the gold-only pathway, the oxygen is adsorbed on the Au nanoparticle, and there is no significant interaction between the oxygen and the support. In the metalloxide-boundary pathway, the adsorbed oxygen interacts with the support, and thus such a mechanism is feasible only at the Au–support interface. On the basis of our data, it is not possible to distinguish between a gold-only and a metalloxide-boundary pathway.

Even if the reaction pathway cannot be deduced from our data, the value of the geometric models is that they allow estimation of the amount of specific CO and oxygen adsorption sites. For example, Molina and Hammer proposed that the reactive molecular oxygen is adsorbed in a concave site formed by the edge of a gold particle and the support surface that is exactly one gold atom high [40–43]. This model resembles the metalloxide-boundary pathway discussed above. The gold particles with an edge length (m) and number of layers (l) that fulfill the condition $l = m + 1$ or $l = 2m$ (examples given in the entire top row and center bottom in Fig. 2) contain sites with exactly that geometry. Counting only the number of corner atoms located at such a site, the turnover frequencies for the Au/TiO_2, Au/$MgAl_2O_4$, and Au/Al_2O_3 catalysts become 4.3, 4.1, and 1.3 s^{-1}, respectively. From this analysis, the turnover frequency over the Au/Al_2O_3 catalyst would be about 3 times lower than that over the other two catalysts. This means that the requirement of such a concave site for oxygen adsorption reduces the difference between the estimated values for the turnover frequencies of Au/TiO_2, Au/$MgAl_2O_4$, and Au/Al_2O_3 but is not sufficient to explain the observed activities. This example clearly shows how the geometric models can be applied to evaluate mechanistic ideas based on atomic-scale models to the activity of a supported catalyst.

Another proposal to explain the activity of a Au/TiO_2 catalyst is that a two-layer structure of Au is required [14,44]. In the Au/TiO_2 catalyst, about 1% of the Au is present in particles with two layers. The amount of Au in two-layer particles is about 1.5% in the Au/$MgAl_2O_4$ catalyst and about 6.5% in the Au/Al_2O_3 catalyst [34]; nonetheless, Au/TiO_2 is the most active catalyst. Furthermore, Au/$MgAl_2O_4$ and Au/Al_2O_3 have approximately the same activity, despite their significantly different amounts of Au in two-layer particles. Therefore, a two-layer structure of Au does not seem to contribute significantly to the overall catalytic activity in supported Au catalysts.

The turnover frequency per corner Au atom for the Au/Al_2O_3 catalyst is 3–4 times lower than that for the Au/TiO_2 and Au/$MgAl_2O_4$ catalysts and is somewhat dependent on which assumptions are made for the active site. A lower turnover frequency for an Al_2O_3-supported catalyst is consistent with the general trend that alumina-supported Au catalysts do not seem very active for CO oxidation, even though they can contain small gold particles [18]. It is interesting to note that the turnover frequencies on the two catalysts with an irreducible support are actually different, supporting the conclusion that the reducibility of the support as such is not critical to the catalytic activity of Au catalysts. The reason for the lower turnover frequency for CO oxidation on a Au/Al_2O_3 catalyst remains unclear, however. A possibility is that the intrinsic turnover frequency per corner Au atom in Au/Al_2O_3 is actually lower compared with that in Au/TiO_2 or Au/$MgAl_2O_4$. This may be due to a different contribution of a metalloxide-boundary pathway, to a more significant electronic effect induced by the higher interface energy of Au on Al_2O_3, or to the smaller size of the Au particles in the Au/Al_2O_3 catalyst [34].

5. Conclusion

The catalytic activity for CO oxidation over Au/TiO_2, Au/$MgAl_2O_4$, and Au/Al_2O_3 catalysts, all containing approximately 4 wt% gold, was related to the atomic-scale geometry of the Au particles in these catalysts. At 0 °C, Au/TiO_2 was about twice as active, on a weight basis, as Au/$MgAl_2O_4$ and Au/Al_2O_3. Using a geometric model of these catalysts, the number of atoms in specific locations was estimated. The difference in activity between the Au/TiO_2 and Au/$MgAl_2O_4$

catalysts matched the difference of low-coordinated Au atoms located at the corners of the Au nanoparticles. The resulting turnover frequency per corner atom in these catalysts was 0.8 s^{-1}. This is an example of a situation in which the difference in catalytic activity of a Au catalyst on a reducible and irreducible support can be entirely explained by a difference in Au particle geometry, by application of the requirement that only the low-coordinated Au corner atoms contribute to the activity. In these cases, the only effect of the support seems to be that the shape of the Au particles is different, as a consequence of a different interface energy, resulting in a different number of low-coordinated Au atoms. The turnover frequency per corner gold atom for the Au/Al_2O_3 catalyst was about 4 times lower than that for the Au/TiO_2 and $Au/MgAl_2O_4$ catalysts, indicating that other support-induced effects may play a role.

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