

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

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Abstract

The CO oxidation activity of a Au/TiO₂, Au/MgAl₂O₄, and Au/Al₂O₃ catalyst, all containing approximately 4 wt% Au, is compared to the detailed size and shape of the gold particles in these supported catalysts. Based on the conclusion that the CO oxidation on Au catalysts requires low coordinated Au atoms, the turn over frequency per Au atom located at the corners of the Au particles is calculated. A value of approximately 0.8 s⁻¹ for both the Au/TiO₂ and the Au/MgAl₂O₄ catalyst is found. This constitutes an example where 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 turn over frequency per corner Au atom in the Au/Al₂O₃ catalyst is approximately 4 times lower, indicating that other support induced effects, not related to the reducibility, may play a role in this case.

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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, in particular at low temperatures [1-6]. Although several explanations have been presented for the catalytic activity of small Au particles, 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 critically depend on the support material, the synthesis method, and the activation procedure [7-14]. The explanations for the catalytic activity of small gold particles presented so far 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 e.g. 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 understand 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 calculation on a variety of gold configurations show that the interaction between CO and O₂ molecules depends on the coordination number of the gold atoms [18,28-30]. The interaction between molecular CO and O₂ and gold atoms with a high coordination number (>8), which are present in the dense (100) and (111)-surfaces of gold, is repulsive, and these atoms are therefore expected not to be catalytically active. However, on Au atoms with a lower coordination number, CO and O₂ adsorption is feasible [18,28], which indicates 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 dominating and a crucial one for catalysis by Au [18]. Other effects, such as strain, support induced effects, electronic effects, or charging of the Au atoms, may also contribute to the catalytic activity of the Au particles, but their influence is significantly smaller. Several IR studies provide strong experimental evidence for the calculated relationship between Au coordination number and CO or oxygen interaction by showing that CO adsorbs on edge and corner sites of Au particles, independent of the size or thickness of the Au particle [31-33].

In supported gold catalysts, the gold atoms at the edges and corners of the nanoparticles have a coordination number lower than 8, and, therefore, the active sites in gold catalysts very probably contain one or more of these atoms. Consequently, the overall activity of a supported Au catalyst should be mainly determined by the total number of atoms located at the corners and edges of the Au nanoparticles in the supported catalyst. The challenge is to find out how many gold atoms are located in those positions in a given supported catalyst. This is achieved with a recently developed method, in which the size and volume of the individual Au particles measured by Scanning Transmission Electron Microscopy is combined with the Au-Au coordination number determined by EXAFS [34]. On the basis of these data, a geometric model for the Au particles in a supported catalyst is constructed, where 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, such as edge, corners or interface, can be estimated. In this way, we can correlate the catalytic activity of a supported catalyst 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 a Au/TiO₂, a Au/MgAl₂O₄, and a Au/Al₂O₃ catalyst is measured. The measured activities are correlated with the atomic scale geometry of the Au nano-particles derived from STEM measurements of the same supported catalysts as used in the activity measurements. When the activity data is combined with the structural information obtained from the geometric models, the turn over frequency per corner, edge, and surface Au atom can be calculated. By comparing these site-specific turn-over frequencies for the Au/TiO₂, Au/MgAl₂O₄, and Au/Al₂O₃ catalysts, a new insight in the catalytic activity of Au based catalysts is obtained.

2. Experimental

The Au/TiO₂, Au/MgAl₂O₄, and Au/Al₂O₃ catalysts used in this study were prepared by homogeneous deposition precipitation of 1.145 g of Au(NH₃)₄(NO₃)₃ [35] with 0.344 g urea in 1200 ml 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 contents found in chemical analysis of the final product were 4.41 wt% Au for the Au/TiO₂, 4.08 wt% Au for the Au/MgAl₂O₄ catalyst, and 3.99 wt% for the Au/Al₂O₃ 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 125-300 μm; the amounts were 21.4 mg (Au/TiO₂), 20.5 mg (Au/MgAl₂O₄), and 20.1 mg (Au/Al₂O₃). Prior to the activity measurement, all catalysts were activated in-situ by heating at 400 °C for 1 hour in a gas mixture containing 1% CO, 21% O₂ in Ar at a flow of 42 Nml/min. Note that this activation procedure has not been optimized to obtain maximum activity; we have chosen a uniform activation procedure for all three

catalysts that results in a 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/TiO₂ 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 is continuously monitored with a calibrated mass spectrometer (Balzers GAM 400), from which data the catalytic activity is 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, and was typically about 1 hour. The microscope used in the STEM experiments was 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% O₂, and 78% Ar, and heated to 400 °C for 1 hour, and cooled down to room temperature. The EXAFS spectra at the Au-L₃ edge (11921.2 eV)

were recorded at room temperature, while keeping the samples in the reaction gas atmosphere. None of the catalysts showed an increase in coordination number upon keeping the samples at room temperature for several hours.

3. Results

The CO oxidation activities of the Au/TiO₂, Au/MgAl₂O₄, and Au/Al₂O₃ catalyst are determined by following the CO, CO₂, O₂, and Ar concentrations at the reactor outlet for about 15 hours at a reactor temperature of 0 °C, using a feed of 1% CO, 21% O₂ and 78% Ar. The time t=0 is set at the point where the temperature reaches 0 °C after the heat treatment. The reaction rate is computed from the data, under the assumption that the reactor operates under plug flow conditions, and that the CO oxidation reaction is pseudo-first order in CO ($r = k p_{CO}$). With these assumptions, the rate constant for the reaction is given by

$$k = \frac{-F \cdot \ln(1 - X)}{W} \quad (\text{Eq.1})$$

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 $X=0$ is used as a measure of the catalytic activity, which is found by multiplication of the rate constant with 0.01, the molar fraction of CO in the feed.

Figure 1 displays the CO oxidation activity at 0 °C as a function of time on stream for the Au/TiO₂, Au/MgAl₂O₄, and Au/Al₂O₃ catalysts. Initially, the Au/TiO₂ catalyst is very active, but the activity gradually drops to only a few percent of its initial value

within the first hours on stream, and reaches a more or less stable level after 10-15 hours on stream. In contrast, the Au/MgAl₂O₄ and Au/Al₂O₃ catalyst reach a stable level within the first hour on stream. The different behavior indicates that the initial deactivation and stabilization of the Au/TiO₂ catalyst is different from that of the Au/MgAl₂O₄ and Au/Al₂O₃ catalysts, which is a reflection of the different nature of the three catalysts in terms of Au/support interaction and interaction of the Au particles and support with the reaction gas. Since the long-term activity is the most relevant for a technical application, we have used the stabilized activity measured after 10-15 hours on stream as a measure of the activity (see inset in Figure 1). Clearly, after 10-15 hours on stream, the Au/TiO₂ is about twice as active (on a weight basis) as both the Au/MgAl₂O₄ and Au/Al₂O₃ catalysts. At the point where the catalysts are transferred to the electron microscope for the STEM analysis, the activities are 8.8 μmol CO/g_{cat} s for Au/TiO₂, 4.8 μmol CO/g_{cat} s for Au/MgAl₂O₄, and 4.2 μmol CO/g_{cat} s for Au/Al₂O₃.

In order to relate a CO oxidation activity with the atomic-scale geometry of the Au particles, a geometric model for the Au particles in the three catalysts is constructed, based on STEM measurements, and the overall Au-Au coordination number derived from EXAFS. The method that is applied and the derivation and exact description of the geometric models for the Au/TiO₂, Au/MgAl₂O₄, and Au/Al₂O₃ catalysts used here is 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 size and shape of the Au particles in the three catalysts is quite different; Figure 2 displays some typical gold particles that result from the geometry analysis for the three catalysts [34].

Clearly, the Au particles in the Au/Al₂O₃ catalyst are small. In addition, the Au particles in the Au/TiO₂ catalyst appear somewhat rounder than those in the Au/MgAl₂O₄ catalyst.

From the geometric models, the number of Au atoms in specific locations in the gold particles is estimated. Table 1 summarizes estimates for the number of Au atoms in some locations, such as 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, the turn over frequency per surface, edge, and corner Au atom are listed in Table 1 as well.

The estimated turn over frequencies per exposed surface atom, per edge atom, and per corner atom do not scale with the measured activities. This indicates that the observed activities for the Au/TiO₂, Au/MgAl₂O₄, and Au/Al₂O₃ catalysts can not 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 for 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 most to the overall activity.

If we consider the turn over frequency per corner Au atom on the Au/TiO₂ and Au/MgAl₂O₄ catalyst, we find approximately the same value of about 0.8 s⁻¹ for both catalysts, even though the Au particle shapes are different in these catalysts (see Figure 2). The turn over frequency becomes 2.4 s⁻¹ if it is assumed that the reaction takes place

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). This means that the requirement for low-coordinated Au atoms alone is sufficient to account for the different overall activity for the Au/TiO₂ and Au/MgAl₂O₄ catalysts, which constitutes an example where the different catalytic activities of Au catalysts on a reducible (TiO₂) support and on an irreducible (MgAl₂O₄) support can be explained by a difference in the Au particle geometry only.

The turn over frequency per Au corner atom in the Au/Al₂O₃ 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 for the Au/TiO₂ and Au/MgAl₂O₄ catalysts. This illustrates that the support still can 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 turn over frequency for the Al₂O₃ 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/TiO₂, Au/MgAl₂O₄, and Au/Al₂O₃ 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 turn over frequency per Au corner atom that is practically the same for both the Au/TiO₂ and the Au/MgAl₂O₄ catalyst, also if the corner atoms in contact or not in contact with the support are counted separately. The fact that the turn

over frequency per Au corner atom is the same for Au/TiO₂ and Au/MgAl₂O₄ 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 earlier proposed support-mediated oxygen transport [20,21], seem to be insignificant for these catalyst systems.

Nevertheless, reducible supports can be advantageous, as they often contain oxygen vacancies which can serve as Au anchor sites [36-38]. For a Au/TiO₂ catalyst, the Au-support interaction becomes more attractive with the oxygen vacancy density [36], and therefore the number of low-coordinated atoms can be expected to increase with the oxygen vacancy density in the support, which undoubtedly affects the catalytic activity of the Au/TiO₂ catalyst. According to this argumentation, the interface energy is a crucial parameter. The final particle size, however, is not only determined by the interface energy, but also by the density of nucleation sites, and consequently, we can not 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 smaller Au particles, in spite of a low interface energy, and therefore result in a different overall catalytic activity.

In our calculation of the turn over 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 turn over frequency at that particular site weighted by the amount that is available in the catalyst. The turn over frequency at a given site can even depend on the way the molecules are adsorbed [39]. As a result, the overall catalytic activity may depend on the particle structure in a complex manner. The similar turn over frequency per corner Au atom for CO oxidation over the Au/TiO₂ and Au/MgAl₂O₄ catalysts, however, suggests that the reaction rate on these catalysts is determined by a single contribution, that involves the Au corner site without significant influence of the support.

Another way to obtain different contributions to the overall activity is by multiple reaction pathways that occur simultaneously. Each pathway will have its own turn over frequency, and the measured overall activity will be a weighted average of these turn over frequencies. In fact, Remediakis et al. proposed two different reaction pathways for CO oxidation on Au nanoparticles, namely a “gold only” and a “metaloxide 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 is the way 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 metaloxide-boundary pathway, the adsorbed oxygen interacts with the support, and therefore such a mechanism is only feasible at the Au/support interface. On the basis of our data, it is not possible to distinguish between a gold-only and a metaloxide-boundary pathway.

Even if the reaction pathway can not be deduced from our data, the value of the geometric models is that the amount of specific CO and oxygen adsorption sites can be

estimated. 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 metaloxide-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 are shown in the entire top row and center bottom in Figure 2) contain sites with exactly that geometry. If we count only the number of corner atoms that are located at such a site, then the turn over frequencies for the Au/TiO₂, Au/MgAl₂O₄, and Au/Al₂O₃ catalysts become 4.3, 4.1, and 1.3 s⁻¹, respectively. From this analysis, the turn over frequency over the Au/Al₂O₃ catalyst would be about 3 times lower compared to 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 turn over frequencies of Au/TiO₂, Au/MgAl₂O₄ and the Au/Al₂O₃ catalyst, but it 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/TiO₂ catalyst is that a two-layer structure of Au is required [14,44]. In the Au/TiO₂ catalyst, about 1% of the Au is present in particles with two layers. The amount of Au in two-layers particles is about 1.5% in the Au/MgAl₂O₄ catalyst, and about 6.5% in the Au/Al₂O₃ catalyst [34]. Nevertheless, the Au/TiO₂ catalyst is the most active one. Furthermore, the activity of the Au/MgAl₂O₄ and Au/Al₂O₃ catalyst is approximately the same, despite the large difference in the amount 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 turn over frequency per corner Au atom for the Au/Al₂O₃ catalyst is 3-4 times lower compared to the Au/TiO₂ and Au/MgAl₂O₄ catalysts, and somewhat dependent on which assumptions are made for the active site. A lower turn over frequency for an Al₂O₃ 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 turn over frequencies on the two catalysts with an irreducible support actually are different, supporting the conclusion that the reducibility of the support as such is not critical for the catalytic activity of Au catalysts. The reason for the lower turn over frequency for CO oxidation on a Au/Al₂O₃ catalyst, however, remains unsolved. A possible conclusion is that the intrinsic turn over frequency per corner Au atom in a Au/Al₂O₃ actually is lower, if compared to a Au/TiO₂ or Au/MgAl₂O₄ catalyst. This may be due to a different contribution of a metaloxide-boundary pathway, to a more significant electronic effect induced by the larger interface energy of Au on Al₂O₃, or to the smaller size of the Au particles in the Au/Al₂O₃ catalyst. [34].

5. Conclusions

The catalytic activity for CO oxidation over a Au/TiO₂, a Au/MgAl₂O₄, and a Au/Al₂O₃ catalyst, all containing approximately 4 wt% gold, has been related to the atomic-scale geometry of the Au particles in these catalysts. At 0 °C, the Au/TiO₂ is about twice as active, on a weight basis, as the Au/MgAl₂O₄ and the Au/Al₂O₃ catalyst.

From a geometric model of these catalysts, the number of atoms in specific locations is estimated. The difference in activity between the Au/TiO₂ and Au/MgAl₂O₄ catalysts matches the difference of low-coordinated Au atoms located at the corners of the Au nanoparticles. The resulting turn over frequency per corner atom in these catalysts is 0.8 s⁻¹. This is an example where 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 turn over frequency per corner gold atom for the Au/Al₂O₃ catalyst is about 4 times lower compared to the Au/TiO₂ and Au/MgAl₂O₄ catalysts. This indicates that other support-induced effects may play a role in that case.

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Table 1. Geometric properties and count of Au atoms located at specific sites, obtained from the geometric models for the Au/TiO₂, Au/MgAl₂O₄, and Au/Al₂O₃ catalysts, as derived in Ref. [34].

Property	Au/TiO₂	Au/MgAl₂O₄	Au/Al₂O₃
Au content (wt%)	4.40	4.10	3.99
Average diameter (nm)	2.10	3.60	1.60
Total Au atoms (μmol/g cat)	223.90	207.14	202.57
Number of Au particles (g ⁻¹ _{cat})	3.49·10 ¹⁷	2.07·10 ¹⁷	9.67·10 ¹⁷
<i>Not in contact with support:</i>			
Corner atoms (μmol/g _{cat})	7.93	4.06	14.08
Edge atoms (μmol/g _{cat})	16.07	12.40	20.38
Surface atoms (μmol/g _{cat})	48.89	43.32	46.48
<i>In contact with support:</i>			
Corner atoms (μmol/g _{cat})	3.47	2.06	9.37
Edge atoms (μmol/g _{cat})	9.74	8.31	20.22
Atoms contact perimeter (μmol/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 (μmol/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 ref. [40-43] for a detailed description of a concave site

Figure captions

Figure 1. CO oxidation activity of Au/TiO₂, Au/MgAl₂O₄, and Au/Al₂O₃ catalysts at 0 °C during the first 10-15 hours of operation. Inset: enlargement of the final part, showing that the Au/TiO₂ catalyst is about twice as active as the Au/MgAl₂O₄ and Au/Al₂O₃ catalysts after 10-15 hours of operation.

Figure 2. Examples of common gold model particles for the Au/TiO₂ (left), Au/MgAl₂O₄ (center), and Au/Al₂O₃ (right) catalysts, see Ref. [34] for more details. The particles in the Au/TiO₂ catalyst are somewhat rounder than in the Au/MgAl₂O₄ catalyst; the Au/Al₂O₃ 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/TiO₂: $m=3$, $l=6$ (top) and $m=4$, $l=6$ (bottom); Au/MgAl₂O₄: $m=4$, $l=5$ (top) and $m=5$, $l=6$ (bottom); Au/Al₂O₃: $m=2$, $l=4$ and $m=3$, $l=3$.

Figure 1

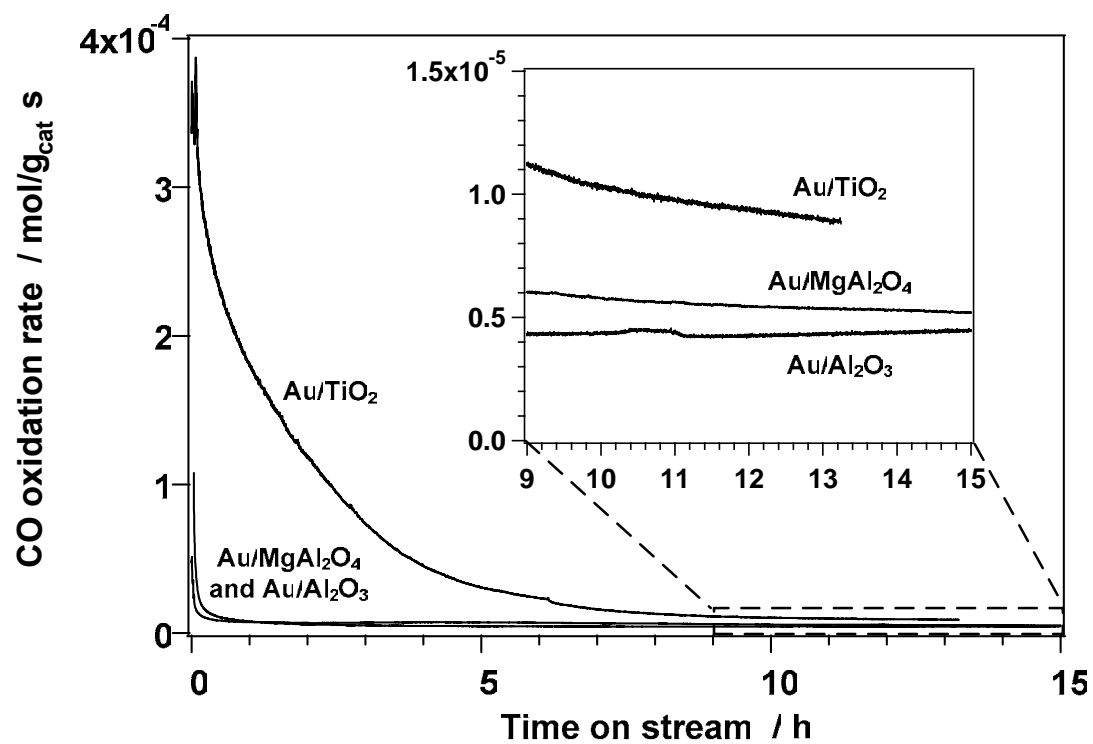


Figure 2

Au/TiO₂



Au/MgAl₂O₄



Au/Al₂O₃

