

Role of promoting oxide morphology dictating the activity of Au/SiO₂ catalyst in CO oxidation

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Abstract

The interfacial interaction of gold nanoparticles deposited on either model SiO₂/Si(100) or high surface area amorphous or mesoporous silica with minute amounts of promoter oxide like “active” FeO_x, TiO₂ and CeO₂ has been discussed. The role of the active oxide, its contribution to the perimeter along the gold nanoparticles has been interpreted. The oxide may invoke electronic interaction and simultaneously the defect structure of oxides likely has a key issue in the formation and stabilization of very small Au particles. The activity of the Au/oxide perimeter depends not only on the size of the Au particles, but also on the size and morphology of the oxide component (likely amorphous structure) regardless of whether it is supporting Au nanoparticles or decorating them. The activity in CO oxidation over Au catalysts is strongly affected by the length of the Au/“active” oxide perimeter which is regarded as the “active interface”. The longer length of the perimeter is evidenced by the enhanced CO oxidation activity.

Keywords: Structure of gold/oxide interface, its effect on CO oxidation, inverse catalysis

1 Introduction

A thorough comparison of the activity of gold nanoparticles deposited on different support materials revealed enhanced CO oxidation rates whether it was deposited on “active” as compared to “non active” supports (e.g. Fe₂O₃, TiO₂, CeO₂, or SiO₂, Al₂O₃, respectively) [1]. It is generally accepted that SiO₂ itself is a non active support regardless of whether the gold-containing samples are prepared by the wet chemical technique [2, 3] or by using the model, SiO₂/Si(100) supported system [4,5]. Only the use of a gold cationic complex precursor [Au(en)₂]³⁺ (en = ethylenediamine) proved the opposite effect. [6, 7] Nevertheless, amorphous silica was also employed to stabilize particle size of gold deposited on TiO₂ support [8].

Large amount of works have described the mechanism of the CO oxidation taking place on gold nanoparticles supported on “active oxide”. The valence state of gold is still a debating factor [9-12]. Earlier the problem has also been addressed in two chapters [13, 14] but apparently the way of preparation, the size of gold nanoparticles, etc. largely influence the valence state of the deposited gold. At the gold/oxide interface many dislocations and irregularities are present thus the coexistence of both species cannot be excluded. Photoelectron spectroscopy not, perhaps EXAFS is suitable experimental technique to give answer to this problem.

There is no unambiguous clarification about the site at which the CO molecules can be activated. The CO molecules can be chemisorbed on gold particles in the size range 2-6 nm, while on larger gold particles (d > 15 nm) no CO chemisorption occurs because the adsorption process is highly endothermic. It is, therefore, more plausible to assume that the the gold sites along the perimeter of gold/support interface serves as the adsorption site.

The active oxide may play a special role in activation of oxygen, although Norskov and his school [15] theoretically established that oxygen can be activated on a 10-atom gold particle. However, Goodman showed that on the Au/TiO₂ system the optimum activity appears in the 2-4 nanometer range, which contains far more than 10-atom gold particles [16]. Behm[1] and later Freund *et al.*[17] found that on Au/Fe₂O₃ large amounts of oxygen can adsorb on the support, which most likely represents the oxygen supply during reaction. The generally accepted view in the literature regarding the reducible oxide supported gold catalysis in CO oxidation, that the active phase is the perimeter, where the reaction takes place between the O₂ activated predominantly on the oxygen vacancies of oxide and CO adsorbed predominantly on Au in close vicinity of each other. [18] Consequently, all the properties of this interface affecting the CO adsorption and O₂ activation (oxygen binding energy, abundance and energetic state and charge of oxygen vacancies etc.) and the quantity of the active sites must affect the catalytic activity.

The aim of the present work is at finding relationship between the different forms of interface (perimeter) between gold (film, nanoparticles) and “active oxide” of different morphology, and developing high activity in the CO oxidation. For this some published and unpublished results will be applied.

2 Factors responsible for optimum activity of gold particles in CO oxidation

The key issue is to interface gold with oxide in creation of active sites determined by: (i) geometry and size of metal and oxide nanoparticles, (ii) morphology of the “active oxide” supporting or decorating the gold nanoparticles and (iii) electron properties of the oxide.

2.1 Size of gold nanoparticles

The presence of nano structured gold particles (2-5 nm) is prerequisite to develop high catalytic activity. In the literature [19] several attempts tried to separate the Au particle size effect from the effect of an active oxide. This can be achieved when either a $\text{SiO}_2/\text{Si}(100)$ model system [20-22], or high surface area SiO_2 aerogel are used as support for preparing Au/ SiO_2 samples. [23] We confined ourselves to apply zero valent gold particles deposited either by pulsed laser deposition technique (PLD), and/or by thermal evaporation, while gold sol was deposited via wet chemical methods on SiO_2 (amorphous or mesoporous). On Au/ $\text{SiO}_2/\text{Si}(100)$ model system the presence of Au nanoparticles was indicated by the shift of the core level binding energy towards positive value by about a 0.5 eV measured by XPS as compared to binding energy characteristic of bulk gold. [5, 21, 22] Sometimes Ar^+ ion bombardment leading to raft like gold nanoparticles was needed for further size reduction. [4] The intrinsic activity of the pure gold nanoparticles in the CO oxidation was significantly higher than that of the bulk like Au thin film. [5]

2.2 Interfacial properties of oxide

The oxide of variable oxidation state affects the catalytic properties of gold nanoparticles in oxidation reactions. One of the important features is that an interface with the gas phase along the gold/oxide boundary (called perimeter) first introduced by Haruta *et al.* [24-28], and later others [29], has a decisive effect. The promoting oxide depending on its nature may enhance the activity on different ways, as taking part in the reactant activation at the perimeter of the Au-oxide interface, via electronic interaction as was shown for TiO_2 as support [30-34], stabilising the metastable small gold nanoparticles against agglomeration and sintering [35,36], stabilising active form of Au (as e.g. $\text{Au}^{\delta+}$ on CeO_2 support).

As we already pointed out the size of gold nanoparticles and the perimeter with an active oxide dictate the efficiency

of the activity. The length of the active Au/oxide perimeter depending mainly on the size and shape of gold and oxide particles and their interface, is difficult to be determined. Moreover, the oxides have various structures, modification and morphology, which influence the gold/oxide interface and possibly the catalytic properties, too.

2.3 Effect of the structure of active support

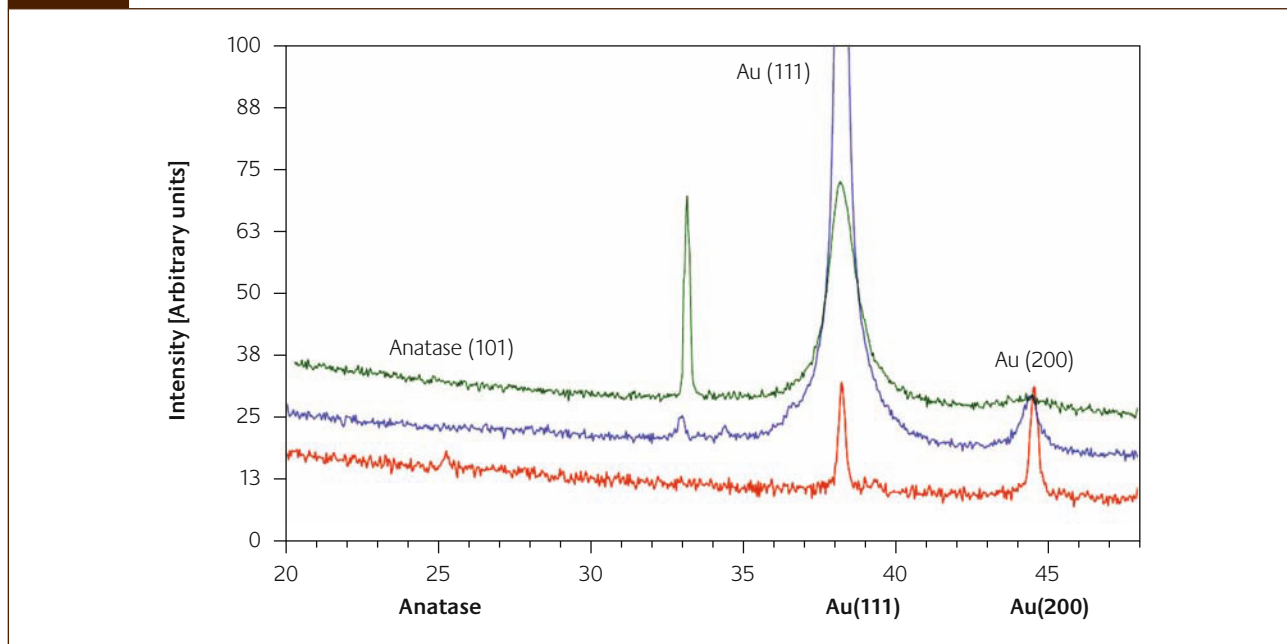
The effect of TiO_2 allotropes (rutile, anatase and brookite) on gold nanoparticles was recently discovered. [35, 36] The gold on different allotropic forms was in fully reduced state [12] indicating that oxidized Au is not necessary for high activity in CO oxidation. Gold nanoparticles on brookite showed the highest activity that was explained by the higher stability of the Au particle size. The surface area of the supporting oxide may influence the Au particle size, its stability against agglomeration and sintering. In Overbury's and coworkers' works the brookite composed of the largest particles has the smallest surface area as compared to the other allotropic forms that would prefer the sintering, but Au is stabilised by brookite more efficiently than anatase or rutile likely based on structural effects. Therefore, by *changing the morphology of the support (e.g. crystalline form), the gold nanoparticles can be stabilized*. The different crystalline form of titania may affect also the specific activity of the Au-oxide perimeter, but it has not been studied.

However, the stabilization of gold particles is not a unique behavior of a given crystal structure of supporting TiO_2 . For instance, Au/ Al_2O_3 was promoted by various oxides (Au/ $\text{MO}_x/\text{Al}_2\text{O}_3$) resulting in enhanced activity. [37] The 6 wt% CoO_x added to Au/ SiO_2 system [38, 39] resulted also in activity increase. Molybdenum oxide has similar effect. [40] Rare earth oxides are proved to be also excellent promoters [41-43]. Note that the effect of the promoting oxides depends on the nature of the combination of additive and support. In most cases the promoter oxide not only stabilizes the gold particle size, but the Au/promoter oxide interface may form having perimeter of increased activity. In such systems it is difficult to determine and control the highly active Au/promoter oxide perimeter dictating interface induced effect. In the three component inert oxide supported Au and promoter oxide systems it has to be considered that the less active Au/inert support and promoter oxide/inert support interface may also be formed on the expense of more active Au/promoter oxide interface. Moreover, the length of perimeter depends also on the shape and the arrangement of the contacting particles (as e.g. one Au interfacing one or more oxide particles or oxide forms an overlayer on Au etc.), all these are difficult to determine, too.

3 Effect of promoting oxide morphology

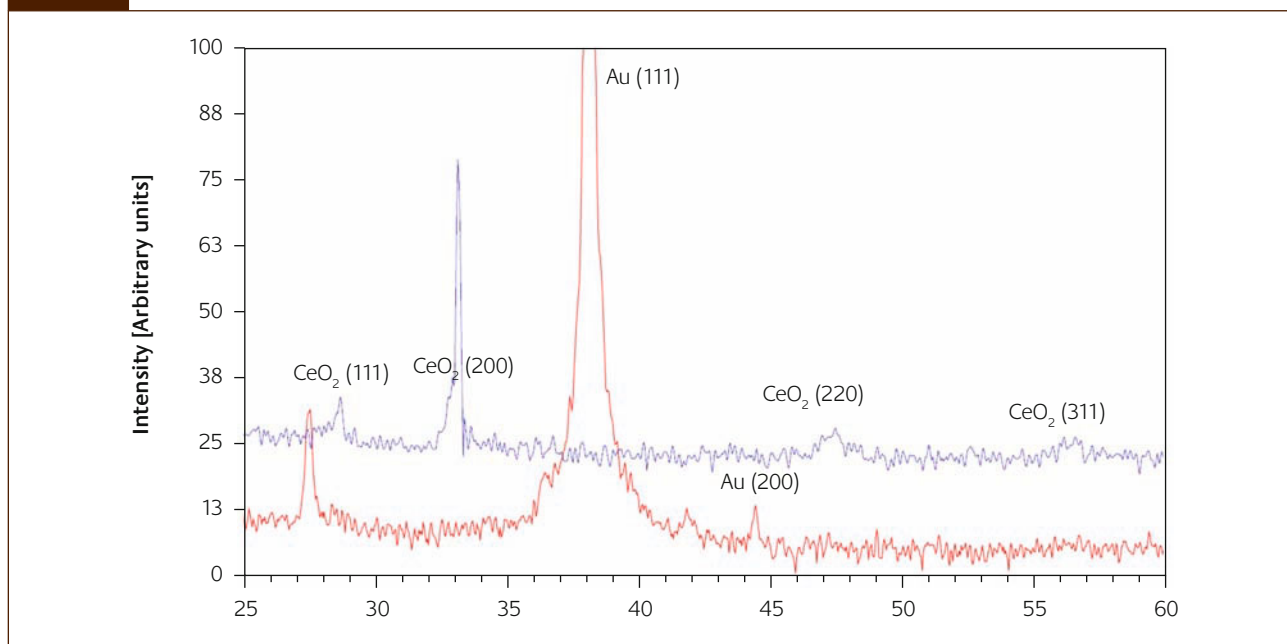
Morphology of promoting oxide comprises the (i) crystalline or amorphous character, (ii) the type of crystalline structure that both may affect for example the oxygen binding energy,

Figure 1



XRD curves of $\text{TiO}_2/\text{Au}/\text{SiO}_2/\text{Si}(100)$ sample. Green curve: 500 pulses of TiO_x on 60nm $\text{Au}/\text{SiO}_2/\text{Si}(100)$ sample, red curve: the same sample after high temperature CO oxidation reaction, blue curve: 500 pulses of TiO_x on 8nm $\text{Au}/\text{SiO}_2/\text{Si}(100)$ sample

Figure 2



XRD of $\text{CeO}_2/\text{Au}/\text{SiO}_2/\text{Si}(100)$ sample. Red curve: 200 pulses of pure CeO_2 on $\text{SiO}_2/\text{Si}(100)$ sample, blue curve: 200 pulses CeO_2 on 20nm $\text{Au}/\text{SiO}_2/\text{Si}(100)$ sample

the abundance of the oxygen vacancies, and (iii) the size and shape of the oxide phase (layers or spherical, hemispherical, polyhedral particles etc.) affecting the length of the perimeter of active Au/promoter oxide interfaces. In the following section we report our work indicating the effect of promoting oxide morphology on the CO oxidation catalyzed by gold nanoparticles. To make the approach easier only prefabricated gold nanoparticles created by PLD deposition or by sol technique were employed.

3.1 $\text{SiO}_2/\text{Si}(100)$ supported model system

As first example the gold-iron oxide system will be discussed. The technique to prepare iron oxide on $\text{SiO}_2/\text{Si}(100)$ followed by gold particle deposition by PLD technique has been described [44]. The major discovery is that after FeO_x and Au deposition and the sequential CO oxidation an amorphous structure of FeO_x was present measured by electron diffraction. The activity sequence of $\text{Au}/\text{FeO}_x/\text{SiO}_2/\text{Si}(100) > \text{Au}/\text{SiO}_2/\text{Si}(100)$ in CO oxidation is indicative of formation of

the more active Au/FeO_x interface perimeter. A drastic decrease in the activity of Au/FeO_x/SiO₂/Si(100) when the sample is treated in hydrogen (called “reduced state”) along with the appearance of the electron diffraction pattern characteristic of maghemite – C ((440), (400), (200) and (220) reflections) is the first sign of the beneficial effect of amorphous oxide layer versus crystalline one. [4] The decrease in activity cannot be ascribed to the change in gold particle size (5.1 nm compared to the original 3.9 nm), thus the possible reason may be due to the change in the crystalline structure of iron oxide in the Au/FeO_x/SiO₂/Si(100) sample. As a further evidence for this interpretation was the same trend observed in the oxidized and reduced co-precipitated Au/Fe₂O₃ samples [2]. From these experimental facts, i.e. *that in the more active as-prepared state mostly amorphous iron oxide layer is present whereas after reduction crystalline oxide structure (maghemite-c) is formed accompanied by lowered activity, even when the gold particle size remains about the same we conclude the importance of oxide morphology in determining the catalytic activity.*

Au/SiO₂/Si(100) sample having low activity, was incidentally decorated by the PLD induced amorphous iron oxide, i.e. a FeO_x/Au/SiO₂/Si(100) system was created. [5] As a consequence of the FeO_x/Au interface formation, the activity considerably increased regardless of the opposite sequence of the Au and oxide deposition forming a so called “inverse” interface. A similar effect was found for Au(111) decorated with an ultra thin TiO₂ layer [45-47]. This experimental finding again underlines the importance of the amorphous metal/oxide interface.

This fact led us to investigate the Au/SiO₂/Si(100) totally covered with FeO_x model catalyst [48,49]. Iron oxide layer of 5–10 nm thickness was deposited by PLD onto nano-sized Au particles on SiO₂/Si(100). The initial activity of FeO_x/Au nano-particles/SiO₂/Si(100) turned out to be the highest compared to both FeO_x/SiO₂/Si(100) and Au/SiO₂/Si(100) reference samples. According to the XPS analysis no Au segregation took place to the surface supported also by ToF SIMS. The catalytic activity of the FeO_x/Au/SiO₂/Si(100) sample must be attributed to the active sites located on the iron oxide overlayer promoted by gold underneath. Since Au caused promotion, we infer that an electronic effect is in operation due to the occurrence of a FeO_x/Au interface. DFT calculation has shown that if thin layer of gold is deposited on thin layer of TiO₂ the adsorbed O₂ molecules induce charge redistribution in the Au nanoparticles that penetrates to the Au/titania interface [46]. Although our FeO_x/Au system is an inverse one the gold nanoparticles penetrating into iron oxide layer might cause structural distortions that lower the total energy of the system promoting thereby the higher activity in CO oxidation.

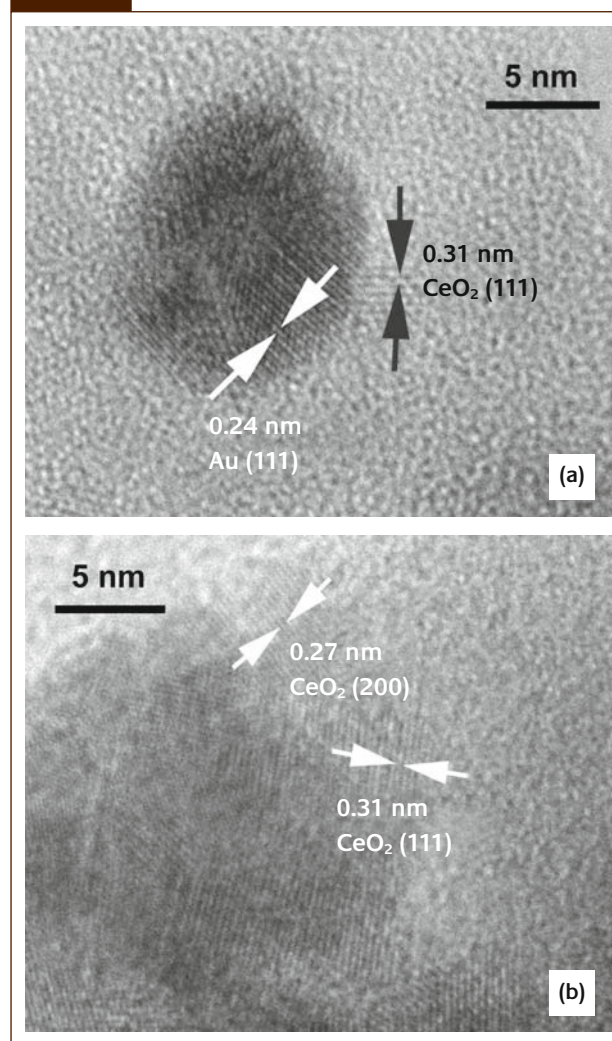
TiO_x/Au/SiO₂/Si(100) as well as CeO_x/Au/SiO₂/Si(100) behaves in an analogue manner. In the first case no anatase signal is visible by XRD in the as prepared state, only after reaction when simultaneous increase in Au particle size is

observable accompanied by restructuring indicated by the reversed intensity ratio between Au(200) and Au(111) reflections as shown Fig 1. All these structural changes resulted in a significantly decreased activity in the repeated catalytic tests. If ceria deposited alone on SiO₂/Si(100) the XRD picture shows crystalline phase while in interaction with gold no ceria signal appears due to the amorphous character of ceria (see Fig. 2). *Consequently, both the small size of gold nanoparticles and the amorphous “active oxide” (iron, titania, ceria) are necessary to develop high activity in the CO oxidation.*

3.2 Promoted silica supported Au catalysts derived from Au sol

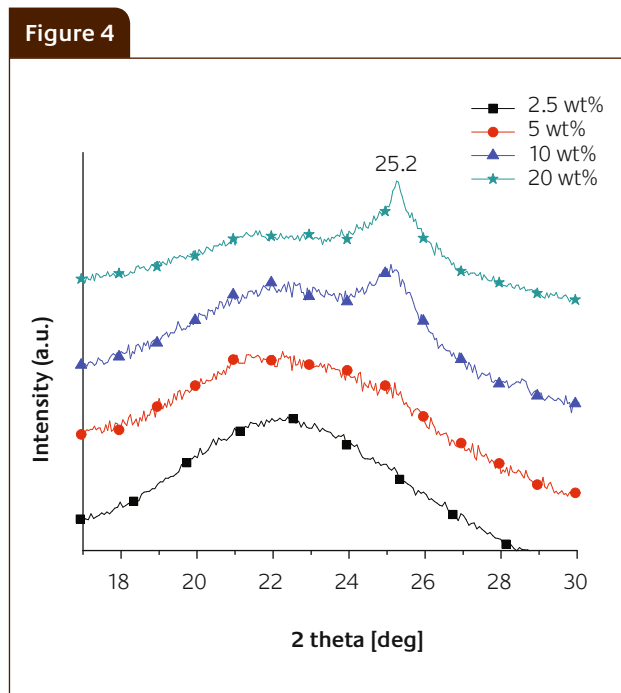
The previous idea has been extended for high surface area Au/SiO₂ decorated with oxide by a wet chemical method. An inverse system, viz., when the surface of Au is decorated with MO_x moieties (“localized oxide promotion” of gold), can provide new insights into the mechanism of CO oxidation on gold [23, 50-52]. Using various precursors (Ti-isopropoxide

Figure 3



HRTEM image of CeO₂/Au/SiO₂. (a) Au particle with a CeO₂ patch on SiO₂, (b) CeO₂ located on SiO₂

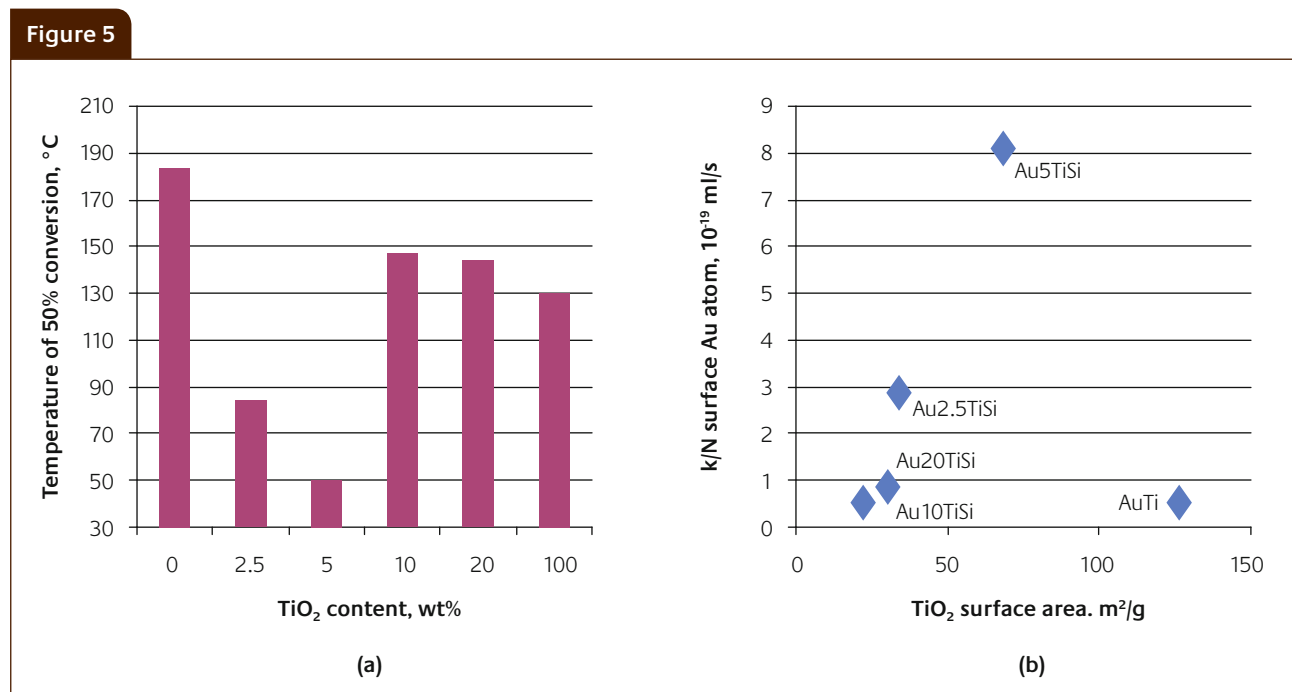
or Ti(IV) bis-(ammoniumlactato)dihydroxide (TALH) and $\text{Ce}(\text{NO}_3)_3$ a decorating amorphous oxide was developed. Careful characterization (XRD, TEM, HRTEM, Raman shift, XPS) revealed the formation of mostly amorphous nanosized TiO_2 and CeO_2 patches and particles interfacing with Au nanoparticles on SiO_2 resulting in higher stability of gold again sintering. Fig. 3a shows an image of $\text{CeO}_2/\text{Au}/\text{SiO}_2$ with



XRD of $\text{TiO}_2/\text{SiO}_2$ of different TiO_2 content prepared by surface initialised hydrolysis of Ti-isopropoxide and calcination at 600°C

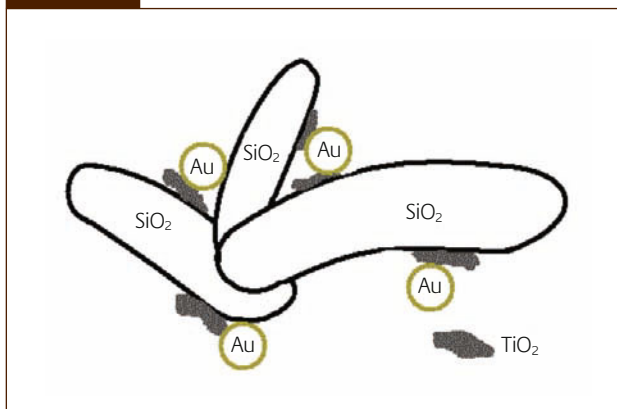
a small CeO_2 patch grown on the gold. However, TiO_2 or CeO_2 may be located on the SiO_2 surface with no connection to gold depending on the way of preparation (see Fig. 3b). According to XRD, TiO_2 formed by the surface induced hydrolysis of Ti-isopropoxide on silica followed by calcination is non crystalline at small concentrations below 5 wt%, but at higher Ti loading the major form is anatase (Fig. 4). The maximum activity of Au deposited on $\text{TiO}_2/\text{SiO}_2$ is at around 4-5 wt% TiO_2 (Fig. 5a) and the decrease of the CO conversion in the case of high TiO_2 loaded silica and pure titania supports is ascribed to the formation/presence of TiO_2 anatase crystallites [50].

It would be very helpful to make some quantitative consideration on the relation between the catalytic activity and the length of Au/promoter oxide perimeter regarded as the location of the most active sites in CO oxidation. We take into account a simplified geometry of the $\text{Au}/\text{TiO}_2/\text{SiO}_2$ (Scheme 1) and Au/TiO_2 (Scheme 2) systems prepared by adsorption of spherical Au colloid on highly dispersed TiO_2 containing SiO_2 and TiO_2 support, respectively, followed by calcination (400°C in air). In the calcined form of $\text{Au}/\text{TiO}_2/\text{SiO}_2$ and Au/TiO_2 we possibly may exclude the anchoring of several Au particles to the same TiO_2 particle/patch, because if even in the “as prepared” state such aggregates could have been present, during the high temperature treatment the Au particles in close vicinity to each other on a small TiO_2 surface are expected to aggregate and sinter. In case of Au/TiO_2 (Eurotitania, $d_{\text{TiO}_2}=8\text{nm}$) Au particles can be surrounded by several TiO_2 particles forming multiplied interface and perimeter. On the contrary, the formation of interface between TiO_2 patches of several surrounding SiO_2 particles

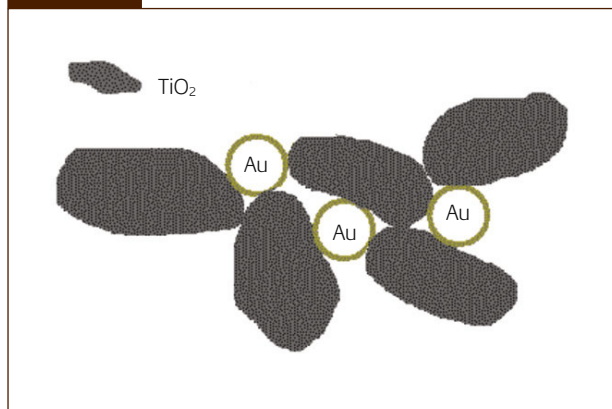


CO oxidation catalytic activity of $\text{Au}/\text{TiO}_2/\text{SiO}_2$ samples prepared by gold deposition on silica supported TiO_2 of different TiO_2 loading. (a) Temperature of 50% conversion vs. TiO_2 content, (b) Rate constant at 67°C related to surface Au atom vs. TiO_2 surface area. (TiO_2 surface was calculated assuming spherical particles of XRD determined size. In case of X-ray amorphous TiO_2 100% dispersity was assumed.)

Scheme 1

Schematic arrangement of particles in Au/TiO₂/SiO₂ systems

Scheme 2

Schematic arrangement of particles in Au/TiO₂ system

with the same Au particle has much less probability regarding the larger size of SiO₂ and the low coverage of silica surface of about 540 m²/g by titania (between about 4-15%). We cannot exclude in such Au/TiO₂/SiO₂ systems the presence of Au nanoparticles with no interface with titania. The exact estimation of the length of perimeter of Au/TiO₂ interface having even such simplified geometrical scheme is not really possible neither in Au/TiO₂/SiO₂ nor even in Au/TiO₂. However, the correlation between the catalytic activity (rate constant) related to surface Au atom and the TiO₂ surface area of Au/x%TiO₂/SiO₂ and Au/TiO₂ samples (see Figure 5b) can make possible a semiquantitative comparison of the specific activity of the Au/promoter oxide perimeter and that of Au/anatase perimeter. The significantly higher activity samples are those (about 6 times for Au/2.5%TiO₂/SiO₂, about 16 times for Au/5%TiO₂/SiO₂) in which the TiO₂ is X-ray amorphous and is in strong interaction with SiO₂. Taking into account the geometrical considerations above in these samples the Au/TiO₂ perimeter cannot be higher than in the less active TiO₂ supported Au sample, so it can be established that the perimeter of Au interface with less crystallised TiO₂ in strong interaction with the silica surface is more active than that of Au with well crystallised anatase.

The phenomenon described above can be attributed to the presence of Au on Ti–O–Si species (amorphous) proved by Raman shift and XPS as compared with Au on Ti–O–Ti containing units (anatase)[50]. The synergy between the advantageous structural, morphological and electronic properties of TiO₂ provided by its stabilization in amorphous form on inert silica support, was achieved using a small amount of TiO₂ forming higher activity interface with Au nanoparticles of increased stability against sintering.

Analogous results were obtained for CeO₂ decorating Au/SiO₂ or Au/SBA-15 compared to the CeO₂ supported Au sample[52]. For the formation of larger Au-active oxide interface with longer perimeter on an inert support the preferential deposition of Au on promoting oxide or vice versa instead of Au and promoting oxide deposition on the

inert support should be provided. One of the most important controlling factors of the interface formation is the electrostatic interaction between the different components during the preparation. The relative surface charges of the stabilized Au particles and the precursors of active oxide or the active oxide itself and the inert silica surface are decisive factors as was demonstrated by our studies on formation activity of TiO₂ and CeO₂ modified SBA-15 supported gold systems. [52] To sum up, (i) for an active oxide supported gold system, the interface between gold and oxide is primarily controlled by the particle size and shape of the two components, (ii) if an inert oxide is applied to support the active oxide and gold, there is a competition between the formation of active interfaces (Au with active oxide) and inactive interfaces (Au or active oxide with inert support). The stronger the attraction between active oxide or its precursors (see e.g. TALH, Ti-propoxide or Ce(NO₃)₃) and stabilized Au particles, the favoured the formation of the more active systems is. (iii) The attraction may be different depending on the sequence of deposition (oxide on Au/SiO₂ or SBA-15 or Au on MO_x/SiO₂ or SBA-15). The effect of size of the active interface and length of the active perimeter has comparable importance in catalytic activity as the Au particle size.

Our observations on the higher activity of the amorphous FeO_x, TiO₂ and CeO₂ promoted Au/SiO₂ are excellent complementary results to what was found by Overbury *et al.* [35] who compared the activity of Au on 3 allotropic titanium oxides and Goodman *et al.* [53] who emphasized the importance of highly reduced TiO_x in the nucleation of gold. Lambert *et al.* [54] observed a large activity on the CeO₂/Pt(111) system in the CO oxidation when the Pt surface was fully covered by ceria. It seems reasonable to associate this catalysis with the morphology of the oxide phase. Schottky barrier formation between Pt and CeO₂ leads to electron transfer from metal to oxide with concomitant decrease in the energy required for oxygen vacancy creation in the latter. Vacancy formation becomes active in CO oxidation by exothermic consumption of lattice

oxygen.[55] Disordered ceria films are much more active than ordered ones because surfaces of the former contain open crystal planes at which oxygen vacancy creation is favored.[55] On reduced TiO₂(110) 3% ML gold was deposited which, after oxidation, had a stronger interaction with the support. Most likely the oxidation made the top layer of TiO₂(110) more oxygen rich which increased the bonding of gold.[56] The importance of structural changes has been found in the NiB amorphous system, i.e. the most active species were neither the amorphous, nor the crystalline states but small nuclei embedded in the amorphous structure.[57]

4 Conclusions

In the highly active Au/oxide catalysts the activity is strongly affected by the length of the Au-oxide perimeter being regarded as the active phase. The presence of such perimeter can be evidenced by the increased CO oxidation activity.

The activity of the Au/oxide perimeter depends on the size of Au particles and also on the nature, size and morphology of the oxide component. For highly active catalysts the Au/oxide interface should be controllable. Controlling the electrostatic interactions between the components during the formation of the composite system is a decisive factor.

It has been established that interaction of gold nanoparticles deposited on either model SiO₂/Si(100) and amorphous or mesoporous silica with minute amounts of amorphous promoter oxide like FeO_x, TiO₂ and CeO₂ dramatically increases the gold activity in CO oxidation. The amorphous oxide not only enhances electronic interaction, but also stabilizes the nano-size gold particles. The defect structure may be important for the formation and stabilization of very small Au particles.

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