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“Catalytically active Au on Titania”: yet another example of a strong metal support interaction (SMSI)?

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In light of the many similarities between previous studies of the so-called strong metal support interaction (SMSI) involving Gr. VIII metals, and catalytically active Au, it is apparent that these two phenomena must be closely related. That active Au on titania spreads to form a bilayer structure, is electron-rich as determined by theory and experiment, nucleates on reduced Ti defects created by annealing to temperatures >750 K, and is deactivated via sintering in oxygen, is convincing evidence that the same basic principles responsible for activation of Au on titania are operative for SMSI involving Gr. VIII metals.

KEY WORDS: gold, titania, CO oxidation, strong metal support interaction, SMSI.

The enhanced catalytic activity of small gold clusters has been ascribed to a number of effects: bilayer structures that exhibit metal–nonmetal transitions [1–3], the metal-support interface [4–7], uncoordinated step- and corner atoms [8–11], strain [11], charge transfer from the support [12, 13], and metal cationic sites [14]. Early work on model Au clusters supported on $TiO_2(110)$ correlated the presence of Au bilayer cluster morphologies (figure 1) with catalytic activity for CO oxidation [1]. These bilayer Au structures have been shown to bind CO approximately 50% more strongly than bulk Au (figure 2) [15]. Furthermore oxygen either alone or in a reaction mixture has been shown to promote sintering of these bilayer Au structures (figure 3) [1]. A recent model study [16] of Au on a highly reduced TiO_x ordered film grown on Mo(112) has demonstrated that a coordinatively unsaturated, continuous Au bilayer structure that precludes assess of the reactant to the support, exhibits an exceptional high activity for catalytic CO oxidation (figure 4). The activity of this Au bilayer film is more than an order of magnitude more active than any previous report on a per Au atom basis [16]. A key feature of Au grown on TiO_x/Mo(112) is the strength of the interaction between the overlayer Au and the support comprised of strong bonding between Au and reduced Ti atoms of the TiO_x support, yielding electron-rich Au [16]. These recent studies are entirely consistent with recent theoretical studies [17] that show the importance of reduced Ti defect sites at the boundary between Au clusters and a TiO_2 interface in determining the Au cluster shape and electronic properties via transfer of charge from the support to Au [18]. Finally a recent theoretical study [19] has shown that a Au-only reaction pathway for a TiO_x supported Au bilayer cluster is energetically competitive with alternative pathways requiring reactant-support interactions.

In summary the essential features of the interaction of Au with TiO_2 that lead to enhanced catalytic activity are: (1) wetting of the support by the cluster; (2) strong bonding between the Au atoms at the interface with surface defects (reduced Ti sites); (3) electron-rich Au; (4) annealing at temperatures in excess of 750 K, sufficient to create and mobilize surface and bulk defects, is crucial in preparing an active catalyst; and (5) oxidation leads to deactivation via sintering of Au.

In the late seventies and eighties considerable attention was given the unusual properties of metals supported on TiO_2 when reduced at relatively high temperatures, results first reported by Tauster et al. for supported Pt and Ir [20], and designated as strong metal-support interaction (SMSI). Associated with SMSI were: (i) CO and H_2 chemisorption suppression [20,21]; (ii) an increase of methanation activity [22,23]; and (iii) a decrease in hydrogenolysis activity [24]. For example, Tauster *et al.* [20,21] showed that H_2 and CO chemisorption on highly dispersed titania-supported catalysts was suppressed. Vannice *et al.* [23,25,26], and Bartholomew *et al.* [27,28], found similar results for titania supported Ni. In addition, the methane yield for titania supported Ni was found to increase by an order of magnitude and the product distribution shifted toward higher hydrocarbons compared with unsupported Ni or Ni on other supports [23,25,27,28]. Chung *et al.* [29,30] and others [31] studied metals deposited on single crystal TiO_2 and determined that electron transfer occurs from the titania support to the metal; theory also supported this conclusion [32]. Work by Huizinga and Prins [33] as well as Baker *et al.* [34], showed that the formation of suboxides of titania in the vicinity of

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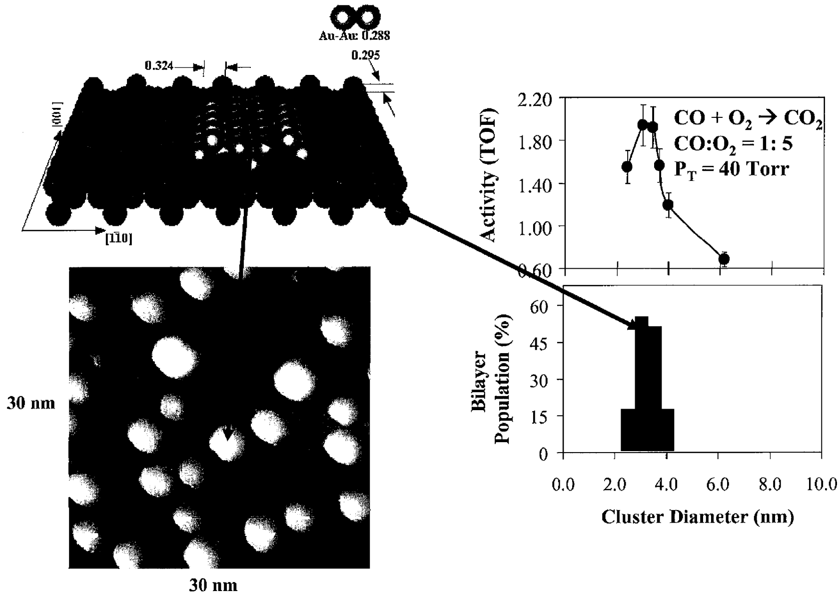


Figure 1. An STM image (bottom left) and schematic (upper left) of Au bilayer clusters on $TiO_2(110)$ whose population are dominant (lower right) for a Au/TiO_2 catalyst most active for CO oxidation (upper right). The activity is expressed as turnover frequency (TOF) in units of CO_2 molecules produced per Au site per second.

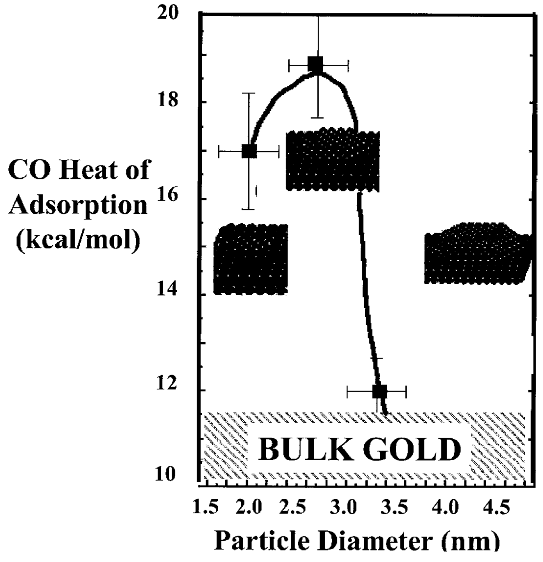


Figure 2. CO heats of adsorption determined by the Clausius-Clapeyron method at a CO coverage of <10% of saturation as a function of Au cluster size on a $TiO_2(110)$ support.

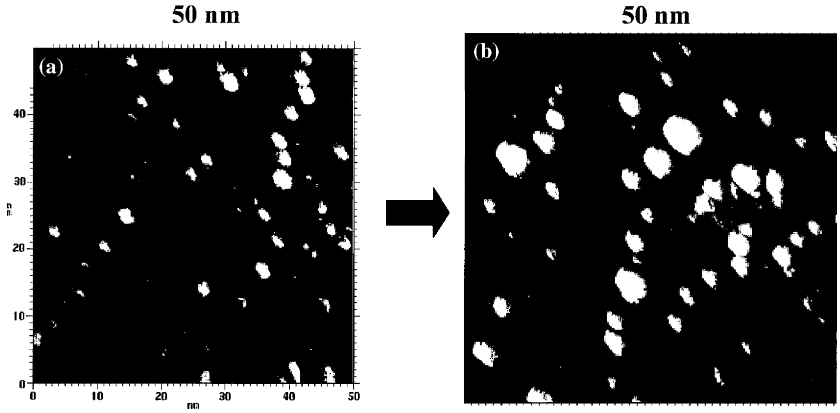
supported metal clusters during high temperature reduction causes spreading of the metal while treatment in O_2 leads to agglomeration of the metal.

These and numerous other researchers in the eighties addressed the SMSI phenomenon and reached the following general conclusions [31,35, and references therein]: (1) high temperature reduction leads to spreading of the metal on the support; (2) strong bonding occurs between the metal and reduced (sub-oxide) support; (3) interaction between the metal and the support leads to the metal becoming electron-rich; (4) reduction temperatures in excess of 750 K lead to SMSI; and (5) SMSI effects are reversed in oxidative environments.

In light of the many similarities between previous studies of SMSI involving Gr. VIII metals and catalytically active Au, it is clear that these two phenomena are very closely related. In fact, that active Au on titania spreads to form a bilayer structure, is electron-rich as determined by theory and experiment, nucleates on reduced Ti defects made by annealing to temperatures >750 K, and sinters in the presence of oxygen is strong evidence that the same basic principles responsible for activation of Au on titania are responsible for SMSI involving Gr. VIII metals.

Specifically the following parallels can be drawn between catalytically active Au on TiO_2 and the SMSI effect:

(1) Reduction in hydrogen at 773 K is the typical condition required to induce SMSI. This temperature has been shown to be sufficient to create surface defects in model studies of single crystal TiO_2 [36] and to be critical in the nucleation and growth morphology of Au clusters [37]. A recent study of supported Au on titania has shown that catalysts prepared at temperatures near 800 K exhibit higher activity and higher dispersion [38].
(2) Inducement of SMSI leads to wetting of the support by the metal [34]. Scanning tunneling microscopy (STM) studies of model Au/TiO_2 catalysts have shown that Au wets titania subsequent to an anneal to 800 K [1].
(3) With SMSI electron transfer occurs from titania to the supported metal yielding an electron-rich metal



Fresh 0.25 ML $Au/TiO_2(110)$

After 120 min exposure to 10 Torr O_2

Figure 3. Two STM images (50 × 50 nm) of a $Au/TiO_2(110)$ catalyst before (a) and after (b) 120 min reaction in 10 Torr O_2.

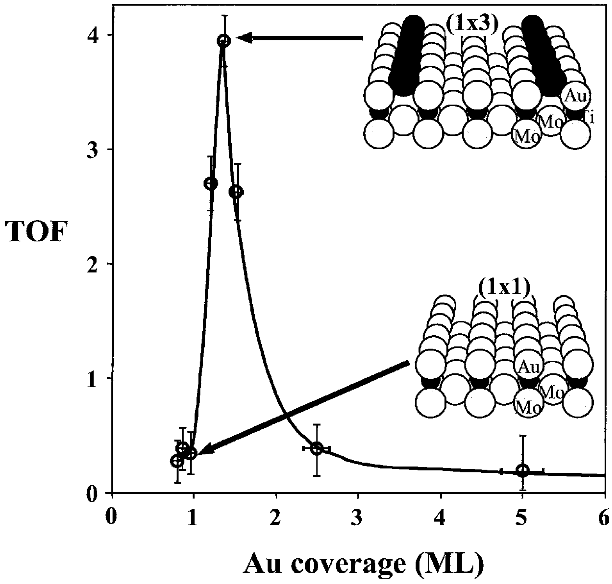


Figure 4. Activity for CO oxidation at room temperature as a function of Au coverage on Mo(112)-(8 × 2)-TiO_x. The CO:O_2 ratio was 2:1, and the total pressure was 5 Torr. Schematic models for the (1 × 1) and (1 × 3)-Au/TiO_x surfaces are shown in the inserts.

[29,30]. For an active Au/TiO_2 model catalyst, core level shifts measured by X-ray photoelectron spectroscopy (XPS) are consistent with electron transfer from titania to Au leading to electron-rich Au [3]. Density functional calculations also are consistent with Au being electron-rich when supported on titania [18,39].

(4) When induced, SMSI leads to suppression of H_2 and CO chemisorption for various metals [22,23]. On the other hand, for an active Au/TiO_2 catalyst CO chemisorption is enhanced [15,38], presumably because electron transfer from titania to Au leads to destabilization of the d-band and to enhanced back-bonding from Au to CO [18,39]. For Gr. VIII SMSI metals electron transfer from the support to the metal and the accompanying destabilization of the d-band may actually lead to a reduction in the metal back-bonding to CO. That is, a similar electronic interaction between the metal and the support for Au compared to Gr. VIII metals may produce a decidedly different chemical (catalytic) result.

(5) Oxidative environments reoxidize the reduced TiO_x support and reverse the SMSI effect [30]. Similarly, for Au on titania an oxidizing environment re-oxidizes the TiO_x support [41] causing de-wetting and sintering of the Au [1].

There is one outstanding discrepancy in the comparison of SMSI and catalytically active Au. This discrepancy is the assertion that SMSI arises from migration of a reduced TiO_x, perhaps TiO, onto the supported metal causing inhibition of chemisorption and modified catalytic properties [31,42]. No such evidence exists for a similar migration of a TiO_x species onto an active Au/TiO_2 catalyst. This discrepancy could be due to the logical, yet possibly incorrect, interpretation of the original data used to deduce migration of TiO_x onto the metal during SMSI. Indeed for a Au/TiO_2 catalyst, inspection shows an enhancement of reduced titania species for the active catalyst compared to a deactivated catalyst due to the critical role of defect sites in the wetting of titania by Au, i.e., the enhancement of TiO_x *at the cluster-support interface* [17]. Assuming this accumulation of defects at the cluster-support interface occurs as well during SMSI formation, this could easily be interpreted as TiO_x formation *on the cluster* because the metal bilayer structure that we now know forms on TiO_2 is relatively transparent to electron probes such as XPS. Likewise, an increase in the Ti feature in low energy ion scattering spectroscopy (LEIS) as a function of anneal temperature, interpreted as migration of TiO onto the metal, could be simply due to the improved accessibility of the probe ions to Ti because of the decrease in the oxygen stoichiometry during reduction. Finally, there is the possibility that decoration occurs for Gr. VIII metals but does not for Au. Nonetheless, the essential feature for the "activation" of both systems is the strong interaction between the metal and defects formed at the surface of the reduced support at elevated temperatures, and the de-wetting and sintering of the Au in an oxidizing environment.

In any case, future work on catalytically active Au on TiO_2 and other supports known to activate Au should be considered in the context of the extensive SMSI literature of the last 30 years. Additional work viewed in this perspective most certainly will illuminate the origin of the exciting and unique properties of catalytically active Au as well as uncover many of the remaining mysteries associated with the SMSI effect.

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