CO and O_2 adsorption on model Au–TiO_2 systems

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Au/TiO_2 catalysts are active for CO oxidation at room temperature and lower. To probe the surfaces of these catalysts, CO and O_2 adsorption and coadsorption on model Au–TiO_2 systems were examined under UHV conditions using TPD, ASE and XPS. No chemisorption of molecular O_2 was detected, as previously reported for clean Au single-crystal surfaces. A low concentration of CO adsorption sites associated with Au was observed; however, no unique interfacial sites could be unambiguously identified on these surfaces.

Keywords: gold–titania catalyst, CO oxidation over Au–TiO_2, CO and O_2 adsorption on Au–TiO_2, TPD, AES, XPS

1. Introduction

Gold is typically considered to be inert as a catalyst for most reactions and is far less catalytically active than other noble metals. However, recent research has shown that highly dispersed gold on reducible metal oxides, such as Fe_2O_3, Co_3O_4, NiO, $Be(OH)_2$, $Mg(OH)_2$ and TiO_2, is remarkably active for low-temperature oxidation of CO [1–7]. For example, high activity for CO oxidation has been reported at temperatures as low as 200 K [3,6]. It has been stated in previous studies that the turnover frequencies for CO oxidation are independent of the oxide support used and increase sharply as gold particles become smaller than 4 nm, and it has been proposed that small gold particles not only provide sites for reversible CO adsorption but may also appreciably increase the amount of oxygen adsorbed on the oxide support [2]. However, large inactive UHP gold powder particles can also be activated to oxidize CO at 300 K by dispersing TiO_x on its surface [8]. For the Au/TiO_2 system, a model invoking CO adsorbed on Au which reacts with oxygen activated at the Au–TiO_x interface has been proposed to interpret experimental results [8]. However, such interfacial sites have not been observed experimentally.

Studies of CO and O_2 adsorption on Au single crystals under ultra-high vacuum conditions have been reported [9–13]. CO weakly adsorbs on Au at temperatures below 125 K, but the coverage of CO at 117 K is only 1/3 the coverage of CO on Pt(110) at 300 K [12,13]. While the relative intensities of the various features in both the core and valance level spectra did not change over the temperature range of 30 to 150 K, attempts to resolve TPD peaks failed. No adsorption of molecular oxygen on Au has been reported between 300 and 500 K, even at O_2 pressures up to 1400 Torr, although atomic oxygen adsorbs and can oxidize CO on Au surfaces [11,12]. An obvious question to be answered is whether new adsorption sites are created in a Au/TiO_x system. This study represents an effort to answer that question.

2. Experimental

This study utilized temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES) to explore possible adsorption sites for CO and O_2 on both Au/TiO_2 and TiO_2/Au systems. Experiments were carried out in a Leybold-Heraeus (L-H) UHV system which has been described in detail elsewhere [14]. Home-made Au and Ti sputter dosers were used to vapor deposit either Au or Ti on a Pt foil which was spot-welded onto a thin tantalum foil was further spot-welded to two Ta metal blocks connected to copper heating leads. The heating leads were passed through a liquid nitrogen reservoir, which allowed the foil to be cooled to below 100 K and heated resistively to above 1300 K. TiO_2 thin films were formed by depositing Ti in 10^{-7} Torr O_2, followed by oxidation to obtain fully oxidized TiO_2. Some carbon contamination was observed during Au deposition and was removed only by sputtering. Both Au and TiO_2 thin films were thick enough to decrease the XPS Pt signal to 5–10% of the original Pt signal. The thickness of the Au and TiO_2 overlayers, based on the attenuation of the Pt 4f XPS peak, were estimated to be 22–29 and 11–15 monolayers, respectively, by assuming a mean free path of 1.3 nm and a monolayer thickness of 0.134 and 0.26 nm for Au and TiO_2, respectively. Au/Pt and TiO_2/Pt surfaces will be referred to as Au and TiO_2 surfaces in this paper. On the Au (or the TiO_2) surface an additional TiO_2 (or Au) overlayer was deposited to form either a Au/TiO_2 (or a TiO_2/Au) surface. For adsorption, O_2 (99.999%, MG Ind.) and CO (99.99%, Matheson) were used by backfilling the UHV chamber via leak valves.

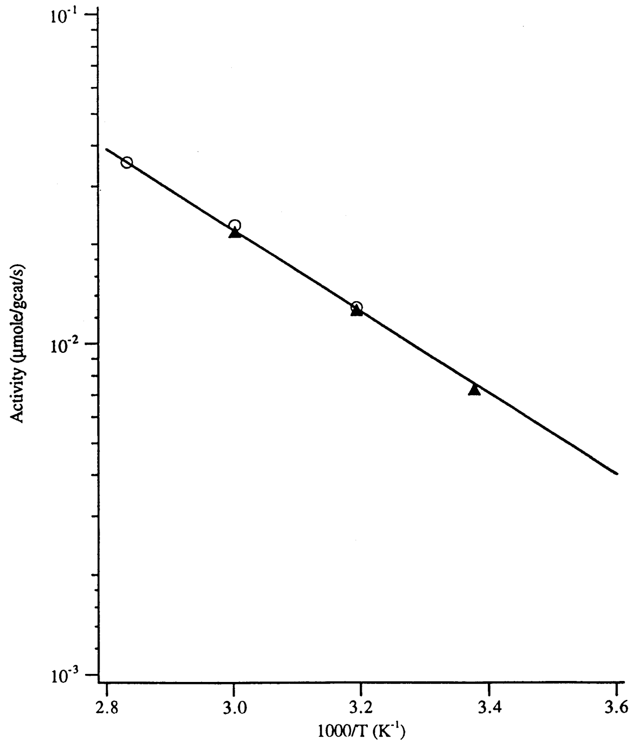

Fig. 1. Arrhenius plot for CO oxidation over UHP Au powder with TiO_2 deposited on its surface: $P_{CO} = P_{O_2} = 38$ Torr. Open symbols represent ascending temperature and filled symbols represent descending temperature.

3. Results and discussion

As reported previously, UHP Au powder (Johnson-Matthey, 99.9994%) is inactive for CO oxidation at low temperatures (below 500 K) as is pure TiO_2 [8]; however, the deposition of titania on this Au powder creates a well-behaved CO oxidation catalyst active at 298 K, as shown in fig. 1. This catalyst has an activation energy of 5.6 kcal/mol and a turnover frequency based on the Au surface area of 0.023 s^{-1}. A comparison of this system to a TiO_2-supported Au catalyst with 33 nm Au crystallites is given in table 1. The activity of the low surface area Au sample relative to the dispersed Au sample is surprising, as indicated by the specific activities.

In an effort to duplicate a similar TiO_2/Au system under UHV conditions, TiO_2 was first sputtered onto a Au film and studied; subsequently, after removing this film, a TiO_2 film was deposited and Au was sputtered onto it. Adsorption and coadsorption of CO and O_2 were studied on these two surfaces as well as on clean Au and clean TiO_2. AES was used to characterize these surfaces, and fig. 2 shows typical AES spectra for the TiO_2/Au surface and the Au/TiO_2 surface. Considering that the AES sensitivity of Au is about the same as that of Pt [17], if the deposition of TiO_2 on Au is assumed to be similar to that on Pt and a previous formula to estimate coverage on Pt is used [18], an estimation of one-half monolayer of TiO_2 on Au is obtained for fig. 2a. A similar calculation gives a coverage of 60% Au on the TiO_2 film in fig. 2b assuming no contribution from the Pt beneath the TiO_2 film.

The dosing temperatures were near 100 K (dosing at 300 K was also tried for TiO_2/Au). No molecular O_2 or CO_2 desorption was observed in any case. Coadsorption experiments gave CO TPD spectra which were the same as that for CO only, regardless of the dosing sequences, as shown in fig. 3. The results suggest that adsorption sites for O_2, either on Au or at the Au–TiO_x interface, are not detected under the experimental conditions employed here. This is consistent with previous studies showing that O_2 uptakes are very low on Au/TiO_2 catalysts and proposing that molecular oxygen is involved in the catalytic cycle [7,8]. The coverage of Au (or TiO_2) on the Au/TiO_2 (or TiO_2/Au) surface was varied, but no significant changes were observed. Consistent with the absence of O_2 adsorption, coadsorption experiments failed to produce any CO_2, which is the reaction product expected. It is also consistent with the recent study of Linsebigler et al. which showed that CO adsorbed on a TiO_2(110) surface did not react with lattice oxygen [15].

Fig. 3 shows CO TPD spectra under different conditions. The desorption of CO below 150 K was not well resolved and was difficult to reproduce. It may include some desorption from the heating leads, but it may also be due to the varying amount of TiO_2. Dosing more than 2 L CO produced a large featureless desorption peak that overlapped the smaller peaks, if they occurred. Figs. 3a and 3b show CO desorption from a TiO_2 surface. The desorption occurs below 150 K. When 5 L O_2 was dosed, only a small amount of desorption due to background CO appeared around 125 K, similar to that reported for CO on TiO_2(110) [15]. Coadsorption showed no desorption above 150 K, similar to that of dosing CO alone. In

Table 1
CO oxidation at 313 K over Au catalysts[a]. $P_{CO} = P_{O_2} = 38$ Torr

Catalyst	Surface area (m^2/g)	Rate (μmol CO/(s g))	Specific activity (μmol CO/(s m^2))
Au powder (99.9994%)	0.025	0	0
TiO_2	50	0	0
TiO_2/Au powder (20 theoretical monolayers TiO_x)	0.070	0.013	0.19
1.0% Au/TiO_2	42	2.3	0.056

[a] From ref. [8].

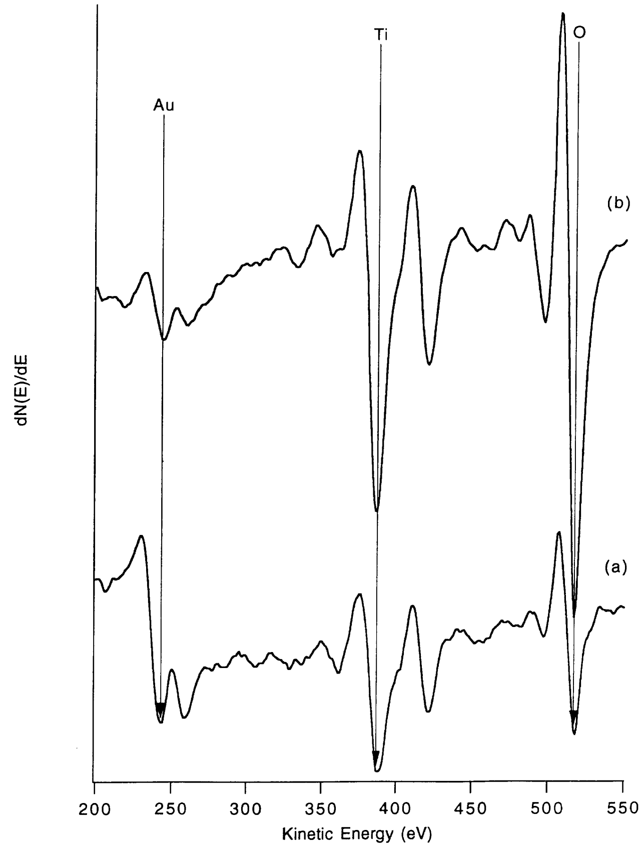

Fig. 2. AES spectra of (a) a TiO_2/Au surface and (b) a Au/TiO_2 surface.

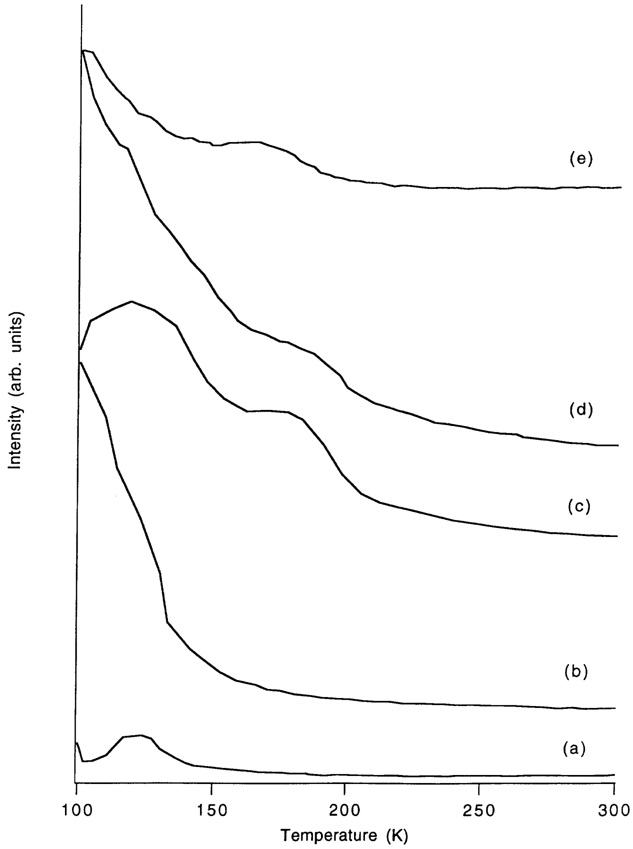

Fig. 3. TPD spectra of CO desorption from various surfaces after: (a) dosing 5 L O_2 on TiO_2; (b) dosing 0.5 L O_2 and 0.5 L CO on TiO_2; (c) dosing 0.5 L CO on Au; (d) dosing 2 L CO on TiO_2/Au (0.5 ML TiO_2); (e) dosing 0.5 L CO on Au/TiO_2 (0.6 ML Au). Dosing temperatures were near 100 K.

contrast, additional CO desorption from Au appeared between 160 and 200 K, as shown in fig. 3c, but compared with the CO desorption from a saturated Pt foil, this peak is about 2% that from the Pt foil. Extending the TPD temperature to 600 K produced no new features in these spectra. This result indicates that the number of sites available for CO adsorption on Au is very small. Nevertheless, as long as Au is available at the surface, this desorption feature exists as shown in figs. 3d and 3e. Either case shows less CO desorption, which suggests that the smaller CO adsorption is due to fewer Au sites available, and no additional CO adsorption sites appear to be produced at the Au–TiO_2 interface. This latter result is consistent with a recent model that CO adsorbs on Au rather than on interface sites [8]. Such a CO desorption peak has not been reported for Au single crystal surfaces; however, when a few layers of Au film were deposited on Pd(110), CO desorption peaks appeared at 225 (the α-state, associated with the first Au monolayer) and 190 K (the β-state, associated with the second Au overlayer) [16]. The β-state desorption peak, which gradually decreased in intensity with higher Au coverages, is very similar to that observed in this study. It is possible that CO may interact more strongly with Au thin films than with Au single crystals under UHV conditions, and thus suggests that CO adsorption on the Au surface may be one key step for CO oxidation on Au/TiO_2 catalysts, as proposed previously [8]. Although we cannot completely rule out a possible influence from the Pt foil substrate, such an influence would have the greatest impact on the first one or two Au layers and would have less impact on TiO_2 layers. In this study, because there were more than then monolayers of either Au or TiO_2 deposited on the Pt substrate, it is very unlikely that adsorbates felt any influence from the Pt foil.

In conclusion, no new adsorption sites in these Au–TiO_2 systems that interacted strongly with molecular O_2 could be detected; however, a low concentration of sites available for CO adsorption on surfaces associated with Au was observed. No unique interfacial sites could be unambiguously identified on these surfaces.

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