The Nanophysics of TiO_2/Au Model Catalyst as a Key to Understanding the High Efficiency of Real Au/TiO_2 Catalyst and Technological Consequences

I.V. Tvauri[*], D.F. Remar[*], A.M. Turiev[*], N.I. Tsidaeva[*], K. Fukutani[**], T.T. Magkoev[*]

[*]Nanophysics Research Centre, University of North Ossetia, Vatutina 46,
Vladikavkaz 362025, Russian Federation, ateia@mail.ru
[**]Institute of Industrial Science, The University of Tokyo, 4-6-1, Komaba,
Meguro-ku, Tokyo 153-8505, Japan

ABSTRACT

Carbon monoxide oxidation on the surface of in-situ prepared direct and inverse model Au/TiO_2 catalyst have been studied in ultra-high vacuum condition by a set of surface science analytical techniques. It is found that a metal/oxide perimeter interface is an active area for CO to CO_2 transformation. Measurements with isotopically labeled $^{18}O_2$ reveal that carbon dioxide is formed over Au/titania via the participation of oxygen specie of titanium oxide. Efficiency of the process is higher for the system consisting of reduced titania (TiO_x, x<2) compared to TiO_2. Results offer a number of possibilities to improve the performance of real Au/TiO_2 catalyst.

Keywords: surface nanostructure, thin films, molecular reaction on surface, gold, titanium oxide.

1 INTRODUCTION

About a decade ago it was found that catalytic activity for a range of oxidation reactions, (most notably carbon monoxide oxidation) of a mixture of Au ultra-small particles with titanium oxide powder considerably exceeds that exhibited by Au or titania on their own [1]. The explanation of high catalytic activity of titania/Au is still controversial. On one hand it is considered that the catalytic efficiency is due to the unique electronic and/or structural properties of oxide supported nanometer-scale Au particles which differ from those of the bulk Au, on the other – to the effect of the Au/titania perimeter interface [2]. To overcome this controversy it would be informative to study the catalytic behavior of the system winch emphasizes one of the two above-mentioned parameters, either an Au ultra-small cluster or titania/Au perimeter interface effect. The real catalyst is hardly suitable for thus purpose, however the corresponding model system might be a good candidate. In relation to this the aim of the present study is to investigate the CO+O_2 interaction on the surface of the system obtained by the controlled growth of titanium oxide sub monolayer to multilayer thin film islands on the surface of atomically clean Au (111). The advantage of this system is that carbon monoxide does not adsorb molecularly on titania and Au (111) [3] under ultra high vacuum (UHV) at a substrate temperature higher than 200 K, thus allowing to attribute any possible CO oxidation effect to the titania/Au interface. This system can be viewed as an inverse model catalyst due to complementary nature to real Au/TiO_2 catalyst [4].

To further elucidate the effect of the titania as well as the metal oxide perimeter interface in catalytic CO oxidation additional set of measurements on CO/Au/TiO_x (x<2) systems consisting of titania films oxidized by isotopically labeled oxygen $^{18}O_2$ have been carried out. Mass-spectroscopic analysis of the formed carbon dioxide specie unequivocally reveal essential role of oxygen of titania in catalytic CO oxidation. Efficiency of the process is notably higher for reduced titanium oxide film (TiO_x, x<2) compared to TiO_2 [5].

2 EXPERIMENTAL

Since gaseous molecules are very sensitive to the influence of electron or ion impact, on which surface probe techniques of electron and ion spectroscopy are based, investigation of CO+O_2 interaction have been carried out by reflection adsorption infrared spectroscopy (RAIRS) – an unrestrictive high-sensitive technique which is well suited for the study of the systems under consideration, i.e., dipole gas molecules on the metal substrate and thin film. For this purpose conventional Fourier-transform spectrometer adapted to measure normal molecular vibrations at grazing incidence and detection beam angles was used. Additional techniques used mainly for characterization of the preparation of titania films were Auger electron spectroscopy (AES) using double-pass cylindrical mirror analyzer with coaxial electron gun, X-ray photoelectron spectroscopy (XPS, Mg K_α anode) and low energy ion scattering (LEIS, He^+ ions) with the aid of a hemispherical analyzer, low energy electron diffraction (LEED) with the rear-view four-grid optics and work function measurements by Anderson method. Mass-spectroscopic analysis of carbon dioxide specie were carried out by thermal desorption spectroscopy (TDS) with the aid of quadrupole mass-spectrometer. For LEIS the chamber was equipped with a differentially pumped ion gun using He^+ ions at a primary energy of 1 keV. All measurements have been carried out in ultra high vacuum chamber with the base pressure normally not exceeding 2×10^{-10} Torr. The Au (111) surface was obtained by the well-known procedure of

growing thick film (50 ML) of Au on Mo (110) at a substrate held at 800 K [4]. Gold of high purity (99.99%) was evaporated from a conical W/Re filament source. It was verified that the film surface prepared in this way is identical to that of bulk Au (111). Titanium oxide was grown by thermal evaporation of metallic titanium (99.996% purity) in oxygen ambient at a substrate held at 700 K. The evaporation rate of Ti was controlled by the work function change of Mo (110) crystal as well as by Mo MNV (188 eV) Auger signal attenuation [5, 6]. One monolayer equivalent (MLE) of Ti is defined as 2.34×10^{15} cm^{-2}. Adsorption of carbon monoxide and oxygen were carried out by backfilling the UHV chamber through the leak valve with the respective spectroscopically pure gas at a partial pressure not exceeding 10^{-6} Torr. The value of exposure of 1 L was defined as 10^{-6} Torr s. In more detail experimental conditions are described elsewhere [5, 7, 8].

3 RESULTS AND DISCUSSION

Initially the Au film of about 50 ML thick was grown by thermal evaporation of metallic Au on the surface of Mo (110) bulk crystal. No impurities as well as Mo (110) substrate signals were detected by AES and XPS after the formation of the Au film. LEED exhibited hexagonal spots characteristic for (111) surface structure. Titanium oxide layers were grown by reactive evaporation of Ti in an oxygen atmosphere at a partial pressure of 10^{-6} Torr at a substrate held at elevated temperature of 700 K. According to LEIS data titanium oxide does not fully cover the Au surface but likely grows via three-dimensional islands beginning from the submonolayer coverage. An observed LEED pattern is and evidence for the formation of TiO_2 (100) structure with some local reconstruction of the surface. Formation of oxide with TiO_2 stoichiometry is corroborated with the XPS data. As has been shown previously [6] the Ti 2p photoelectron line is very sensitive to the degree of Ti oxidation. The corresponding spectra are shown in Fig. 1. Curves 1 and 2 correspond to the oxide films obtained by the above mentioned procedure with the difference that the latter one was not exposed to oxygen after stopping the Ti atom flux. The curve 1 indicating a "deeper" oxidation of Ti is close to the spectrum of the bulk TiO_2 crystal [6], whereas the curve 2 is an evidence of sub-stoichiometric oxide film.

The RAIRS measurements of carbon monoxide adsorption separately on pure Au (111) and TiO_2 films held at 200 K have shown that CO does not easily adsorb on these surfaces. The spectrum of the system obtained after exposing the titanium oxide film (30 MLE) corresponding to curve 1 of Fig. 1 to about 100 L of carbon monoxide consists of only one low intensity absorption line at a wavenumber of 2180 cm^{-1} (see Fig. 2, inlay). No lines have been detected upon exposing the Au (111) to CO up to exposure value of 400 L (wavenumber range probed: 1800 – 2200 cm^{-1}). In addition, no C 1s lines have been observed by XPS. However quite noticeable IR absorption line at 2114 cm^{-1} has been detected when CO was adsorbed on the surface consisting of titania clusters on Au (111). The corresponding spectrum for titania 5 MLE at CO exposure of 100 L is shown in Fig. 2 (curve 1). Exposure of about 100 L corresponds to CO saturation. Up to this exposure the IR intensity gradually increases with the total blue shift of intramolecular vibration frequency of 8 cm^{-1}. The latter can be attributed to increasing dipole-dipole interaction with CO coverage increase. Above 100 L exposure the CO IR intensity and line position do not noticeably change. Therefore one can consider that the interface area created by the contact of Au (111) and titanium oxide becomes an active place for CO adsorption while titania and Au (111) separately are poor substrates for CO bonding at this temperature. Such a dramatic change of the adsorption capability is an evidence of considerable change of the electronic and/or structural properties of both titania and Au when they are in contact. According to literature data on

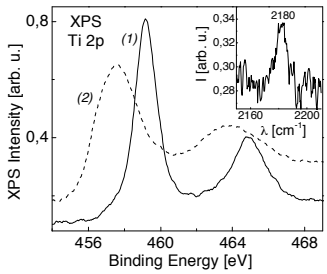

Figure 1: Ti 2p photoelectron spectra of thick (30 MLE) titanium oxide film on Au (111) annealed (1) and unannealed (2) in an oxygen ambient after stopping the Ti evaporation flux. Inlay: Infrared absorption line (intensity I versus wave-number λ) observed after exposing the titanium oxide film, corresponding to curve (1), to 100 L of carbon monoxide at a substrate held at 200 K.

titanium dioxide growth on different metal substrates the stoichiometry as well as the electronic structure of Ti and O ions of the oxide layer which is in direct contact with the metal is different from that of TiO_2. Moreover the electronic state of the topmost layer of the metallic substrate also changes. The Au atoms at the oxide/Au perimeter interface acquire some anionic character. Thus adsorption of the titanium oxide on Au (111) results in a formation of a ternary Ti-O-Au system at the interface with a chemisorptive properties which are notably different from those of TiO_2 and Au separately [8].

Upon subsequent inlet of the molecular oxygen into the UHV chamber the intensity of the CO absorption line gradually decreases with a slight blue shift (total detected shift is about 10 cm^{-1}) (see Fig. 2, curves 1 and 7). Possible explanations of such IR intensity depletion are 1) oxygen adsorption stimulated CO desorption; 2) formation of CO_2 and its subsequent desorption; 3) change of the CO molecular axis tilt in the way that intramolecular vibrations are no longer accessible by RAIRS in the configuration

used. However, the latter one might not be the case since XPS measurements before and after oxygen inlet revealed that in the latter case the C 1s intensity is by the order of magnitude lower than in the former case. (It should be noted that the C 1s line intensity decrease is not accompanied by the change of its binding energy which indicates that CO does not dissociate on the surface). This means that the IR line intensity depletion is due to CO surface concentration decrease, rather than to molecular reorientation on the surface. The reason for CO concentration decay is CO_2 formation and its subsequent desorption.

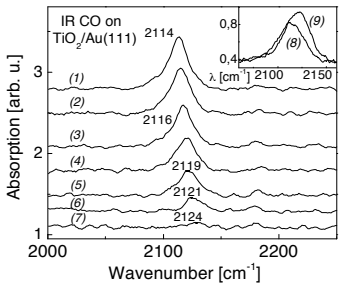

Figure 2: Change of the infrared absorption spectra during exposure of the CO/titania/Au (111) system to oxygen at a substrate held at 200 K. Carbon monoxide initial exposure and oxygen partial pressure are 100 L and 10^{-6} Torr, respectively. Oxygen exposure time (min): 1-0; 2-5; 3-10; 4-15; 5-20; 6-25; 7-30. Inlay: Comparison of IR absorption bands of CO on bare (8) and oxygen predosed 5 MLE titania/Au (111) held at 200 K

In the previous studies it was shown that CO, as well as NO, coadsorbed with atomic oxygen on a number of substrates exhibit an increase of the vibrational frequency caused by molecular-oxygen interaction. An observed blue shift of CO vibrational mode in this case (see Fig. 2, inlay) can be viewed as an evidence that oxygen is accommodated by the surface prior to interaction with preadsorbed CO. Accommodation by the surface results in the formation of some anionic species at the oxide/Au interface which cause an observed increase of the CO intramolecular vibrational frequency and which are active for CO oxidation. In addition, coexistence of a negatively charged species on the surface in the vicinity of a polar molecules like CO and NO results in an effective increase of their dynamical dipole moment [9]. The latter one leads to the enhanced infrared light absorption which results in the increase of IR line intensity. In relation to this, the observed increase of the CO IR intensity for the reversed order of adsorption (see Fig. 2, curves 8 and 9) is a further evidence of appearance of anionic species upon oxygen adsorption on titania/Au. Thus oxygen and carbon monoxide adsorption on titania/Au (111) results in the change of the electronic state of the interface in addition to the change of the electronic state of both titania and Au when they form the interface. Such a complex transformation of the electronic state of the system resulting from titania/Au (111) formation and subsequent adsorption of oxygen and carbon monoxide leads to an adsorption and catalytic behavior of the interface which are dramatically different from those exhibited by titania and Au on their own. Also taking into account a rather high CO IR intensity decay rate (see Fig. 2) one can conclude that the titania/Au perimeter interface is a place for efficient carbon monoxide and oxygen chemical interaction.

Above consideration relates to saturation coverage of CO which can be achieved at an exposure of 100 L. Similar CO IR intensity degradation was also observed for lower CO initial coverage. Moreover, it was found that the rate of the CO IR line intensity decay is higher at lower initial CO coverage. In order to find the corresponding dependence the four types of CO/oxide/Au systems differing only by the initial CO exposure have been investigated measuring the CO IR intensity versus oxygen exposure time. In this case the scan area was restricted to 2070 – 2150 cm^{-1} with the increase of the number of scans to increase signal to noise ratio. The corresponding plots for titania 5 MLE and different CO initial exposures are shown in Fig. 3 (curves 1 to 4). It is seen that the lower the CO initial coverage the higher is its decay rate upon oxygen exposure. Assuming that this decay is due to CO_2 formation and its subsequent desorption the initial slopes of the corresponding curves (slope angles (α) of the initial part of the curves (see Fig. 3) are proportional to the $CO+O_2$ interaction efficiency (σ), σ = tg (α). This value plotted versus the CO initial exposure is shown in Fig. 3 (inlay). It is seen that at lower concentration the CO molecules more efficiently interact with oxygen: The reaction rate varies by a factor of two or even higher depending on the CO initial coverage. Possible explanation of this might be the fact that the reactant species may need a free space on the surface (specifically at the oxide/Au perimeter interface) for the reaction to occur.

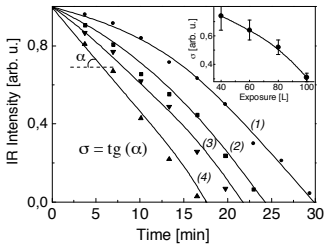

Figure 3: Dependence of the CO IR intensity line on the oxygen exposure time for different initial CO exposures of titania/Au (111) system (L): 1-100; 2-80; 3-60; 4-40. Inlay: Dependence of the value of σ characterizing the CO surface concentration decay rate upon the initial CO exposure

It may turn out that this space is necessary because the reaction between species proceeds via the mobile precursor. At higher CO coverage when the concentration of free sites is lower, the mobility of the species is suppressed due to site blocking effect so that the reaction rate decreases, and vice versa. As some CO adsorption sites become unoccupied due to CO_2 formation and desorption, the

reaction rate increases as follows from the corresponding curves shown in Fig. 3.

Results with titania formed by oxidation in an isotopically labeled oxygen ($^{18}O_2$) ambient corroborate above conclusion of the essential role of the titania surface in CO oxidation. Reduced (TiO_x, x<2) and totally oxidized TiO_2 films were prepared by the technique mentioned above. The formed Au/TiO_2 and Au/TiO_x systems after cooling down to 80K were exposed to carbon monoxide at an exposure of 100 L. Afterwards molecular oxygen $^{16}O_2$ was supplied into the UHV chamber to a partial pressure of 10^{-6} Torr. The thermal desorption spectra of particles recorded by the quadrupole mass analyzer at a temperature sweep rate of 2 K/s, tuned to the mass of 46 m/z ($C^{16}O^{18}O$), are shown in Fig. 4. Appearance of this desorption peak is a clear indication of direct participation of oxygen of titania in catalytic oxidation of CO over Au/TiO_2 and Au/TiO_x. Notably higher intensity of the desorption peak in the latter case is an indication of higher efficiency of reduced titania film in CO oxidation, despite lower oxygen concentration compared to fully oxidized titanium oxide.

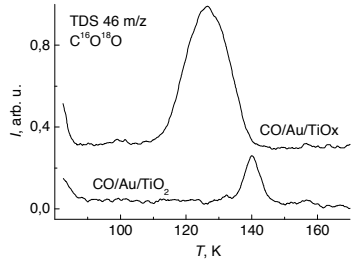

Figure 4: Thermal desorption spectra of isotopically labeled carbon dioxide specie ($C^{16}O^{18}O$) formed over Au/TiO_2 and Au/TiO_x (x<2).

In this sense one should attribute the main effect of CO oxidation not to the absolute concentration of available oxygen atoms but mainly to their specific electronic state in the oxide as well as at the metal/oxide perimeter interface. Repeated cycles of the above adsorption-desorption process of oxygen and carbon mono- and dioxide does not change the Ti 2p photoelectron line both for the reduced and totally oxidized titania (see Fig. 1), whereas one should expect further reduction because of the oxygen loss due to $C^{18}O^{16}O$ formation. Such stability of the stoichiometry of the titania during catalytic CO oxidation can be explained assuming oxygen exchange between the gas phase and titania, maintaining oxygen concentration of the oxide at an initial level. Higher efficiency of the oxidation process for the reduced titania film indicates that higher delocalization and lower bonding energy of oxygen of oxide is a key factor governing the catalytic effect.

4 CONCLUSIONS

Reflection absorption infrared spectroscopy in combination with other surface sensitive techniques of electron and ion spectroscopy (XPS, AES, LEED, LEIS, TDS) was used to study catalytic CO oxidation effect on the model direct and inverse Au/titania supported catalysts in ultra-high vacuum condition. It was found that in both cases the metal/oxide perimeter interface is a key factor for adsorption and CO oxidation. Efficiency of the effect is higher for lower CO concentration on the surface, pointing at a crucial role of the free sites for catalytic CO oxidation. For technological perspective the results obtained offer the following steps to gain the performance of the Au/TiO_2 catalysts: 1) to produce smaller gold particles to increase the Au/TiO_2 perimeter interface length; 2) to supply the reaction $CO+O_2$ mixture to the catalyst at lower pressure to enhance the oxidation rate.

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