Surface Science 606 (2012) 1581–1585

Contents lists available at SciVerse ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Influence of Au and TiO_2 structures on hydrogen dissociation over TiO_2/Au(100)

I. Nakamura, H. Mantoku, T. Furukawa, A. Takahashi, T. Fujitani *

Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8569, Japan

ARTICLE INFO

Article history:
Received 20 February 2012
Accepted 18 June 2012
Available online 14 July 2012

Keywords:
Au catalyst
Ti oxides
Structure dependence
Hydrogen dissociation
Perimeter interface

ABSTRACT

We performed H_2–D_2 exchange reactions over TiO_x/Au(100) and compared the observed reaction kinetics with those reported for TiO_x/Au(111) in order to clarify the influence of the Au and TiO_2 structures on dissociation of H_2 molecules. Low energy electron diffraction observations showed that the TiO_2 produced on Au(100) was disordered, in contrast to the comparatively ordered TiO_2 structure formed on Au(111). The activation energies and the turnover frequencies for HD formation over TiO_2/Au(100) agreed well with those for TiO_2/Au(111), clearly indicating that the hydrogen dissociation sites created over TiO_2/Au(100) were the perimeter interface between stoichiometric TiO_2 and Au, as was previously concluded for TiO_2/Au(111). We concluded that the creation of active sites for hydrogen dissociation was independent of the Au and TiO_2 structures consisting perimeter interface, and that local bonds that formed between Au and O atoms of stoichiometric TiO_2 were essential for the creation of active sites.

1. Introduction

Au nanoparticles supported on metal oxides are known to exhibit high catalytic activity and excellent selectivity for various oxidation reactions such as CO oxidation, hydrocarbon oxidation, and propylene epoxidation [1]. Numerous investigations have been carried out to elucidate the source of the nanoparticles' high catalytic activity for CO oxidation, and different types of catalytically active sites, such as low-coordinated Au atoms and negatively charged Au particles, have been proposed [1–11]. Recently, some studies have reported that the Au–TiO_2 interface is the active site for oxidation reactions. Yates et al. reported that CO oxidation occurs at a perimeter zone on an Au/TiO_2 catalyst [12]. We measured the kinetics of CO oxidation and H_2–D_2 exchange reactions using Au/TiO_2(110) [13,14] and TiO_x/Au(111) [15] surfaces, and demonstrated that the perimeter interface between Au and TiO_2 was the active site for both CO oxidation at low temperature and dissociation of H_2 molecules. At present, the perimeter interface between Au and metal oxide seems to be the most likely active site for Au nanoparticle catalysis.

The structure of the Au–TiO_2 interface has been examined using high-resolution transmission electron microscopy [16], which has revealed that Au particles are supported on anatase TiO_2 with the Au(111) plane parallel to the TiO_2(112) plane. In contrast, for rutile TiO_2, Au particles are supported with the Au(111) plane parallel to the TiO_2(110) plane. Furthermore, the interface structure has been investigated using an Au/TiO_2(110) model surface [17]; three kinds of Au planes parallel to the TiO_2(110) surface were observed for deposited Au nanoparticles. The structures of interfaces between Au and other oxides such as Fe_2O_3, Co_3O_4, and NiO have also been investigated [18]. Thus, the structures of the perimeter interfaces between Au and oxide supports have become apparent, but whether these structures affect the Au nanoparticles' catalytic activity remains unknown. The morphologies of Au nanoparticles supported on CeO_2 during CO oxidation have been recently studied by means of in situ environmental transmission electron microscopy [19]. In that study, the morphology of the Au nanoparticles changed from the form of a stable polyhedron enclosed by the major (111) and (100) facets to spherical in the presence of O_2, and the authors concluded that this change in particle morphology correlated well with the catalytic activity of Au nanoparticles supported on CeO_2. However, these results were still insufficient to explain the relationship between changes in morphology and catalytic activity. To clarify the relationship between nanoparticle structure and catalytic activity, reaction kinetics must be compared among uniform catalyst surfaces with different structures of Au or metal oxide. In this study, we carried out H_2–D_2 exchange over TiO_x/Au(100), and we clarified the influence of the Au crystal structure and Ti oxide structure on the creation of active sites for hydrogen dissociation by comparing the reaction kinetics over TiO_x/Au(100) with those over TiO_x/Au(111) [15].

2. Experimental methods

X-ray photoelectron spectroscopy (XPS, VG ESCALAB 220-i), polarization modulation infrared reflection absorption spectroscopy (PM-IRAS, Mattson RS/2), low-energy electron diffraction (LEED, OCI LPS075/300), and H_2–D_2 exchange reaction experiments were performed in an ultrahigh vacuum apparatus described in detail elsewhere [15]. Briefly,

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* Corresponding author at: Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan. Tel.: +81 29 861 8377; fax: +81 29 861 8374.
E-mail address: t-fujitani@aist.go.jp (T. Fujitani).

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doi:10.1016/j.susc.2012.06.012

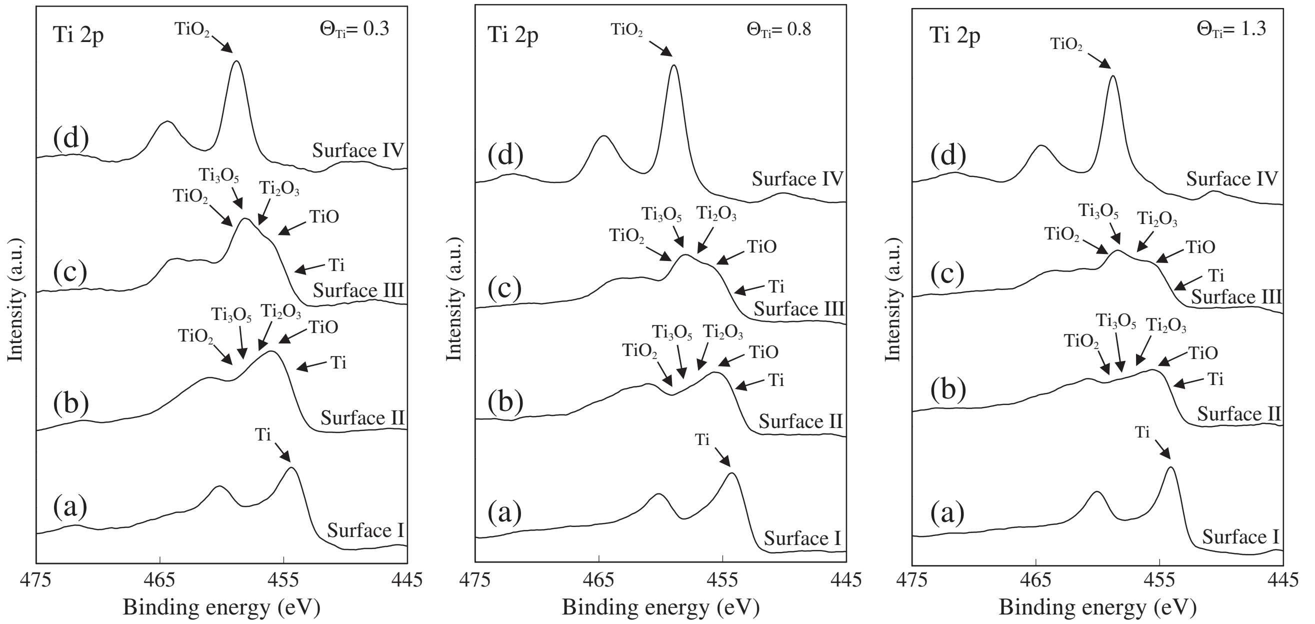

Fig. 1. Ti 2p XP spectra before (a) and after (b–d) oxidation of Ti-deposited Au(100) surfaces at $\Theta_{Ti} = 0.3$, 0.8, and 1.3. Oxidation conditions: (b) 7 L O_2 exposure at 500 K; (c) 35 L O_2 exposure at 500 K; (d) 300–700 K in 3×10^{-7} Torr O_2, then 200 L O_2 exposure at 700 K, and then cooling to 400 K in O_2.

the apparatus was composed of four chambers: a load-lock chamber; a preparation chamber equipped with an ion gun for Ar^+ sputtering and an evaporator for Ti deposition; an analysis chamber containing probes for XPS, LEED, and quadrupole mass spectroscopy; and a reaction chamber equipped with an infrared spectrometer. XP spectra were measured with Mg Kα radiation. LEED patterns were obtained with a gun emission current of about 2 μA at energies of 50 eV. PM-IRA spectra were recorded at a resolution of 4 cm^{-1} with 500 scans. Noncontact atomic force microscopy (NC-AFM, Veeco CP-II) images were obtained at room temperature under atmospheric pressure with a silicon cantilever with a resonance frequency of 273–326 kHz and a spring constant of 20–80 N/m.

An Au(100) single-crystal disk (8-mm diameter, 1-mm thickness, 99.999% purity) polished on one side only was used in this study. The crystal orientation was accurate to within 1°, and the surface roughness was <0.03 μm on the polished side. The sample was mounted using two 0.25-mm-diameter tungsten wires for resistive heating. The temperature of the sample was measured by a chromel–alumel thermocouple spot-welded to the back of the crystal. The polished Au surface was cleaned by Ar^+ sputtering and annealed at 900 K for 10 min under vacuum. The cleanliness of the sample surface was verified by XPS.

Ti was deposited at 300 K onto the clean Au(100) surface by evaporation from a Ti rod (1.5-mm diameter, 99.9% purity) by means of a commercial evaporator (AVC AEV-1). After Ti deposition, the surface was annealed at 500–700 K in O_2 (7–200 L; 1 L = 10^{-6} Torr s). The coverages (Θ) of Ti and O were determined from the Ti $2p_{3/2}$/Au $4f_{7/2}$ and O 1s/Au $4f_{7/2}$ peak area ratios, respectively, using the O 1s/Au $4f_{7/2}$ peak area ratio yielded from the saturation oxygen coverage obtained by exposure of the Au(111) surface to ozone at 323 K [20], the ratio of Au surface atom densities between Au(111) and Au(100), and the sensitivity factors for O 1s and Ti $2p_{3/2}$: Θ = 1 corresponded to an Au(100) surface atom density of 1.21×10^{15} atoms/cm^2.

The H_2–D_2 exchange reaction was performed at 350–475 K with a mixture of 6 Torr H_2 and 6 Torr D_2 in the reaction chamber. The reaction gases were introduced into the analysis chamber at constant pressure of 4×10^{-9} Torr through a leak valve from the reaction chamber, and the pressures of H_2, D_2, and HD were measured in real time during reaction by monitoring mass numbers 2, 4, and 3, respectively, using quadrupole mass spectrometry. Then, the concentrations of H_2, D_2, and HD were calculated from the pressure of each gas using sensitivity factors of 0.44, 0.35, and 0.42, respectively. We obtained the initial formation rates of HD from the initial slopes of plots of HD molecules formed *vs.* reaction time. We have confirmed that the H_2–D_2 exchange reaction depends on the first-order rate law from the following equation:

$$\ln[HD_e/(HD_e - HD_t)] = (k_1/2 + k_2)t \equiv kt,$$

where HD_e and HD_t are the number of HD moles at equilibrium and time, t (s), and k_1 and k_2 are the rate constants for the forward and the reverse reaction of H_2–D_2 exchange. The estimated rate constant (k) was regarded as an apparent rate constant because it consists of k_1 and k_2. CO exposure experiments were carried out at 10 Torr and at a sample temperature of 273 K.

Table 1
Atomic ratios for Ti oxides on TiO_x/Au(100) surfaces under different Ti coverage and oxidation conditions.

Θ_{Ti}	Surface	Temp. (K)	O_2 exposure (L)	O/Ti ratio	Atomic ratio (%)				
					Ti	TiO	Ti_2O_3	Ti_3O_5	TiO_2
0.3	I	300	0	0	100	0	0	0	0
	II	500	7	1.16	11	49	17	13	10
	II	500	7	1.16	11	49	17	13	10
	III	500	35	1.57	3	10	37	26	24
	IV	700	200	2.03	0	0	0	0	100
0.8	I	300	0	0	100	0	0	0	0
	II	500	7	1.22	9	46	19	15	11
	III	500	35	1.59	2	11	34	28	25
	IV	700	200	2.01	0	0	0	0	100
1.3	I	300	0	0	100	0	0	0	0
	II	500	7	1.27	7	43	21	17	12
	III	500	35	1.59	2	10	36	27	25
	IV	700	200	2.02	0	0	0	0	100

3. Results and discussion

3.1. Ti oxidation on an Au(100) substrate

The oxidation of Ti over Au(111) has been examined by means of XPS and scanning tunnelling microscopy, demonstrating that Ti oxides with different oxidation states are formed depending on O_2 exposure and annealing temperature [15,21,22]. However, the influence of the Au