



Structurally defined SnO₂ substrates, nanostructured Au/SnO₂ interfaces, and their distinctive behavior in benzene and methanol oxidation



Wu Jiang^a, Yijun Pang^a, Lingli Gu^a, Yao Yao^a, Qin Su^a, Weijie Ji^{a,*}, Chak-Tong Au^b

^a Key Laboratory of Mesoscopic Chemistry, MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

^b Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong

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ABSTRACT

SnO₂ crystallites of regular morphology [rhombohedral dodecahedra (*r.d*-SnO₂), elongated octahedra (*e.o*-SnO₂), and octahedra (*o*-SnO₂)], together with low-dimensional rod-clusters (*r.c*-SnO₂) and plates (*p*-SnO₂), were controllably synthesized. Based on (HR)TEM, SEM, and SEAD characterizations, the SnO₂ facets were identified as {111}, {110}, and {101}. Au nanoparticles of 2.2–2.4 nm with narrow particle size deviation (±0.6–0.7 nm) were monodispersed on the SnO₂ substrates. Au/SnO₂ interfacial structures with structurally defined oxide substrate and comparable Au particle size and morphology were accomplished. The systems achieved made it possible to study the distinct interfaces in catalytic benzene combustion and methanol oxidation. H₂ TPR, O₂ TPD, and XPS characterizations revealed that the specific Au–SnO₂ interaction has a strong effect on the reactivity of surface and bulk lattice oxygen, the oxidation state of surface Sn atoms, and the sort and relative concentration of surface oxygen adspecies. The Au/SnO₂{110} and Au/SnO₂{101} interfaces favor selective oxidation of methanol, whereas Au/SnO₂{111} enhances total oxidation of both benzene and methanol. These interfacial structures were rather stable in both reactions. Through structural analysis of SnO₂ facets, the evolution of active oxygen species and the possible reaction pathways of benzene combustion have been proposed. The involved reaction pathways are notably influenced by the specific Au/SnO₂ interfacial structure and the nature of the reactant molecule, as well as the reaction temperature. The current study gained insight into the significance of specific Au/SnO₂ facets determining the catalytic activity of benzene and methanol oxidation.

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1. Introduction

In recent years, nanostructures with specific morphologies and facets have been fabricated, which demonstrate different behavior in various reactions [1–7]. Without controllable synthesis, oxide support is generally in a polycrystalline state, dispersion of metal particles on the support surface is highly random, and the observed metal–support interaction is an average of various metal–oxide interfacial effects. Because of this complexity at the metal/support interface, understanding inherent metal–support interactions is rather challenging.

This development in the synthesis of nanomaterials has provided opportunities to gain deep insight into the metal–support interaction. Controllable synthesis of nanocrystals with structurally defined facets is considered an important prerequisite for better understanding of catalytic chemistry over different surfaces and/or interfaces [8–11]. Oxide nanoparticles (NPs) with certain

dimensions and morphology can be obtained through a controlled synthetic approach. The oxide facet structure can be identified by means of high-resolution transmission electron microscopy (HRTEM). Therefore, different interfacial structures can be assembled upon deposition of precious metal particles onto regularly shaped metal oxide substrates. This is very helpful in studying the actual metal–support interaction as well as the related catalytic mechanism.

Tin dioxide (SnO₂) is an important *n*-type semiconductor with a wide band gap. Because of its unique physical and chemical properties, it has been extensively studied for various applications, including semiconductor sensors [12], batteries [13], and catalysts [14–23]. It was found that the performance of SnO₂ greatly depends on its morphology and facet structure, and the observation motivated extensive studies on synthesis and application of a variety of morphologically distinctive SnO₂ nanostructures [24–27], especially those reported by Zheng's group [25–27].

Early examples of gold catalysis were made in the 1970 s. Bond and Sermon [28], as well as Parravano and co-workers [29,30], reported that olefin hydrogenation, hydrogen/carbon monoxide

* Corresponding author. Fax: +86 25 83317761.

E-mail address: jwjj@nju.edu.cn (W. Ji).

oxidation, and NO reduction by H₂ could be catalyzed by small Au particles supported on SiO₂, MgO, and Al₂O₃, although their activities were not high. There were two breakthroughs in Au catalysis [31]: in 1985, Hutchings observed that nanosized Au particles were the most active for vapor phase hydrochlorination of acetylene [32]; and in 1987, Haruta et al. reported the remarkably high activity of supported Au catalysts for low-temperature CO oxidation [33]. Since then, Au catalysts of different types have been continuously developed for various reactions [34–38]. It is generally recognized that not only the Au NPs but also the generated Au-oxide interfaces and the involved Au-oxide interaction are critical to catalyst activity [39–48]. Recently, Kung and co-workers [49] reviewed the Au-metal oxide support interface as an active site for CO oxidation, water gas shift reaction, and selective oxidation of propane. Although many studies have focused on the role of the particle size and electron density of Au clusters, there is a tendency to shift attention to the function of the Au-oxide boundary/interface. Carley et al. [50] recently investigated CO oxidation on Au/Fe₂O₃ and found that oxygen molecules dissociatively co-adsorbed with CO on the boundary Au atoms where oxidation underwent. It is technically challenging, however, to establish clear interface structure for in-depth understanding of the effect of Au-oxide interfacial structure on target reactions. So far, there are limited examples of Au/SnO₂ systems reported [51–53], most of the SnO₂ substrates were polycrystallites, and the metal-oxide interfaces were not structurally controlled.

In recent years, catalytic removal of VOCs over metal oxides and metal oxide-supported metals has gained great interest. Among various reports [54–62], Taylor's [56–59] and Liotta's [60–62] groups made significant progresses in this field. In this study, morphologically uniform rhombic dodecahedra, elongated octahedra, and SnO₂ octahedra were first synthesized, and then Au deposition with a narrow particle size distribution on these substrates was achieved to obtain unique Au/SnO₂ interfaces. The catalytic behavior of the resulting interfaces in benzene combustion/methanol oxidation was compared in detail. Low-dimensional SnO₂ rod-clusters and SnO₂ plates were also prepared for comparison. Insights into the significance of specific Au/SnO₂ interfaces determining the catalytic activity of two target reactions were gained.

2. Experimental

2.1. Catalyst preparation

2.1.1. Reagents

SnCl₄·5H₂O, aqueous tetramethylammonium hydroxide (TMAH; 25%), anhydrous alcohol (99.7%), ammonia solution (25–28%), HAuCl₄·4H₂O, SnSO₄, and NaF were purchased from Sino-pharm Chemical Regent Company Limited (Shanghai) and used as received without further purification.

2.1.2. Synthesis of SnO₂ rhombic dodecahedra (r.d-SnO₂)

Tetramethylammonium hydroxide solution [w(H₂O):w(TMAH) 25%, aq) = 55:25.11] was added dropwise to a conical flask containing 12 ml of aqueous solution of SnCl₄·5H₂O (1.4024 g) employing a constant pressure drop funnel. The mixture was continuously stirred for 6 h and then divided into two parts, transferred into a 60 ml Teflon-lined stainless steel autoclave, and subjected to hydrothermal treatment at 200 °C for 12 h. After the autoclave was cooled to room temperature (RT), the precipitate was collected via centrifugation and washed repeatedly with distilled water. The sample was dried at 80 °C for 12 h and calcined in air at 400 °C for 3 h (with a heating rate of 1 °C min⁻¹ from RT).

2.1.3. Synthesis of SnO₂ elongated octahedra (e.o-SnO₂) and octahedra (o-SnO₂)

Tetramethylammonium hydroxide solution [w(H₂O):w(TMAH) 25%, aq) = 43:24.82 and 40:30.65] was added dropwise, employing a constant-pressure-drop funnel, to a conical flask containing a 25 ml mixture of H₂O and ETOH (v:v = 12:13) in which 1.4024 g SnCl₄·5H₂O was dissolved, and the mixture was continuously stirred for 12 h. The following steps were the same as those employed in synthesis of r.d-SnO₂.

2.1.4. Synthesis of SnO₂ plates (p-SnO₂)

Tetramethylammonium hydroxide solution [w(H₂O):w(TMAH) 25%, aq) = 56.98:21.90] was added dropwise, employing a constant-pressure-drop funnel, to a conical flask containing 12 ml aqueous solution of SnSO₄ (1.074 g), and the mixture was continuously stirred for 5 h. The following steps were the same as those employed in synthesis of r.d-SnO₂.

2.1.5. Synthesis of SnO₂ rod-clusters (r.c-SnO₂)

SnCl₄·5H₂O, 1.050 g, and NaF, 0.12 g, were dissolved in 20 ml of H₂O and ETOH (v:v = 1:1) in a conical flask. A volume of 60 ml NaOH (1.280 g) ethanol-water solution [v(H₂O):v(ETOH) = 1:1] was added dropwise to the conical flask, and the mixture was continuously stirred for 4 h. The mixture was divided into two parts, transferred into a 60 ml Teflon-lined stainless steel autoclave, and subjected to hydrothermal treatment at 200 °C for 24 h. After the autoclave was cooled to RT, the precipitate was collected via centrifugation and washed repeatedly with 5 wt.% ammonia solution and distilled water. The following steps were the same as those employed in the synthesis of r.d-SnO₂.

2.1.6. Preparation of Au-loaded samples

A controlled deposition-precipitation process was employed to load Au species onto various SnO₂ substrates. A certain amount of SnO₂ was dispersed in distilled water, and then a HAuCl₄·4H₂O solution (0.0085 mol L⁻¹) was added slowly with a nominal Au loading of 2 wt.%. A diluted ammonium solution was added into the suspension to adjust the pH value to 9. After that, the mixture was put into a water bath, kept at 50 °C, and continuously stirred for 3 h. The product was collected by centrifugation and dried at RT overnight. The dried sample was further calcined at 250 °C for 2 h (with a heating rate of 1 °C min⁻¹ from RT). The Au content measured by ICP-AES is 1.7–1.8 wt.% for the five Au-loaded samples.

2.2. Materials characterization

X-ray diffraction (XRD) measurements were conducted on a Bruker D8 Advance X-ray diffractometer with Co K α radiation ($\lambda = 0.1790$ nm). Au content was measured using ICP-AES on a J-A1100 Versa Probe spectrometer.

TEM images were taken with a JEOL JEM-1010 microscope operated at 100 kV. HRTEM images and SAED were taken with a JEOL JEM-2010 microscope operated at 200 kV to determine the Au particle size distribution and exposed crystal facets of different SnO₂ substrates.

N₂ adsorption measurements were performed on a NOVA-2020 material physical structure determinator. Before measurement, samples were degassed at 300 °C for 4 h. BET surface areas were calculated based on a multipoint BET analysis of the nitrogen adsorption isotherms.

Hydrogen temperature-programmed reduction (H₂ TPR) was carried out using a U-shaped quartz reactor. The catalyst (100 mg) was first pretreated in a He stream (40 ml min⁻¹) at 120 °C for 2 h. After the temperature was lowered to RT, the sample was heated to 950 °C at a rate of 10 °C min⁻¹ in a 5% H₂-Ar flow

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