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Layered sphere-shaped TiO₂ capped with gold nanoparticles on structural defects and their catalysis of formaldehyde oxidation

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ABSTRACT

We describe here a one-step method for the synthesis of Au/TiO₂ nanosphere materials, which were formed by layered deposition of multiple anatase TiO₂ nanosheets. The Au nanoparticles were stabilized by structural defects in each TiO₂ nanosheet, including crystal steps and edges, thereby fixing the Au–TiO₂ perimeter interface. Reactant transfer occurred along the gaps between these TiO₂ nanosheet layers and in contact with catalytically active sites at the Au–TiO₂ interface. The doped Au induced the formation of oxygen vacancies in the Au–TiO₂ interface. Such vacancies are essential for generating active oxygen species (*O) on the TiO₂ surface and Ti³⁺ ions in bulk TiO₂. These ions can then form Ti³⁺–O[–]–Ti⁴⁺ species, which are known to enhance the catalytic activity of formaldehyde (HCHO) oxidation. These studies on structural and oxygen vacancy defects in Au/TiO₂ samples provide a theoretical foundation for the catalytic mechanism of HCHO oxidation on oxide-supported Au materials.

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Introduction

Although gold (Au) is chemically inert, Au nanoparticles supported on metal oxides exhibit high catalytic activity for various oxidation reactions, including carbon monoxide (CO) oxidation (Knudsen et al., 2010; Han et al., 2010; Jia et al., 2010), ethylene oxidation (Ma et al., 2010), and formaldehyde (HCHO) oxidation (Zhang et al., 2009; Ma et al., 2011). Several factors control the catalytic activity of Au nanoparticles on oxide supports, and the size of the Au nanoparticles has a significant effect on catalytic activity (Herzing et al., 2008; Okatsu et al., 2009; Ishida et al., 2010; Ma et al., 2013). Many

surface chemical reactions are catalyzed on Au nanoparticles 2–5 nm in diameter (Okatsu et al., 2009; Ishida et al., 2010; Ma et al., 2013). Other important factors include the nature of the metal oxide support (Abad et al., 2005; Su et al., 2008; Dobrosz-Gómez et al., 2008), and the charge transfer efficiency between the support and Au particles (Porta et al., 2002; Haruta, 2007). In recent reports, perimeter interface sites between Au nanoparticles and metal oxide supports have been regarded as reaction sites (Green et al., 2011; Widmann and Behm, 2011).

Crystalline titanium dioxide (TiO₂) is a good dispersant and catalytic promoter when used as a support in Au/TiO₂

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catalysts (Erjavec et al., 2013; Kim et al., 2013; Li et al., 2013; Wang et al., 2014; Liu et al., 2010; Zhang et al., 2010). TiO₂ crystallizes in three different phases: rutile, anatase, and brookite. Anatase TiO₂-supported Au catalysts boast the highest catalytic activity among the three crystal phases (Benjamin and Graeme, 2010; Li et al., 2008a,b; Pillai et al., 2007; Yang et al., 2008; Peng et al., 2008). The unique catalytic performance of Au/TiO₂ catalysts has been attributed to the Au–TiO₂ perimeter interface, which contains activating sites for reactants (Fujitani and Nakamura, 2011). These sites can be optimized by controlling the defect sites in anatase TiO₂. Crystal steps and edges are important defect features in TiO₂ surfaces (Derdour and Skliar, 2012) and are involved in several processes, including nucleation of Au particles and adsorption of molecules. The relatively low density of point defects, such as surface oxygen vacancies on TiO₂, which play an important role in catalytic oxidation (Strunk et al., 2010; Namai and Matsuoka, 2005), is also related to these perimeter sites (Fujitani and Nakamura, 2011). Both theoretical calculations and experimental results concerning the effects of oxygen vacancies in TiO₂ on catalytic reactions have been widely investigated. In contrast, the effects of the location of Au nanoparticles on the marked crystal steps of TiO₂ have not been adequately explored. Therefore, the development of a simple strategy that allows the synthesis of a Au/TiO₂ material with defects, including TiO₂ crystal steps and oxygen vacancies, would provide an excellent means of studying active sites and the reaction mechanisms of catalysis on such materials.

HCHO is emitted from common decorative materials and becomes a major indoor pollutant in airtight buildings. Studies have suggested that nasopharyngeal or nasal cancer can result from prolonged exposure to HCHO concentrations that exceed safe limits. Therefore, the exploration of catalysts that can eliminate HCHO at room temperature with no additional light and/or heat is of value. Research on the active sites in supported Au catalysts has primarily focused on CO oxidation. HCHO oxidation on supported Au catalysts may be a suitable model for learning the reaction mechanism and nature of active sites in such materials.

The synthesis and catalytic performance of yolk-shell spheres containing one or more noble metal nanoparticle core(s) and a mesoporous shell of oxides have been reported (Hampsey et al., 2005; Wang et al., 2011; Lee et al., 2011). Reactants pass through the mesopores of the shell to be activated by the noble metal nanoparticles. However, the metal nanoparticles in these systems are still tightly encapsulated by oxides, and not easily accessible to the reactants. Thus, reactants passing along the mesoporous shell may not come into sufficient contact with the encapsulated metal nanoparticles. Herein, we describe a simple one-step method to manipulate the hydrolysis of Ti-containing precursors in a nano-Au sol to obtain layered Au/TiO₂ nanospheres. Each layer consisted of a single anatase TiO₂ nanosheet, and Au nanoparticles about 6 nm in diameter were positioned at crystal steps or edges on the TiO₂ nanosheet. The structure differs significantly from that of conventional core-shell Au/TiO₂ nanospheres (Lee et al., 2011). The layered Au/TiO₂ nanospheres showed catalytic activity and stability for HCHO oxidation at room temperature. The crystal steps and edges

stabilized the Au nanoparticles to form a fixed Au–TiO₂ perimeter interface. The structural and electronic properties of this Au–TiO₂ interface were characterized. Oxygen vacancies resulted in the formation of active oxygen-rich species at the Au–TiO₂ interface and enhanced the catalytic efficiency of the system. The proposed catalytic mechanism for HCHO oxidation on Au/TiO₂ catalysts increases our understanding of molecular oxidation on supported Au catalysts.

1. Experimental section

1.1. Preparation of Au/TiO₂ nanosphere material

A suitable amount of PVP solution (2 wt.%) was added to an aqueous HAuCl₄ solution (0.39 mg Au/mL) under vigorous stirring. Then, a freshly prepared solution of NaBH₄ was slowly added dropwise into the mixture (molar ratio NaBH₄/Au = 4). A TiF₄ aqueous solution was added into the mixture afterwards and stirred at room temperature for 10 min, then transferred into a Teflon-lined stainless steel autoclave. Then the autoclave was sealed and heated at 180°C for 48 hr in an electric oven. Anatase TiO₂ nanocrystals were generated through a crystallization process as follows:

After completion of the reaction, the autoclave was taken out and cooled to room temperature. The product was washed with ultrapure water several times. Then the powder was recovered by centrifugation and dried at 70°C for 5 hr. Finally, the Au/TiO₂ sample was calcined at 300°C for 3 hr and designated as Au/TiO₂-300. The obtained Au/TiO₂ nanospheres were finally harvested and then kept carefully for further characterization and subsequent experiments. The Au/TiO₂ nanospheres calcined at 200 and 400°C were designated as Au-TiO₂-200 and Au/TiO₂-400.

1.2. Material characterization

Scanning electron microscopy (SEM) were taken using a Hitachi SU 8020 instrument. Studies on the buildup of nanosheet layers were conducted by atomic force microscopy (AFM, Nanoscope IIIa MultiMode, Digital Instruments, American). High-resolution transmission electron microscopy (HRTEM) observations were conducted with a JEOL 2100F instrument at the accelerating voltage of 200 kV. The specimens were prepared by ultrasonic dispersion in ethanol, evaporating a drop of the resultant suspension onto a copper grid previously covered with a thin carbon layer. The powder X-ray diffraction (XRD) pattern was recorded on an X'pert PRO equipment using Cu K α radiation ($\lambda = 0.15418$ nm). The data was collected in a 2θ range of 10–90° with a scanning step size of 0.02°. X-ray photoelectron spectroscopy (XPS) was conducted on a Kratos Axis Ultra DLD spectrometer with a monochromated Al-K α X-ray source ($h\nu = 1486.6$ eV), hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector (DLD). All binding energies were referenced to the position of the adventitious C 1s peak at 284.8 eV. Low temperature electron spin resonance (ESR) spectra were

recorded on a JES FA200 spectrometer. The catalyst (10 mg) was placed in a quartz ESR tube, which was evacuated for 2 hr and analyzed at 77 K. O_2 was introduced into the tube and kept for 1 hr. The tube was then evacuated for 2 hr to remove excess O_2 and analyzed at 77 K. Infrared (IR) spectra were recorded by a Nicolet 560 spectrometer equipped with an airtight chamber, whose base is composed of a horizontal Attenuated Total Refraction (ATR) accessory using a ZnSe crystal as the substrate, and scanned from 1300 to 3400 cm^{-1} . A small amount of catalyst was spread on the ZnSe substrate uniformly, and the gas mixture of 300 ppm HCHO/ N_2 passed through the airtight chamber for 10 min, then the gas mixture of 300 ppm HCHO/22% O_2 / N_2 passed at a flow rate of 10 mL/min. The *in situ* IR spectra were recorded by passing gas mixtures (300 ppm HCHO/22% O_2 / N_2) through the catalysts for 1 min.

1.3. Activity measurement of the catalyst for formaldehyde oxidation

The catalytic activity tests were carried out in a fixed-bed quartz reactor by passing a gas mixture of HCHO/ O_2 / N_2 = 300 ppm/22 vol%/balance at a total flow rate of 120 mL/min. The relative humidity of the reaction gas was 15%. 0.35 g catalyst (40–60 mesh) was loaded into the darkened reactor and the catalyst temperature was maintained at 30°C. The concentration of CO_2 resulting from formaldehyde oxidation was measured with a gas chromatograph equipped with a TCD detector connected to a Porapak-Q column. The conversion of formaldehyde over the catalysts was calculated on the basis of the CO_2 content of the effluent.

2. Results and discussion

2.1. Characterization of Au/TiO₂ materials

Fig. 1A–C shows scanning electron microscopy (SEM) micrographs of Au/TiO₂-300 samples. Perfect layered spheres with diameters ranging from 800 to 1500 nm were evenly distributed (Fig. 1A). More micrographs of Au/TiO₂-300 are provided in Appendix A Fig. S1. The resulting layered spheres were coated with staggered TiO₂ nanosheets containing crystal steps and edges. Au nanoparticles mainly having diameter of about 6 nm were located on the crystal steps and edges of TiO₂. The layered structure is similar to that of Rh particles in the interlayer space of layered silicates (Papp et al., 2004), Pd/layer silicates (Kun et al., 2005), and TiO₂/montmorillonite materials (Kun et al., 2006). The gap between TiO₂ nanosheet layers was beneficial for the transfer of reactants and products, and allowed them to come in contact with the Au nanoparticles (Fig. 1C). The lamellar structure characteristic of Au/TiO₂-300 spheres is discernible in the AFM micrograph shown in Fig. 1D. Scanning electron microscopy (SEM) micrographs of Au/TiO₂-200 and Au/TiO₂-400 are shown in Appendix A Fig. S2. The layered spherical structure of the above two samples is well ordered. The Au nanoparticles in Au/TiO₂-400 were a little larger than those in Au/TiO₂-200 and Au/TiO₂-300, due to the higher calcination temperature. A model showing the Au/TiO₂ layers is shown in Fig. 5A. The steps and edges of the TiO₂ nanosheets are well defined, and Au nanoparticles were preferentially located at these steps and edges. The resulting layered Au/TiO₂ structure

Fig. 1 – Scanning electron microscopy (SEM) (A, B and C) and atomic force microscopy (AFM) micrographs (D) of Au/TiO₂-300.

shows all the characteristics of an efficient configuration for catalysis.

The HRTEM micrographs of Au/TiO₂-300 shown in Fig. 2 and Appendix A Fig. S3 reveal that the original sheetlike shape of TiO₂ was maintained, which agrees with the SEM observations. Au nanoparticles (imaged as black dots) are evident as pseudospherical particles on the TiO₂ nanosheets with diameters about 6 nm, and are composed of hundreds to thousands of Au atoms. Fig. 2A shows a 6-nm Au particle in an epitaxial relationship with the TiO₂ substrate. The lattice distances of the Au are 0.23 and 0.20 nm, corresponding to the spacings of the (111) and the (002) planes, respectively. The interface between Au particles and the TiO₂ substrate is flat. The intensity profiles for the Au (111) lattice planes are parallel to the interface. The Au (111) planes are not clearly observed in Fig. 2C, but the Au (002) planes are tilted with respect to the interface. The angle between the Au (002) surface and the interface (Fig. 2C) is equal to the angle between the Au (002) and Au (111) surfaces (Fig. 2A). Thus, the interface of Au–TiO₂ is parallel to the Au(111) planes. One pair of fringes measuring 0.22 nm × 0.15 nm corresponds to the TiO₂(101) and TiO₂(110) planes. Fig. 2B shows a corresponding fast Fourier transform (FFT) pattern of Fig. 2A. The FFT image confirms that the TiO₂ nanosheets are composed of crystalline anatase TiO₂. This conclusion was corroborated by XRD studies. The diffractogram in Fig. 2D contains peaks at $2\theta = 25.3^\circ$, 37.8° , and 48.1° corresponding to the (101), (004), and (200) crystal planes of anatase TiO₂ (tetragonal, I₄/amd, JCPDS 21-1272), respectively, and indicating a pure anatase TiO₂ phase. The diffraction peak at 38.2° corresponds to the Au (111) plane (Lee et al., 2008), which overlaps slightly with

that of TiO₂ (004). The peak observed at 38.2° was barely detectable, indicating that the Au nanoparticles measuring less than 5 nm in diameter were uniformly dispersed (Avgouropoulos et al., 2008).

The N₂ physisorption results (Appendix A Fig. S4) show that all of the Au/TiO₂ catalysts exhibit type IV isotherms. The Barrett–Joyner–Halenda (BJH) pore size distributions of the Au/TiO₂ catalysts are shown in Appendix A Fig. S5. The most probable pore diameters of Au/TiO₂ catalysts are larger than 30 nm, which indicates that the pores do not exist in the TiO₂ nanosheet. However, the pore diameters matched the distance between the TiO₂ nanosheets. The physical structure parameters of Au/TiO₂ catalysts are compared in Table S1. The Brunauer–Emmett–Teller (BET) specific surface area of Au/TiO₂-300 is higher than that of Au/TiO₂-200 and Au/TiO₂-400.

The XPS of O (1s), Ti (2p) and Au (4f) in the Au/TiO₂-300 samples are shown in Fig. 3A. The oxidation state of Ti in the materials (Ti (2p_{3/2}), binding energy 458.6 eV; Ti (2p_{1/2}), binding energy 464.3 eV) was identical to that of Ti⁴⁺, as reported previously (Pillai et al., 2007; Jiang et al., 2012). The O (1s) line in TiO₂ was composed of two or three components. The presence of O²⁻ species is unequivocally evidenced by the clear peak at 529.8 eV in the O (1s) XPS spectrum. The addition of Au shifts the O²⁻ peak to a higher binding energy, (531.0 eV) and can be ascribed to a Ti–O bond at the Au–TiO₂ interface. The peak at 532.4 eV in the O (1s) XPS spectrum can be assigned to the ionization of oxygen species such as *O⁻ or OH⁻ that compensate for deficiencies in the surface of TiO₂ (Kruse and Chenakin, 2011). The amount of *O⁻ or OH⁻ on the Au/TiO₂ surface was 3.51%, which also corresponds to

Fig. 2 – High-resolution transmission electron microscopy (HRTEM) micrographs (A and C), and a representative X-ray diffraction (XRD) pattern of Au/TiO₂-300 (D); Fast fourier transformation (FFT) pattern of image Fig. 2A (B).

Fig. 3 – X-ray photoelectron spectra (XPS) spectra of Au/TiO₂-300, showing the three characteristic peaks of O, Ti and Au (A), and electron spin resonance (ESR) spectra measured at 77 K in a vacuum for Au/TiO₂-300 and Au/TiO₂-300 with adsorbed atmospheric oxygen (B).

the deficiency content, and the number of surface oxygen vacancies (Vo) (Kim et al., 2008; Petrik and Kimmel, 2011). The XPS spectra of O (1s), Ti (2p) and Au (4f) in the Au/TiO₂-200 and Au/TiO₂-400 samples are shown in Appendix A Fig. S6. The *O⁻ species are also detected in the above two samples as seen by the obvious peak at 532.4 eV. There seems to be no obvious difference between Au/TiO₂-200, Au/TiO₂-400 and Au/TiO₂-300 XPS spectra.

Typical Au (4f_{7/2}) binding energies for Au⁰ are near 83.8 eV (Somodi et al., 2008). In our experiments, the Au (4f) binding energy was 83.3 eV. This negative shift in binding energy is due to an electron transfer from Vo to Au (Wörz and Heiz, 2005). In this process, Vo is a donor defect site that converts to Vo⁺ after an electron is transferred to Au. The electron and oxygen molecule easily adsorb at Vo sites to form oxygen species such as *O₂⁻. The formation rate of *O₂⁻ was directly coupled to the consumption rate of Vo.

*O₂⁻ species are easily converted to *O₂²⁻ by *O₂⁻ + e⁻ → *O₂²⁻. When oxygen gas was adsorbed at Vo sites, the O–O bond weakened to facilitate the dissociation of *O₂²⁻ to *O⁻. *O₂⁻ species may have been directly converted to *O⁻ by *O₂⁻ + Vo⁺ → *O⁻. *O⁻ species are thought to behave as active oxygen species in catalytic oxidation reactions.

The existence of Vo, due to the loss of one oxygen atom, is hypothesized to generate Ti³⁺ ions. Low temperature ESR spectra, shown in Fig. 3B, were collected to test for the existence of Ti³⁺ and active oxygen species. Au/TiO₂-300 yielded an ESR signal at g = 1.991, which was attributed to Ti³⁺ in the anatase lattice. Other observed g-values, 1.967 and 1.985, have been assigned to paramagnetic Ti³⁺ (Dimitrijevic et al., 2011; D'Arienzo et al., 2011). Surface Ti³⁺ would tend to adsorb atmospheric oxygen, which would then be reduced to O₂⁻, producing an ESR signal at g = 2.02 (Anpo et al., 1999; Zuo et al., 2010). However, we observed that Ti³⁺ adsorbed atmospheric oxygen to form O⁻, producing an enhanced ESR signal at g = 1.991. The absence of a peak at g = 2.02 in Fig. 3B indicates that the Ti³⁺ was present in the bulk of the sample (Zuo et al., 2010). This conclusion is supported by surface XPS spectra of the Au/TiO₂ samples, which contained no Ti³⁺ peaks. Since surface Ti³⁺ would be easily oxidized to Ti⁴⁺, Ti³⁺ in the bulk would be more stable and more capable of forming *O⁻ species. Therefore, the introduction of Ti³⁺ accounts for the observed enhancement in catalytic activity (Zuo et al., 2010). The layered Au/TiO₂ nanosphere rich in bulk Ti³⁺ would be an effective catalyst for oxidation reactions.

2.2. Room-temperature activity of formaldehyde oxidation

An initial HCHO concentration of 300 ppm was used to analyze the catalytic activity of the Au/TiO₂ samples at 30°C.

Fig. 4 – Reaction tests at 30°C for formaldehyde oxidation with time-on-stream over Au/TiO₂ (A). In situ Infrared (IR) spectra of formaldehyde adsorption and oxidation on the Au/TiO₂-300 for increasing time-on-stream (B).

Anatase TiO₂ prepared with a hydrothermal method without Au loading did not oxidize HCHO under the same reaction conditions. This indicated that the gold dopant is essential for the obtained catalytic activity in formaldehyde oxidation. Because of the highly dispersed gold nanoparticles, the CO₂ yield over the Au/TiO₂ nanosphere catalyst calcined at 300°C reached 6.38%, which is higher than the CO₂ yields obtained over Au/TiO₂ calcined at 400°C. The catalysts were inherently stable, as evidenced by the constant activity as a function of reaction time (Fig. 4A). HCHO cannot be converted to CO₂ over Au/TiO₂ catalysts prepared by impregnation methods at 20°C (Zhang and He, 2007), and Fe₂O₃- and CeO₂-supported Au catalysts can generally decompose HCHO into CO₂ only at temperatures at or above 60°C (Shen et al., 2008; Li et al., 2008a, b). Thus, the catalytic activity of the layered Au/TiO₂-300 nanospheres was higher than that reported in previous studies and is indicative of the structural benefits of Au/TiO₂ for HCHO oxidation.

2.3. Reaction mechanism of formaldehyde oxidation

Fig. 4B shows an in situ infrared spectrum of surface species on layered Au/TiO₂-300 at 30°C in a flow of 300 ppm HCHO/22% O₂/N₂. Several absorption peaks are evident between 1350 and 1710 cm⁻¹ and between 2250 and 3350 cm⁻¹. The band at 2845 cm⁻¹ was assigned to the methylene (CH₂) asymmetric stretch of HCHO. The bands at 1562, 1370, 1700, and 2916 cm⁻¹ were ascribed to $\nu_{as}(\text{COO}^-)$, $\nu_s(\text{COO}^-)$, $\nu_s(\text{CO})$, and the C–H stretch, respectively, of bidentate formate (Ma et al., 2011; Busca et al., 1987). The bands at 1460 and 1395 cm⁻¹ were attributed to $\delta(\text{CH}_2)$ and $\nu(\text{OCO})$ in dioxymethylene (DOM), respectively (Chen et al., 2014). The above results indicate that HCHO was quickly oxidized to formate and dioxymethylene by surface oxygen species. In addition, monodentate carbonate (1513 cm⁻¹) and hydrocarbonate species (1628 cm⁻¹) were also detected. One may reasonably assume that subpopulations of formate species were oxidized to hydrocarbonate and carbonate species. The bands appearing at 2360 and

2326 cm⁻¹ were ascribed to the asymmetric stretch of CO₂ adsorbed on the catalyst surface. Taken together, these data indicate that HCHO adsorbed on the catalyst surface was quickly oxidized to formate, and further oxidized to carbonate or hydrocarbonate before decomposing into CO₂ and H₂O.

Based on the above structural and electronic analyses of the obtained Au/TiO₂, as well as the observed catalysis in HCHO oxidation, we propose the following reaction mechanism. (1) The Au dopant facilitates the formation of Vo at the Au–TiO₂ interface, where Vo accepts an electron and an oxygen molecule from the gas phase to generate the active oxygen species *O⁻ on an oxygen vacancy (Fig. 5B). (2) HCHO adsorbed on the Au/TiO₂ surface is oxidized by *O⁻ to form CO₂ and H₂O (Fig. 5C–E). (3) The desorption of CO₂ and H₂O repairs the oxygen vacancy and restores the surface to its initial composition (Fig. 5F). In contrast to reported oxidation mechanisms on supported Au catalysts, which identify Au⁰ or Au^{δ+} as the active phase (Porta et al., 2002; Haruta, 2007), we propose that negatively charged Au functions as the active phase. Our results are consistent with those of Liu (Zhu et al., 2012), in which negatively charged Au was thought to be the active component in the visible-light photocatalytic degradation of Rhodamine B in aqueous solution. The existence of oxygen vacancies at the Au–TiO₂ interface results in the generation of Ti³⁺ in the bulk of the particle, which can be described as Ti³⁺–Vo–Ti⁴⁺ (Fig. 5B). Since *O⁻ is generated on Vo, the real species is Ti³⁺–O⁻–Ti⁴⁺ (Fig. 5C). Previous results also demonstrated that Au nanoparticles dispersed on a reducible oxide support are better catalysts than those supported on non-reducible supports. This effect is due to the ability of Ti³⁺ to efficiently form an active oxygen-rich Au–TiO₂ interface (Weiher et al., 2007). Oxygen vacancy defects reportedly stabilize Au monomers and Au trimers, but larger Au clusters cannot be sufficiently stabilized (Matthey et al., 2007). In the Au/TiO₂ obtained in this study, the Au cluster nanoparticles were stabilized by structural defects in which the crystal steps and edges in the anatase TiO₂ crystal nanosheets fixed the Au–TiO₂ perimeter

Fig. 5 – Proposed morphology model (A) and ball and stick models (B–F) of Au/TiO₂ catalysts for HCHO oxidation. Initially, electrons migrate to the surface Vo, which is generated from the loss of one surface oxygen atom and results in an bulk Ti³⁺ ion. The oxygen molecules from the atmosphere attach to the Vo (B). The oxygen molecules adsorb electrons (O₂[−]), and then decompose to O[−], which fills the Vo site (C). The C–H bond of the adsorbed HCHO breaks and the carbon site links to the O[−]. In this step, formate species are generated (D). The C–H bond of the adsorbed formate species also breaks. After the consumption of O[−], carbonate species are generated (E). In the final step, the adsorbed carbonate species decompose to CO₂ and H₂O and restore the surface to its initial composition (F). (yellow ball: gold atom; light-gray ball: titanium atom; red ball: oxygen atom; dark-gray ball: carbon atom; white ball: hydrogen atom). HCHO: formaldehyde.

interface, resulting in the stable catalytic oxidation of HCHO (Fig. 5A).

3. Conclusions

A one-step method to synthesize Au/TiO₂ nanospheres was developed in which staggered TiO₂ nanosheets were covered by other TiO₂ nanosheets. Au nanoparticles of about 6 nm in diameter were located on the crystal steps and edges of the TiO₂ nanosheets, and these structural defects stabilized the Au nanoparticles and fixed the Au–TiO₂ perimeter interface. The doped Au is essential for the generation of oxygen vacancies at the Au–TiO₂ perimeter interface. Gas phase oxygen was absorbed into these vacancies to form active oxygen species that reacted with HCHO to generate CO₂ and H₂O. The enhanced catalytic performance of Au/TiO₂ for the

oxidation of HCHO was explained in terms of the structural and electronic properties of the nanospheres themselves.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2015.12.004>.

REFERENCES

- Abad, A., ConcepciOn, P., Corma, A., Garcia, H., 2005. A collaborative effect between gold and a support induces the selective oxidation of alcohols. *Angew. Chem. Int. Ed.* 44 (26), 4066–4069.
- Anpo, M., Che, M., Fubini, B., Garrone, E., Giamello, E., Paganini, M.C., 1999. Generation of superoxide ions at oxide surfaces. *Top. Catal.* 8 (3–4), 189–198.
- Avgouropoulos, G., Manzoli, M., Boccuzzi, F., Tabakova, T., Papavasiliou, J., Ioannides, T., Idakiev, V., 2008. Catalytic performance and characterization of Au/doped-ceria catalysts for the preferential CO oxidation reaction. *J. Catal.* 256 (2), 237–247.
- Benjamin, J.M., Graeme, W.W., 2010. Intrinsic n-type defect formation in TiO₂: a comparison of rutile and anatase from GGA+U calculations. *J. Phys. Chem. C* 114 (5), 2321–2328.
- Busca, G., Lamotte, J., Lavalley, J., Lorenzelli, V., 1987. FT-IR study of the adsorption and transformation of formaldehyde on oxide surfaces. *J. Am. Chem. Soc.* 109 (17), 5197–5202.
- Chen, D., Qu, Z., Sun, Y., Gao, K., Wang, Y., 2014. Identification of reaction intermediates and mechanism responsible for highly active HCHO oxidation on Ag/MCM-41 catalysts. *Appl. Catal. B Environ.* 142–143, 838–848.
- D'Arienzo, M., Carbajo, J., Bahamonde, A., Crippa, M., Polizzi, S., Scotti, R., Wahba, L., Morazzoni, F., 2011. Photogenerated defects in shape-controlled TiO₂ anatase nanocrystals: a probe to evaluate the role of crystal facets in photocatalytic processes. *J. Am. Chem. Soc.* 133 (44), 17652–17661.
- Derdour, L., Skliar, D., 2012. Crystallization from solutions containing multiple conformers. 1. modeling of crystal growth and supersaturation. *Cryst. Growth Des.* 12 (11), 5180–5187.
- Dimitrijevic, N.M., Vijayan, B.K., Poluektov, O.G., Rajh, T., Gray, K.A., He, H., Zapol, P., 2011. Role of water and carbonates in photocatalytic transformation of CO₂ to CH₄ on titania. *J. Am. Chem. Soc.* 133 (11), 3964–3971.
- Dobrosz-Gómez, I., Kocemba, I., Rynkowski, J.M., 2008. Au/Ce_{1-x}Zr_xO₂ as effective catalysts for low-temperature CO oxidation. *Appl. Catal. B Environ.* 83 (3–4), 240–255.
- Erjavec, B., Kaplan, R., Djinić, P., Pintar, A., 2013. Catalytic wet air oxidation of bisphenol a model solution in a trickle-bed reactor over titanate nanotube-based catalysts. *Appl. Catal. B Environ.* 132–133, 342–352.
- Fujitani, T., Nakamura, I., 2011. Mechanism and active sites of the oxidation of CO over Au/TiO₂. *Angew. Chem. Int. Ed.* 50 (43), 10144–10147.
- Green, I.X., Tang, W., Neurock, M., Yates Jr., J.T., 2011. Spectroscopic observation of dual catalytic sites during oxidation of CO on a Au/TiO₂ catalyst. *Science* 333 (6043), 736–739.
- Hampsey, J.E., Arsenault, S., Hu, Q., Lu, Y., 2005. One-step synthesis of mesoporous metal-SiO₂ particles by an aerosol-assisted self-assembly process. *Chem. Mater.* 17 (9), 2475–2480.
- Han, M.M., Wang, X.J., Shen, Y.N., Tang, C.H., Li, G.S., Smith Jr., R.L., 2010. Preparation of highly active, low Au-loaded, Au/CeO₂ nanoparticle catalysts that promote CO oxidation at ambient temperatures. *J. Phys. Chem. C* 114 (2), 793–798.
- Haruta, M., 2007. New generation of gold catalysts: nanoporous foams and tubes—is unsupported gold catalytically active? *Chem. Phys. Chem.* 8 (13), 1911–1913.
- Herzing, A.A., Kiely, C.J., Carley, A.F., Landon, P., Hutchings, G.J., 2008. Identification of active gold nanoclusters on iron oxide supports for CO oxidation. *Science* 321 (5894), 1331–1335.
- Ishida, T., Watanabe, H., Bebeko, T., Akita, T., Haruta, M., 2010. Aerobic oxidation of glucose over gold nanoparticles deposited on cellulose. *Appl. Catal. A-Gel.* 377 (1–2), 42–46.
- Jia, C.J., Liu, Y., Bongard, H., Schüth, F., 2010. Very low temperature CO oxidation over colloidal deposited gold nanoparticles on Mg(OH)₂ and MgO. *J. Am. Chem. Soc.* 132, 1520–1522.
- Jiang, X.D., Zhang, Y.P., Jiang, J., Rong, Y.S., Wang, Y.C., Wu, Y.C., Pan, C.X., 2012. Characterization of oxygen vacancy associates within hydrogenated TiO₂: a positron annihilation study. *J. Phys. Chem. C* 116 (42), 22619–22624.
- Kim, H.Y., Lee, H.M., Pala, R.G.S., Shapovalov, V., Metiu, H., 2008. CO oxidation by rutile TiO₂(110) doped with V, W, Cr, Mo, and Mn. *J. Phys. Chem. C* 112 (32), 12398–12408.
- Kim, S.H., Jung, C.H., Sahu, N., Park, D., Yun, J.Y., Ha, H., Park, J.Y., 2013. Catalytic activity of Au/TiO₂ and Pt/TiO₂ nanocatalysts prepared with arc plasma deposition under CO oxidation. *Appl. Catal. A-Gel.* 454, 53–58.
- Knudsen, J., Merte, L.R., Peng, G., Vang, R.T., Resta, A., Lægsgaard, E., Andersen, J.N., Mavrikakis, M., Besenbacher, F., 2010. Low-temperature CO oxidation on Ni(111) and on a Au/Ni(111) surface alloy. *ACS Nano* 4 (8), 4380–4387.
- Kruse, N., Chenakin, S., 2011. XPS characterization of Au/TiO₂ catalysts: binding energy assessment and irradiation effects. *Appl. Catal. A Gen.* 391 (1–2), 367–376.
- Kun, R., Mogorósi, K., Németh, J., Körösi, L., Papp, S., Dékány, I., 2005. Thermoanalytical and structural properties of metal oxide semiconductor and palladium/layer silicate nanocomposites. *J. Therm. Anal. Calorim.* 79 (3), 595–604.
- Kun, R., Mogorósi, K., Dékány, I., 2006. Synthesis and structural and photocatalytic properties of TiO₂/montmorillonite nanocomposites. *Appl. Clay Sci.* 32 (1–2), 99–110.
- Lee, J., Park, J.C., Song, H.A., 2008. Nanoreactor framework of a Au@SiO₂ yolk/shell structure for catalytic reduction of p-nitrophenol. *Adv. Mater.* 20 (8), 1523–1528.
- Lee, I., Joo, J., Yin, Y., Zaera, F., 2011. A yolk@shell nanoarchitecture for Au/TiO₂ catalysts. *Angew. Chem. Int. Ed.* 50 (43), 10208–10211.
- Li, C., She, Y., Jia, M., Sheng, S., Adebajo, M.O., Zhu, H., 2008a. Catalytic combustion of formaldehyde on gold/iron-oxide catalysts. *Catal. Commun.* 9 (3), 355–361.
- Li, C.M., Zhang, S.T., Zhang, B.S., Su, D.S., He, S., Zhao, Y.F., Liu, J., Wang, F., Wei, M., Evans, D.G., Duan, X., 2013. Photocatalytic oxidation-assisted anchoring of ultra-small Ru clusters onto TiO₂ with excellent catalytic activity and stability. *J. Mater. Chem., A* 1 (7), 2461–2467.
- Li, S.C., Dulub, O., Diebold, U., 2008b. Scanning tunneling microscopy study of a vicinal anatase TiO₂ surface. *J. Phys. Chem. C* 112 (42), 16166–16170.
- Liu, J., Xu, J., Zhao, Z., Duan, A., Jiang, G., Jing, Y., 2010. A novel four-way combining catalysts for simultaneous removal of exhaust pollutants from diesel engine. *J. Environ. Sci.* 22 (2010), 1104–1109.
- Ma, C.Y., Mu, Z., Li, J.J., Jin, Y.G., Cheng, J., Lu, G.Q., Hao, Z.P., Qiao, S.Z., 2010. Mesoporous Co₃O₄ and Au/Co₃O₄ catalysts for low-temperature oxidation of trace ethylene. *J. Am. Chem. Soc.* 132 (5), 2608–2613.
- Ma, C.Y., Wang, D.H., Xue, W.J., Dou, B.J., Wang, H.L., Hao, Z.P., 2011. Investigation of formaldehyde oxidation over Co₃O₄-CeO₂ and Au/Co₃O₄-CeO₂ catalysts at room temperature: effective removal and determination of reaction mechanism. *Environ. Sci. Technol.* 45 (8), 3628–3634.
- Ma, C.Y., Xue, W.J., Li, J.J., Xing, W., Hao, Z.P., 2013. Mesoporous carbon confined Au catalysts with superior activity for selective oxidation of glucose to gluconic acid. *Green Chem.* 15 (4), 1035–1041.
- Matthey, D., Wang, J.G., Wendt, S., Matthiesen, J., Schaub, R., Lægsgaard, E., Hammer, B., Besenbacher, F., 2007. Enhanced bonding of gold nanoparticles on oxidized TiO₂(110). *Science* 315 (5819), 1692–1696.
- Namai, Y., Matsuoka, O., 2005. Chain structures of surface hydroxyl groups formed via line oxygen vacancies on TiO₂(110) surfaces studied using noncontact atomic force microscopy. *J. Phys. Chem. B* 109 (50), 23948–23954.
- Okatsu, H., Kinoshita, N., Akita, T., Ishida, T., Haruta, M., 2009. Deposition of gold nanoparticles on carbons for aerobic glucose oxidation. *Appl. Catal. A-Gel.* 369 (1–2), 8–14.

- Papp, S., Szél, J., Oszkó, A., Dékány, I., 2004. Synthesis of polymer stabilized rhodium nanoparticles in the interlayer space of layer silicates. *Chem. Mater.* 16 (9), 1674–1685.
- Peng, C.W., Ke, T.Y., Brohan, L., Richard-Plouet, M., Huang, J.C., Puzenat, E., Chiu, H.T., Lee, C.Y., 2008. (101)-exposed anatase TiO₂ nanosheets. *Chem Mater* 20 (7), 2426–2428.
- Petrik, N.G., Kimmel, G.A., 2011. Oxygen photochemistry on TiO₂(110): recyclable, photoactive oxygen produced by annealing adsorbed O₂. *J. Phys. Chem. Lett.* 2 (21), 2790–2796.
- Pillai, S.C., Periyat, P., George, R., McCormack, D.E., Seery, M.K., Hayden, H., Colreavy, J., Corr, D., Hinder, S.J., 2007. Synthesis of high-temperature stable anatase TiO₂ photocatalyst. *J. Phys. Chem. C* 111 (4), 1605–1611.
- Porta, F., Prati, L., Rossi, M., Scari, G., 2002. New Au(0) sols as precursors for heterogeneous liquid-phase oxidation catalysts. *J. Catal.* 211 (2), 464–469.
- Shen, Y., Yang, X., Wang, Y., Zhang, Y., Zhu, H., Gao, L., Jia, M., 2008. The states of gold species in CeO₂ supported gold catalyst for formaldehyde oxidation. *Appl. Catal. B Environ.* 79 (2), 142–148.
- Somodi, F., Borbath, I., Hegedűs, M., Tomopos, A., Sajo, I.E., Szegedi, A., Rojas, S., Fierro, J.L.G., Margitfalvi, J.L., 2008. Modified preparation method for highly active Au/SiO₂ catalysts used in CO oxidation. *Appl. Catal. A-Gel.* 347 (2), 216–222.
- Strunk, J., Vining, W.C., Bell, A.T., 2010. A study of oxygen vacancy formation and annihilation in submonolayer coverages of TiO₂ dispersed on MCM-48. *J. Phys. Chem. C* 114 (40), 16937–16945.
- Su, F.Z., Liu, Y.M., Wang, L.C., Cao, Y., He, H.Y., Fan, K.N., 2008. Ga–Al mixed-oxide-supported gold nanoparticles with enhanced activity for aerobic alcohol oxidation. *Angew. Chem. Int. Ed.* 47 (2), 334–337.
- Wang, S., Zhang, M., Zhang, W., 2011. Yolk–shell catalyst of single Au nanoparticle encapsulated within hollow mesoporous silica microspheres. *ACS Catal.* 1 (3), 207–211.
- Wang, Y., He, Y., Lai, Q., Fan, M., 2014. Review of the progress in preparing nano TiO₂: an important environmental engineering material. *J. Environ. Sci.* 26 (11), 2139–2177.
- Weiher, N., Beesley, A.M., Tsapatsaris, N., Delannoy, L., Louis, C., van Bokhoven, J.A., Schroeder, S.L.M., 2007. Activation of oxygen by metallic gold in Au/TiO₂ catalysts. *J. Am. Chem. Soc.* 129 (8), 2240–2241.
- Widmann, D., Behm, R.J., 2011. Active oxygen on a Au/TiO₂ catalyst: formation, stability, and CO oxidation activity. *Angew. Chem. Int. Ed.* 50 (43), 10241–10245.
- Wörz, A.S., Heiz, U., 2005. Charging of Au atoms on TiO₂ thin films from CO vibrational spectroscopy and DFT calculations. *J. Phys. Chem. B* 109 (39), 18418–18426.
- Yang, H.G., Sun, C.H., Qiao, S.Z., Zou, J., Liu, G., Smith, S.C., Cheng, H.M., Lu, G.Q., 2008. Anatase TiO₂ single crystals with a large percentage of reactive facets. *Nature* 453 (7195), 638–641.
- Zhang, C., He, H., 2007. A comparative study of TiO₂ supported noble metal catalysts for the oxidation of formaldehyde at room temperature. *Catal. Today* 126 (3–4), 345–350.
- Zhang, J., Jin, Y., Li, C.Y., Shen, Y.N., Han, L., Hu, Z.X., Di, X.W., Liu, Z.L., 2009. Creation of three-dimensionally ordered macroporous Au/CeO₂ catalysts with controlled pore sizes and their enhanced catalytic performance for formaldehyde oxidation. *Appl. Catal. B Environ.* 91 (1–2), 11–20.
- Zhang, Z., Chen, M., Jiang, Z., Shangguan, W., 2010. Performance and mechanism study for low-temperature SCR of NO with propylene in excess oxygen over Pt/TiO₂ catalyst. *J. Environ. Sci.* 22 (9), 1441–1446.
- Zhu, S.Y., Liang, S.J., Gu, Q., Xie, L.Y., Wang, J.X., Ding, Z.X., Liu, P., 2012. Effect of Au supported TiO₂ with dominant exposed {001} facets on the visible-light photocatalytic activity. *Appl. Catal. B Environ.* 119–120, 146–155.
- Zuo, F., Wang, L., Wu, T., Zhang, Z., Borchardt, D., Feng, P., 2010. Self-doped Ti³⁺ enhanced photocatalyst for hydrogen production under visible light. *J. Am. Chem. Soc.* 132 (34), 11856–11857.