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Article

Facet-dependent anchoring of gold nanoparticles on TiO₂ for CO oxidation

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ARTICLE INFO

Article history:

Received 26 June 2019

Accepted 27 July 2019

Published 5 October 2019

Keywords:

Au nanoparticles

Titanium dioxide

Stability

Interfacial perimeter

CO oxidation

ABSTRACT

The interfacial perimeter of gold nanocatalysts is popularly viewed as the active sites for a number of chemical reactions, while the geometrical structure of the interface at atomic scale is less known. Here, TiO₂-nanosheets and nanospindles were adapted to accommodate Au particles (~2.2 nm), forming Au-TiO₂{001} and Au-TiO₂{101} interfaces. Upon calcination at 623 K in air, HAADF-STEM images evidenced that the Au particles on TiO₂{101} enlarged to 3.1 nm and these on TiO₂{001} remained unchanged, suggesting the stronger metal-support interaction on TiO₂{001}. Au/TiO₂{001} was more active for CO oxidation than Au/TiO₂{101} system.

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1. Introduction

Since the discovery that gold nanoparticles (NPs) on TiO₂ are exceptionally active for low-temperature oxidation of CO, great efforts have been made to explore the chemical nature of the catalytically active sites on Au/TiO₂ catalysts, which largely depends on the size of gold particles [1–8]. It is generally acknowledged that the active sites locate at the gold-support interface, based on the experimental observation that the activity is often proportional to the total length of the interfacial perimeter [9–13]. The reaction occurs at the Au-oxide interfacial perimeter: CO is adsorbed and activated on the gold nanoparticle while molecular oxygen is activated by the perimeter of Au-oxide interface [8–11]. With this respect, both the size of gold particles and the chemical properties of TiO₂ surfaces

played critical roles in determining the Au-TiO₂ interfacial structure and consequently the catalytic activity, involving both electronic and geometric interactions between Au particles and TiO₂ surfaces.

The commercial P25, a mixture of anatase- and rutile-TiO₂, has been commonly used to support gold nanoparticles for examining the size effect of the metal particles [5,14]. However, the diversity of TiO₂ surfaces makes it difficult to straightforwardly identify the atomic structure of the interfacial perimeters. Tailoring the morphology of TiO₂ provides a possibility to anchor gold nanoparticles on a specific facet of the oxide-support, forming relatively uniform Au-TiO₂ interfaces [15–17]. For example, TiO₂{001} favoured an intimate contact and a stronger interaction with gold particles, as compared with TiO₂{101}. While the intimate contact of Au-TiO₂{001}

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This work was supported by Liaoning Revitalization Talents Program (XLYC1807121) and National Natural Science Foundation of China (20673054). DOI: S1872-2067(19)63388-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 10, October 2019

improved the electron transfer from Au NPs to the adsorbed O_2 , thus being in favour of oxygen dissociation and promoting the catalytic activity in CO oxidation [18,19]. Recently, the stronger bonding of Au nanoparticles on $TiO_2\{001\}$ than that on $TiO_2\{101\}$ has been directly visualized by in situ transmission electron microscopy (TEM) [20]. Au NPs of 4–8 nm, immobilized on $TiO_2\{101\}$, were sintered to large particles through the Ostwald ripening and particle migration coalescence as being heated to 773 K in the presence of oxygen, but no sintering was observed on the anatase- $TiO_2\{001\}$ under the identical conditions. It was attributed to the much higher adsorption energy of gold on $TiO_2\{001\}$ than that on $TiO_2\{101\}$ [20].

In this work, anatase TiO_2 -nanosheets and nanospindles were used to support Au particles of ~ 2.2 nm, and the resulting Au/ $TiO_2\{001\}$ and Au/ $TiO_2\{101\}$ interfacial perimeters were examined for CO oxidation. It was found that the Au/ $TiO_2\{001\}$ interface is more active for CO oxidation than the Au/ $TiO_2\{101\}$ system under identical reaction conditions.

2. Experimental

2.1. Synthesis of Au/ TiO_2 catalysts

The anatase TiO_2 nanosheets (TiO_2 -P) and nanospindles (TiO_2 -S) were synthesized by a hydrothermal method, as we previously described [21–23]. Au colloids of about 2.2 nm (Fig. S1) were prepared by reduction of $HAuCl_4$ with $NaBH_4$ in the presence of polyvinyl alcohol (PVA), following a typical procedure [24]. The Au/ TiO_2 catalysts were then prepared by immobilizing Au colloids on TiO_2 . The oxide-support was mixed with the Au colloidal solution under vigorous stirring, and the pH of the mixture was adjusted to ca. 6.0 by adding 0.1 M HNO_3 aqueous solution. After stirring for 1 h at room temperature, the solid was collected by filtration and washed thoroughly with distilled water. The sample was dried under vacuum at room temperature overnight and calcined at 623 K for 4 h in air. ICP analysis showed the actual loading of Au was 0.80 wt% for Au/ TiO_2 -nanospindle (Au/ TiO_2 -P) and 0.81 wt% for Au/ TiO_2 -nanosheet (Au/ TiO_2 -S).

2.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2500PC with $Cu K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV, 200 mA. TEM images were recorded on a Hitachi 7700 microscope operated at 120 kV. Aberration-corrected STEM (ac-STEM) images were taken on a JEM-ARM200F at 200 kV. The specimen was prepared by ultrasonically dispersing the sample powder into water or ethanol, and the drops of the suspension were deposited on a carbon-coated copper grid and dried at room temperature in air. The lattice spacing and the morphology of Au nanoparticles was analyzed by a Digital Micrograph software. X-ray photoelectron spectra (XPS) were recorded with an ESCALAB 250 Xi spectrometer (ThermoFisher) using an Al $K\alpha$ radiation source operated at an accelerating voltage of 15 kV. The charge effect was corrected by adjusting the binding energy of C 1s to 284.6 eV.

2.3. Catalytic test

CO oxidation over the Au/ TiO_2 catalysts was performed in a U-shape quartz tubular reactor (inner diameter 6 mm) under atmospheric pressure. 150 mg catalyst was loaded between two layers of quartz wool and pretreated with a 20.0 vol% O_2 /Ar mixture at 623 K for 4 h. The feed gas of 1.0 vol% CO/20.0 vol% O_2 /He (50 mL min^{-1}) was introduced through a mass-flow controller, and the temperature was gradually increased from 198 to 473 K. The effluent from the reactor was analyzed by an online gas chromatogram (Agilent-GC7890B). The reaction rate was measured at the temperature range of 263–293 K and the conversion of CO was controlled to be 8%–15% by varying the gas flow rate for assuring a differential reactor condition.

3. Results and discussion

3.1. Synthesis and characterization of Au/ TiO_2

XRD patterns of the Au/ TiO_2 -P and Au/ TiO_2 -S samples show prominent diffraction lines at 25° , 38° , 48° , 54° , and 55° (Fig. S4), which are assigned to the anatase- TiO_2 facets of (101), (103), (004), (112), and (200) [JCPDS # 21-1272]. There were no diffraction lines of Au particles, primarily because of the well dispersion of particles in small sizes or the lower Au loading (ca. 0.8 wt%). Fig. 1 shows XPS of Au 4f in the Au/ TiO_2 catalysts. The binding energies (BEs) of Au 4f_{7/2} and 4f_{5/2} at 83.1 and 86.8 eV indicated the presence of metallic gold, which are the typical values (~ 83.2 eV of Au 4f_{7/2} and ~ 86.9 eV of Au 4f_{5/2}) for gold nanoparticles dispersed TiO_2 [25–30]. The slightly lower binding energies as compared with bulk gold might be caused by the size effect gold nanoparticles and the possible electron transfer from gold to TiO_2 in the Au/ TiO_2 catalysts.

The spatial and size distributions of TiO_2 nanosheets and nanospindles are analyzed by TEM. As we previously reported [22], TiO_2 -P exhibits a spindle shape with an average size of 50 nm (length) and 20 nm (width) and is enclosed by $TiO_2\{101\}$ (81%) on the isosceles trapezoidal surface and $TiO_2\{001\}$

Fig. 1. XPS spectra of Au 4f in the Au/ TiO_2 catalysts.

Fig. 2. HAADF-STEM images and the size distribution of Au particles in the Au/TiO₂-P sample. The statistics was done by counting 1431 particles.

(19%) on the top surface. TiO₂-S has a sheet-like morphology with an average particle size of 75 nm length and 7 nm thickness, and predominantly expose TiO₂{001} (84%) and TiO₂{101} (16%) facets. On TiO₂-P, gold NPs are preferentially anchored on the TiO₂{101}. The majority of the Au NPs on TiO₂{101} were in the size range of 2.6–4.2 nm, with a mean diameter of 3.1 nm and a typical height of 2.63 nm (ca. 12 layers of Au atoms, Fig. 2). STEM analysis on the atomic structures of Au NPs and the metal-support interfaces found that the Au NPs adopt a morphology of quasi-truncated octahedron, which is consistent with our previous work [24]. The prominent Au{100} and Au{111} are clearly identified by the lattice spacing of 0.21 and 0.23 nm on the gold crystallites (Fig. 2).

On TiO₂-S, the distribution of gold NPs showed a dual-model pattern; 76% metal particles located on TiO₂{001} while 24% gold particles deposited to TiO₂{101}, based on the statistics for 556 particles in the sample. The Au NPs on TiO₂{101} had a mean size of 3.2 nm (Fig. 3), similar to the situation of the Au/TiO₂-P sample. On TiO₂{001}, the majority of the Au NPs on TiO₂{001} were in the size range of 1.7–2.7 nm, with a mean

diameter of 2.2 nm (Fig. 3), which is the same as the starting Au colloids. It is most likely that TiO₂{001} bonded Au NPs more tightly than TiO₂{101}. That is, the strong metal-support interaction stabilized the 2.2 nm Au NPs on TiO₂{001} and retarded the aggregation of the small gold particles under the thermal treatment (623 K in air).

Based on the STEM observations, the atomic configuration of Au particles and the Au-TiO₂ interfacial structures were quantitatively analyzed (Table 1). For Au/TiO₂{101}, the total number of Au atoms per gold particle is 1228, in which 108 atoms are low-coordinated at the edges and corners. While on Au/TiO₂{001}, the gold NPs contain 549 atoms and 78 atoms are low-coordinated. Particularly, the numbers of the gold atom at the interfacial perimeters, on the basis of a single particle, are 27 for Au/TiO₂{101} and 21 for Au/TiO₂{001}.

3.2. Catalytic activity of Au/TiO₂ in CO oxidation

Fig. 4(a) shows the catalytic activities of the Au/TiO₂ catalysts for CO reaction in the temperature range 198–473 K. The conversion of CO over Au/TiO₂-S was readily 15% at 243 K, and sharply approached to 100% at 280 K. On the Au/TiO₂-P catalyst, the conversion of CO was 14% at 243 K while the full conversion of CO (99%) was achieved at 468 K. This clearly demonstrates that the superior activity of the Au/TiO₂-S to the Au/TiO₂-P. TEM analysis on the spent catalysts confirmed that the size and shape of gold nanoparticles kept almost unchanged (Figs. S8 and S9).

The reaction kinetics of CO oxidation over the Au/TiO₂ catalysts were then investigated by controlling the conversion of

Fig. 3. HAADF-STEM images and the size distributions of Au particles in the Au/TiO₂-S catalyst. The statistics was done by counting 556 particles (421 particles on TiO₂{001} and 135 on TiO₂{101} of the TiO₂-S samples).

Table 1
Geometrical properties of the Au NPs on the TiO₂ surfaces.*

Catalyst	Au/TiO ₂ {101}	Au/TiO ₂ {001}
Diameter of Au particle (nm)	3.4	2.6
Height of Au particle (nm)	2.63	2.07
Layers of Au atoms	12	9
Total number of Au atoms	1228	549
Number of atoms at corners	24	24
Number of atoms at edges	84	54
Number of atoms on flat surfaces	292	142
Number of atoms at the interfacial perimeter	27	21

* The geometric configuration of Au particles was calculated by the Wulff modes (Figs. S2 and S3), and the number of gold particles calculated based on actual loading of gold per gram of catalyst.

Fig. 4. Performance of the Au/TiO₂ catalysts for CO oxidation. (a) CO conversion as a function of reaction temperature with a feed gas of 1 vol% CO/20 vol% O₂/79 vol% He; (b) Activation energies were measured at 263–293 K.

CO at 8%–15% (Fig. 4(b)). The apparent activation energy of CO oxidation over the Au/TiO₂-P and Au/TiO₂-S was 30.0 and 28.2 kJ mol⁻¹, respectively, in the temperature range of 263–293 K. They are similar to the general values for CO oxidation over gold nanocatalysts at this temperature range [31–33]. At room temperature (298 K), the reaction rate on Au/TiO₂-P was 0.17 mmol_{CO} g_{Au}⁻¹ s⁻¹, while it was 0.41 mmol_{CO} g_{Au}⁻¹ s⁻¹ over Au/TiO₂-S (Table 2). By taking the size distributions of gold particles on TiO₂{001} and TiO₂{101} in the Au/TiO₂ catalysts into account, the reaction rate was estimated to be 0.17 mmol_{CO} g_{Au}⁻¹ s⁻¹ on Au/TiO₂{101} and 0.46 mmol_{CO} g_{Au}⁻¹ s⁻¹ on Au/TiO₂{001}. It indicates that the small sized Au NPs (2.2 nm) on the TiO₂{001} exhibit the higher catalytic activity than the corresponding large sized Au NPs on the TiO₂{101}, consist-

ence with the previous results [34].

Since the interfacial perimeter is associated with the active sites in CO oxidation over Au/TiO₂, the reaction rates further were normalized with the total number of the perimeter Au atoms, estimated according to the mean size of the Au NPs and the Au-TiO₂ interfacial models as determined by TEM/STEM analysis. For the Au-TiO₂-P catalyst, Au-TiO₂{101} is the only interface, and the total number of perimeter gold atoms was 5.38×10^{17} per gram. For the Au-TiO₂-S sample, both Au-TiO₂{001} and Au-TiO₂{101} interfaces are presented and their proportions were calculated to be 7:3. Accordingly, their perimeter gold atoms were 7.17×10^{17} and 2.96×10^{17} per gram, respectively. The turnover frequency (TOF) on the perimeter Au atoms was determined to be 1.52 s⁻¹ for Au/TiO₂{101} and 2.34 s⁻¹ for Au/TiO₂{001}. This result evidences that the Au NPs (average 2.2 nm) on TiO₂{001} are intrinsically more active than these (3.1 nm) on TiO₂{101}, which is mainly because of the unique atomic arrangement of TiO₂{001} that bonded gold particles more strongly.

4. Conclusions

The gold-support interaction in Au/TiO₂ is governed by the surface orientation of TiO₂. TiO₂{001} had a stronger interaction with Au NPs, and thus avoiding the aggregation of Au NPs (2.2 nm) during calcination at 623 K in air. The Au NPs dispersed on TiO₂{001} exhibited a much higher activity than the particles on TiO₂{101} in CO oxidation, primarily because of intrinsic coordination patterns of the interfacial gold atoms on TiO₂ facets.

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Table 2

Reaction rates and turnover frequencies (TOFs) of CO oxidation on the Au/TiO₂ catalysts.

Catalyst	Au/TiO ₂ -P	Au/TiO ₂ -S ^d
Conversion ^a (%)	11.67	11.28
Reaction rate (mmol _{CO} g _{Au} ⁻¹ s ⁻¹)	0.17	0.41 (0.46)
Total number of Au particles ($\times 10^{16}$) ^b	1.99	4.51 (3.41)
Total number of perimeter Au atoms at perimeter site ($\times 10^{17}$) ^c	5.4	9.5 (7.2)
Total length of the interfacial perimeter ($\times 10^{17}$ nm)	1.42	2.57 (1.19)
Normalized reaction rate with the perimeter length ($\times 10^{-23}$ mol _{CO} s ⁻¹ nm ⁻¹)	0.96	1.29 (3.30)
TOF of gold atoms at perimeter site (s ⁻¹)	1.52	2.10 (2.34) ^e

^a Taking the average conversions for 2 h.

^b Calculated from the geometrical models.

^c Calculated by assuming that the activity of Au NPs on the TiO₂{101} is the same.

^d Values in parentheses refer to the Au/TiO₂{001}.

^e The normalized TOF is calculated based on the interface perimeter gold atom of gold catalysts, as follows:

$TOF(Au/TiO_2-S) = TOF(Au/TiO_2\{101\}) \times (1 - P_1) + TOF(Au/TiO_2\{001\}) \times P_1$
 $(P_1 = \frac{S_1 \times N_1}{S_1 \times N_1 + (1 - S_1) \times N_2})$, where, S_1 is the spatial distribution of Au particles on the TiO₂{001}, N_1 and N_2 are the number of Au atoms at the perimeter per particle on the TiO₂{001} and TiO₂{101} in the Au/TiO₂-S, respectively. Of note, $TOF(Au/TiO_2-P) = TOF(Au/TiO_2\{101\})$.

Graphical Abstract

Chin. J. Catal., 2019, 40: 1534–1539 doi: S1872-2067(19)63388-7

Facet-dependent anchoring of gold nanoparticles on TiO₂ for CO oxidation

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Two different Au/TiO₂ catalysts, prepared via colloid-immobilized method, showed significant morphological effect in CO oxidation. The TiO₂{001} can well stabilize the 2–3 nm Au nanoparticles and exhibit higher catalytic activity in CO oxidation.

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二氧化钛负载金催化剂：界面效应

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摘要: 自从发现TiO₂负载金纳米粒子对CO氧化具有催化活性以来, 人们努力探索Au/TiO₂催化剂上催化活性位点的化学本质。大量研究表明, Au/TiO₂催化反应的活性位点位于金颗粒-TiO₂载体界面处, 催化剂活性通常与界面周长成正比。因此,

无论是金颗粒的大小还是二氧化钛表面的化学性质都决定着Au-TiO₂界面结构和催化活性,即Au颗粒和二氧化钛表面之间的电子结构和几何相互作用。

商用P25是锐钛矿相和金红石相以80/20比例混合的二氧化钛,通常用于负载金纳米粒子。然而,由于P25表面的多样性和复杂性,很难直接区分界面的原子精细结构,给研究载体表面结构对催化性能的影响带了一定困难。设计特定形貌TiO₂(合成暴露特定晶面的TiO₂),形成均匀的Au-TiO₂界面成为研究该课题的突破口。目前,随着纳米材料设计的日渐成熟,氧化物形貌甚至晶面的可控合成已经实现。最近原位透射电镜发现,与TiO₂{101}相比金颗粒与TiO₂{001}具有更强的相互作用。氧气在773 K焙烧,负载在TiO₂{101}的Au粒子通过Ostwald熟化和粒子的迁移聚结而烧结成颗粒;反之,负载在TiO₂{001}上的Au粒子则非常稳定。这主要归结于Au粒子在TiO₂{001}上的吸附能比在TiO₂{101}上高很多。Au与TiO₂{001}的强相互作用可以促进电子从Au纳米粒子到吸附的O₂上的转移,从而有利于氧离解和提高CO氧化活性。

本文采用水热法合成选择性暴露TiO₂{001}和TiO₂{101}的锐钛矿TiO₂:暴露TiO₂{001}比例84%的纳米片(TiO₂-S)和19%的纺锤体(TiO₂-P),然后分别负载上2 nm左右的Au溶胶颗粒并在623 K空气下进行烧结。通过X射线光电子能谱(XPS),高分辨透射电镜(HRTEM/STEM)等表征手段研究了Au纳米粒子的尺寸分布、电子结构以及原子结构。XPS结果表明,Au物种为金属态Au⁰颗粒。对Au粒子尺寸进行统计,发现在TiO₂{001}上的Au粒子尺寸大小无明显变化(2.2 nm),而在TiO₂{101}上的Au粒子尺寸由2.2 nm长到3.1 nm。结果表明,在TiO₂{001}与Au粒子相互作用更强,能更好地稳定Au粒子。在CO氧化反应测试中发现,Au/TiO₂{001}具有比Au/TiO₂{101}更高的催化活性;但是两个催化剂的表观活化能相近(Au/TiO₂-P为30.0 kJ mol⁻¹,Au/TiO₂-S为28.2 kJ mol⁻¹),且与典型的Au/TiO₂催化CO氧化反应动力学数据一致进行分析,表明催化剂载体的晶面并未影响反应路径。进一步结合原子结构模型,将反应速率归一化到Au-TiO₂界面,发现两者界面原子的转化频率(TOF)相差较大;Au/TiO₂-P,即Au/TiO₂{101}界面Au原子在室温下的TOF为1.52 s⁻¹,而Au/TiO₂-S催化剂的为2.10 s⁻¹,其中Au/TiO₂{001}的转化频率为2.35 s⁻¹。这表明,在TiO₂{001}界面上的Au粒子(粒径2.2 nm)不仅热稳定性比较好,且催化性能比在TiO₂{101}上的Au粒子(粒径3.1 nm)更高,这主要是由于TiO₂{001}表面独特的原子排列使金颗粒与之结合更为强烈。

关键词: 金纳米粒子; 二氧化钛; 稳定性; 界面; CO氧化

收稿日期: 2019-06-26. 接受日期: 2019-07-27. 出版日期: 2019-10-05.

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基金来源: 兴辽英才计划(XLYC1807121)和国家自然科学基金(20673054).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).