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Enhanced liquid phase catalytic hydrogenation reduction of bromate over Pd-on-Au bimetallic catalysts

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The catalytic bromate reduction TOF first increased and then decreased with Au core size.

Highlights

• Pd-on-Au core-shell like bimetallic nanoparticles were prepared by the sequential photocatalytic deposition method.

- The bimetallic catalyst exhibited a substantially higher catalytic activity for the liquid phase catalytic reduction of bromate than the monometallic ones.
- The catalytic activity of bimetallic catalyst first increased then decreased with Au core size.
- Both the H₂ activation and reactant adsorption play important roles on the catalytic hydrogenation reduction of bromate.

Abstract

Pd-Au/TiO₂ bimetallic catalysts with varied Au contents were prepared by the sequential photocatalytic deposition method and the liquid phase catalytic hydrogenation reduction of bromate over these catalysts was investigated. The catalysts were characterized using X-ray diffraction, transmission electron microscope, UV-Vis diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy, H₂ chemisorption and energy dispersive spectroscopy. Characterization results showed that Pd atoms were site-deposited on the surface of varied size Au cores and formed Pd-on-Au coreshell like bimetallic nanoparticles on TiO₂. The bimetallic catalysts showed higher Pd dispersions and more exposed active sites than that of Pd/TiO₂, and the amount of exposed active sites first increased then decreased with Au content. For a similar Pd loading, the bimetallic catalyst exhibited volcano-shape activity as a function of Au loading and the highest activity was identified on Pd-Au(1.0)/TiO₂ with Au core size around 8.4 nm. In addition, the catalytic reduction of bromate could be well-fitted by the Langmuir-Hinshelwood model, reflecting an adsorption controlled mechanism.

Keywords: Liquid phase catalytic hydrogenation; Bromate; Pd-Au/TiO₂; Photocatalytic deposition; core-shell structure

1. Introduction

Bromate (BrO₃⁻) is a common disinfection byproduct generated from bromide-containing source waters undergo ozonation or chlorination [1]. Bromate is considered as a potential carcinogen to human beings [2,3], the maximum concentration in the drinking water regulated by the U.S. Environmental Protection Agency (EPA) and World Health Organization (WHO) is 0.01 mg l⁻¹ [4,5].

Nowadays varies treatment methods have been developed to eliminate bromate from drinking water, such as biological treatment [6,7], activated carbon adsorption/reduction [8], photocatalytic reduction [9,10], electrochemistry reduction [11,12] etc. Alternatively, catalytic hydrogenation reduction is one of the clean and efficient methods to deal with the halogen-containing compounds and high valence ions [13-15].

Supported noble metal catalysts usually applied in the hydrogenation reduction reaction involved the activation of H₂ [16,17]. Pd-based catalysts were the most frequently used materials due to its superior hydrogen dissolving capacity [18]. Our previous studies showed that the catalyst performance were intimately related to the supports and preparation methods which could adjusted Pd particle size, electronic state and so on [19-21]. Significantly, the properties of the monometallic catalyst could be further improved by decorating with another metal to form bimetallic systems and metal Au as the modifier has received great interest. For example, Kittisakmontree et al. [22] found that the liquid phase hydrogenation of 1-heptyne could be greatly enhanced over Au-Pd bimetallic catalyst compared to the pure metal catalyst. Zhou et al. [23] suggested that the activities of Pd-Au bimetallic catalysts were much higher than the monometallic ones for the catalytic hydrodechlorination of 2,4dichlorophenol. Pongthawornsakun et al. [24] improved the selective hydrogenation of acetylene using Au-Pd-TiO₂ bimetallic catalysts.

To deeper understand the catalyst properties or catalytic mechanism, many studies concentrated on better control of the bimetallic nanostructure to modulate the configuration of bimetallic particles

and/or valence electron density of the combined metals [25-27]. The Core-shell Pd-Au bimetallic catalysts have received great interest because of the controllable structure and special catalytic performance, which frequently applied in the oxidation [28,29], hydrogen peroxide synthesis [30,31], hydrogenation [32,33], and electrochemistry reactions [34]. The catalytic activity and selectivity of the core-shell structure bimetallic catalyst mainly improved by regulating the core size or metal coverage. Accordingly, the improvement of the bimetallic catalyst performance is generally due to the geometric and electronic effects. For example, Zhang et al. [35] prepared Au-Pd/SiO₂ catalysts using the electroless deposition method and found that higher coverages of Au on Pd resulted in smaller ensembles of Pd sites, which favored the hydrogenation of acetylene to ethylene by adsorbing as a π bonded species of acetylene on Pd sites. Pretzer et al. [36] prepared Pd-on-Au nanoparticles and adjusted the Pd surface coverages using the magic cluster model on Au core with varied diameters and concluded that both the Au particle size and Pd surface coverage affected the catalytic activity remarkably. Nutt et al. [37] synthesized Pd/Au nanoparticles with different Pd loadings and suggested that the electronic structure of metal Pd could be modified by Au only when the Pd-Au metal were in intimate contact, and the intimate interface supplied additional active sites for the hydrodechlorination of trichloroethene.

The photocatalytic deposition method with semiconductor material as the support is one of the alternative methods to simply obtain uniform bimetallic nanostructure [38,39]. For the preparation of TiO_2 supported Pd-on-Au bimetallic catalyst via the two-step photocatalytic deposition method, TiO_2 acted as the catalyst to generate photoelectrons for the reduction of metal ions. During the second deposition process metal Au acted as the sink of photo-induced electrons and Pd atoms were site deposited on the surface of Au particles, forming Pd-on-Au core-shell like bimetallic nanoparticles on TiO_2 [40,41], which may exhibit interesting catalytic performance. However, thus far few studies have

been conducted on the behavior of Pd-Au bimetallic catalysts for the catalytic hydrogenation reduction of bromate. Hence, it is of interest to examine the catalytic reduction of bromate by Pd-Au/TiO₂ prepared using the photocatalytic deposition method.

In the present study, we prepared monometallic and Pd-on-Au core-shell like bimetallic catalysts with varied Au contents supported on TiO_2 by the two-step photocatalytic deposition method, and investigated the liquid phase catalytic hydrogenation reduction of bromate.

2. Experimental

2.1. Catalyst preparation

The monometallic and bimetallic Pd-Au catalysts with varied Au deposition amounts were prepared using the photocatalytic deposition method. For the preparation of Pd/TiO₂ with Pd deposition amount at 1.0 wt%, 2 g of TiO₂ (P25, Degussa) was suspended in 480 ml of distilled water and added a desired amount of PdCl₂ solution and 10 ml of methanol. After purging with a N₂ flow (50 ml min⁻¹) under stirring for 1 h in the dark, the mixture was exposed to ultraviolet (UV) irradiation with a high pressure Hg lamp (500W) for 4 h. The Pd/TiO₂ sample was obtained by filtration, followed by washing thoroughly with distilled water, drying at 110 °C for 8 h under vacuum. For the bimetallic Pd-Au/TiO₂ catalysts, Pd deposition amount was kept around 1.0 wt% and Au loading amount was varied. Typically, metal Au was first deposited onto TiO₂ with HAuCl₄·4H₂O as the precursor and followed the same procedure as the preparation of Pd/TiO₂, then, the sample experienced a second deposition with PdCl₂ as the precursor, and monometallic Au/TiO₂ were synthesized for comparison. The collected bimetallic catalyst was referred to as Pd-Au(*x*)/TiO₂, where *x* is the Au actual deposition amount (wt. %) detected by ICP-AES.

2.2. Catalyst characterization

Brunauer-Emmett-Teller (BET) surface areas of the samples were collected using a Micromeritics

ASAP 2020 instrument (Micromeritics Instrument Co., Norcross, GA, USA) at -196 °C. The X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku D/max-RA powder diffractionmeter with a Cu *Ka* radiation (Rigaku, Tokyo, Japan). The Pd content in the catalyst was measured on an inductive coupled plasma emission spectrometer (ICP) (J-A1100, Jarrell-Ash, USA). The X-ray photoelectron spectroscopy (XPS) was tested by a PHI5000 VersaProbe equipped with a monochromatized Al *Ka* excitation source (hv= 1486.6 eV) (ULVAC-PHI, Japan). The C 1s peak (284.6 eV) was used as the calibration of binding energy. The UV-vis spectra were analyzed using SHIMADZU UV-2450 UV/vis spectrophotometer (Shimadzu Co., Kyoto, Japan) with BaSO4 as a reference. Energy dispersive X-ray spectroscopy (EDS) elemental mapping was collected from an X-MAX energy dispersive spectrometer (Oxford, UK) equipped with an ARM-200F transmission electron microscope (JEOL Co., Japan.).

The TEM images of the catalysts were obtained on a JEM-200CX electron microscope (JEOL Co., Tokyo, Japan). The average metal particle sizes of the catalysts were obtained using Eq (1) [42]:

$$\overline{\mathbf{d}_{s}} = \sum n_{i} d_{i}^{3} / \sum n_{i} d_{i}^{2}$$
(1)

Where n_i is the number of counted metal particles with diameter of d_i , and the total number of counted particles ($\sum n_i$) is larger than 300.

The zeta potentials of the materials were tested on a Zeta Potential Analyzer (Zeta PALS, Brookhaven Instruments Co.). Typically, 40 mg of the materials were ultrasonic dispersed in 400 mL distilled water, then the solution pH was adjusted using 0.1 M HCl and 0.1 M NaOH, the measurement was conducted after the suspension standing at room temperature for 12 h.

Pd dispersion of the samples was performed using the H₂ chemisorption method. Simply, 200 mg of catalyst was pressed into pieces and loaded in a U-shaped quartz tube, and heated at 120°C in a H₂ flow (40 ml min⁻¹) for 1h. Then, the tube was purging with a Ar flow (40 ml min⁻¹) for 1h. After

cooling to room temperature, the H_2 chemisorption was started using the pulse titration model with H_2 partial pressure below 0.011 atm. H_2 contents were tested using an online gas chromatograph (GC) with a thermal conductivity detector (TCD).

2.3. Liquid phase catalytic reduction reaction

The liquid phase catalytic reduction of bromate was carried out under atmospheric pressure in a 250 ml of four-necked flask equipped with a sample port, pH-stat, H₂ inlet and outlet. The reaction temperature was stabilized at 20±0.5 °C by a water-bath (SDC-6, scientz Co., China). Typically, 20 mg of catalyst was suspended in 200 ml of 0.4 mol 1⁻¹ potassium bromate solution. The reactor was purging with a N₂ flow (50 ml min⁻¹) under stirring for 30 min, and then the N₂ flow was switched into a H₂ flow (150 ml min⁻¹) during the reaction process. Samples were collected at selected time intervals and the catalyst particles were removed using 0.45 µm filter. The concentrations of reactant and products in the filtrate were analyzed using Ion Chromatography (ICS1000, Dionex) with a mobile phase of 18 mM KOH solution. The initial activities were calculated using Eq (2), and the turnover frequency (TOF), defined as the reduction rate of bromate over per exposed active site, was determined by Eq (3):

Initial Activity =
$$\frac{C_0 - C_t}{W_{cat} \times t}$$
 (2)

$$TOF = \frac{Initial \ Activity}{N_{Pd}}$$
(3)

In which, C_0 is the initial concentration of BrO₃⁻; C_t is the concentration of BrO₃⁻ at reaction time *t*; W_{cat} is catalyst dosage; N_{Pd} is the number of exposed Pd atom per gram catalyst, which determined by the H₂ chemisorption data [43].

3. Results and discussion

3.1. Catalyst characterization

The zeta potentials of TiO₂, Pd/TiO₂ and Pd-Au(1.0)/TiO₂ as a function of pH are presented in Fig. 1. Clearly, the zeta potentials decreased with pH, and all the isoelectric points (IEPs) of the materials were around 6.0, implying that the catalyst surface was positively charged when pH was lower than 6.0, while negatively charged when solution pH was higher than 6.0.

The XRD patterns of Pd/TiO₂ and Pd-Au bimetallic catalysts with varied Au loading amounts are presented in Fig. 1S, supporting information. All the samples displayed diffraction peaks at 25.2°, 27.6°, 37.9°, 48.6°, 54.1°, 55.3° and 62.7°, respectively characterize the anatase and rutile phases of TiO₂ [44]. However, characteristic peaks of Pd were not identified, likely due to the small metal particle size and/or the low metal loading amounts. Additionally, only Pd-Au(4.3)/TiO₂ showed the diffraction peak of metal Au around 44.4° [45], reflecting more exposed Au particles which may ascribe to the lower Pd surface coverage on Au particle.

The Pd-Au bimetallic nanostructure was tested by UV-vis and the UV-vis spectra of monometallic and Pd-Au bimetallic catalysts are shown in Fig. 2 and Fig. 2S, supporting information. All samples presented strong absorbance below 400nm, attributed to anatase and rutile phases of support TiO₂ [46]. Additionally, there was another peak around 550 nm for Au(1.0)/TiO₂ while no peak was observed for Pd/TiO₂, reflecting that only metal Au particles exhibited surface plasmon resonance. Comparing with Au(1.0)/TiO₂, Pd-Au(1.0)/TiO₂ displayed a much weaker absorbance peak, which may due to the surface of Au particles covered by Pd atoms and resulted in the disappearance of Au plasmon band, conforming that metal Pd tended to site grow on Au ensemble and formed Pd shell-Au core like bimetallic nanostructure. For bimetallic catalysts, the absorbance peak become stronger with Au loading, reflecting decreased Pd surface coverage and increased exposed Au species with Au loading.

TEM images and histograms of metal particle size distributions of monometallic Au catalysts with varied Au loadings are shown in Fig. 2S, supporting information. Increasing Au amount from 0.5 to

4.3%, the metal particle size increased from 5.8 to 10.1 nm, implying that Au particles aggregated and formed larger Au ensembles with the loading amount gradually. TEM images and histograms of metal particle size distributions of Pd/TiO₂, Au(1.0)/TiO₂ and the bimetallic catalysts are shown in Fig. 3. The calculating metal particle sizes are listed in Table 1. For all samples, TiO₂ particles with irregular shape and sizes around 30-40 nm were clearly observed. The average metal particle was 4.7 nm for Pd/TiO₂, much smaller than that of Au(1.0)/TiO₂ (8.4 nm). In addition, the monometallic and bimetallic catalysts with the same Au loadings exhibited similar metal particle size. For example, the metal particle sizes were 5.8, 8.4, 9.3 and 10.1 nm for Au(0.5)/TiO₂, Au(1.0)/TiO₂, Au(2.1)/TiO₂ and Pd-Au(4.3)/TiO₂, respectively, suggesting that Pd mainly coated on metal Au instead of forming discrete Pd particles on TiO₂ directly.

To further study the morphology of the bimetallic particles in the catalysts, EDS elemental mapping was performed on Pd-Au(1.0)/TiO₂, and the images are compared in Fig. 4. The high intensity signal of Ti and O elements can be clearly tested and the Pd and Au intensity profiles were collected from a spherical particle of 8.5 nm (Fig. 4a). The elemental mapping of Au showed a sphere with higher atomic density in the center region, and a similar distribution of Pd element to that of Au element was observed. Besides, the signal of Pd and Au elements displayed in the same region, the excellent overlapping of element Pd on Au suggested that Pd and Au were in close contact, confirming the site-specific deposition of Pd on Au rather than on TiO₂. In addition, Pd element showed uniform and much lower atomic density than that of Au element, implying a high Pd dispersion on the surface of Au particle.

Pd dispersions were evaluated by H_2 chemisorption and the results are compiled in Table 1. Because metallic Au is incapable of adsorbing H_2 , the H_2 adsorption amounts only related to the

exposed Pd sites in the catalysts. All the bimetallic catalysts showed higher Pd dispersions than that of Pd/TiO₂ at the same Pd loading amounts, suggesting that metal Au facilitated the dispersion of Pd particles. Increasing Au content from 0.5 to 1.0%, Pd dispersion increased from 20.5 to 25.8%, while further increase Au content to 4.3%, Pd dispersion decreased to 17.2%. Notably, for Pd-Au(4.3)/TiO₂, Pd dispersion was similar to the monometallic Pd catalyst, reflecting that Pd dispersion could not be improved over large Au aggregates. In parallel, the H₂ adsorption amount first increased and then decreased with Au content and the maximum value was observed on Pd-Au(1.0)/TiO₂.

The structural properties of metal Pd and Au are further verified by XPS analysis and the results are compared in Fig. 5 and Fig. 4S, supporting information, the relative parameters are shown in Table 2. Because the Pd $3d_{5/2}$ peak was overlapped by Au $4d_{5/2}$ peak, the surface properties of the Pd-Au bimetallic particles were identified using Pd 3d_{3/2} and Au 4 f_{7/2}. For Pd/TiO₂ and Au(1.0)/TiO₂, the binding energies were observed at 340.7eV and 83.7eV, respectively assigned to Pd 3d_{3/2} and Au 4f_{7/2} [47]. For the bimetallic catalysts, the binding energies of metal Pd had a negative shift with the increase of Au loading amount. Similarly, the Au binding energies also had a slight blue shift, resulted in enhanced electronegativity of the nanoparticles, reflecting electron transfer between Pd and Au. Lee et al. [48] and Yi et al. [49] studied the properties of Pd-Au bimetallic catalysts and also found blue shifts of binding energies in the bimetallic Pd-Au particles and proposed a charge compensation model that Pd loses sp-electrons and gains d-electrons while Au gains sp-electrons and loses d-electrons. Here, the electron transfer between Pd and Au could be described by the same mechanism. Notably, Pd-Au(0.5)/TiO₂ and Pd/TiO₂ showed the same Pd binding energy (340.7 eV), which can be explained by no intimate contact between surface Pd atoms and inner Au particles in Pd-Au(0.5)/TiO₂. In addition, the Pd/Au surface ratios are much higher than the Pd/Au bulk ratios, further implying that Pd particles mainly site deposited on the surface of Au and formed Pd-on-Au core-shell like structure.

3.2. Liquid phase catalytic reduction of bromate

3.2.1 Bromate reduction over mono- and bi-metallic catalysts

The liquid phase catalytic reduction of bromate over Pd/TiO₂, Au(1.0)/TiO₂ and Pd-Au(1.0)/TiO₂ are shown in Fig. 6. Notably, the catalytic activities of the catalysts differed with metals at a similar metal loading level. For example, after reaction for 50 min, negligible bromate conversion was observed on Au(1.0)/TiO₂, while approximately 49.5 and 94.6% of bromate was reduced on Pd/TiO₂ and Pd-Au(1.0)/TiO₂, respectively, suggesting that the bimetallic core-shell like catalyst had much higher catalytic activity than the monometallic ones. During the reaction, H₂ was adsorbed and dissociated into active H by the Pd active sites and formed Pd-H and/or β-PdH phase [35,50], which then converted BrO₃⁻ into Br⁻ [51]. The hydrogenation reduction of bromate over Pd-based catalyst are illustrated in Scheme 1. As indicated by H₂ chemisorption, Pd-Au(1.0)/TiO₂ had much higher H₂ adsorption amount than that of Pd/TiO₂ and Au(1.0)/TiO₂, providing more active sites in the reduction reaction and resulted in much higher bromate conversion.

3.2.2 Effect of Au deposition amount

To further research the activities of the core-shell like structure catalysts with varied Au core sizes, the catalytic hydrogenation reduction of bromate over bimetallic catalysts with different Au amounts are compiled in Fig. 7 (a). Increasing Au deposition amount from 0.5 to 4.3%, the catalyst activities first increased and then decreased and Pd-Au(1.0)/TiO₂ showed the highest activity. More insight into the active dependence of exposed active sites on Au core size can be obtained by comparing the TOF. The results are shown in Fig. 7 (b) and the TOF value displayed a volcano-like dependence on Au core size. For the liquid phase catalytic hydrogenation reactions over supported Pd catalyst, the affinity of Pd particles with the reactant and H₂ are considered to be the crucial steps [19]. Generally, lower Pd dispersion with larger Pd particle size facilitates H₂ solubility and formation of β -

PdH phase, thus exhibited stronger catalytic ability for H₂ activation [50]. For the bimetallic Pd-Au catalysts, Pd dispersion first increased and then decreased and resulted in negative peak like H₂ activation ability with Au core size. On the other hand, the affinity between Pd active sites and bromate varied with valence electron density of Pd particles. As evidenced by XPS analysis, Pd surface became electron-rich with Au content, which inhibited the hydrogenation reduction of bromate as a result of the electrostatic repulsion between the anionic reactant (BrO₃⁻) and Pd surface. Hence, for the bimetallic catalysts with Au core size larger than 8.4 nm, the activation of H₂ was enhanced while the adsorption of bromate over Pd particles was attenuate with the increase of Au core size, and finally resulted in reduced TOF, indicating that the surface adsorption was more important than the activation of H₂. However, Pd-Au(0.5)/TiO₂ had larger Pd particle size and attenuate electronegativity than that of Pd-Au(1.0)/TiO₂, but showed lower TOF value. For the Pd-on-Au bimetallic nanoparticles, different Pd islands formed on Au core with varied diameters, and more highly active Pd ensembles (as small as 2-3 Pd atoms) may form on larger Au core as a result of Pd-Au interaction [37]. In this study, Pd-Au(1.0)/TiO₂ had larger Au core size than that of Pd-Au(0.5)/TiO₂ and may show more active Pd ensembles as well as higher TOF value because of stronger Pd-Au interaction. Undoubtedly, more research should be warranted in the future to determine the Pd-Au coordination effect on the liquid phase catalytic activity.

3.2.3 Effect of bromate adsorption

For a heterogeneous catalytic reaction, the reaction was conducted on the surface of the catalyst, thus the role of bromate adsorption is extremely important. The catalytic reduction of bromate with different initial concentrations over Pd-Au(1.0)/TiO₂ was performed and the results are shown in Fig. 8 (a). The bromate reduction efficiency increased with the initial concentration, suggesting that the adsorption of bromate on the catalyst surface facilitated the hydrogenation reduction reaction. The

results can be described using the Langmuir-Hinshelwood model [52]:

$$r_0 = k\theta_s = k\frac{bC_0}{1+bC_0} \tag{4}$$

$$\frac{1}{r_0} = \frac{1}{kbC_0} + \frac{1}{k}$$
(5)

where r_0 is the initial reduction rate at bromate concentration of C_0 , θs is the coverage of bromate adsorption on the catalyst surface, *k* is the reaction rate constant, and *b* is the adsorption equilibrium constant for bromate.

The linear plot of $1/r_0$ with $1/C_0$ is shown in Fig. 8 (b), the good liner relationship (R²>0.98) indicated that the reduction of bromate could be well fitted by Langmuir-Hinshelwood model and bromate pre-adsorption on the catalyst surface was the rate-controlling step [53].

More insight into the role of bromate adsorption, the catalytic reduction of bromate was conducted with varied solution pH and the results are compiled in Fig. 9. Increasing the solution pH from 2.1 to 8.1, the initial reduction rate decreased from 105.5 to 3.18 mM $g_{cat}^{-1}h^{-1}$, implying that the reduction reaction was inhibited by increasing the solution pH. As suggested by IEP results, the catalyst surface was positively charged when pH was lower than 6.0 while negatively charged when pH>6.0. Therefore, the interaction between the catalyst surface and bromate changed from electrostatic absorption to electrostatic repulsion with solution pH, resulted in weaker adsorption and declined reduction rate of bromate.

4. Conclusions

In the present study, bimetallic Pd-Au/TiO₂ catalysts with different Au loading amounts were prepared by the stepwise photocatalytic deposition method and the liquid phase catalytic hydrogenation reduction of bromate over the catalysts was investigated. Characterization results showed that the bimetallic particles formed Pd-on-Au core-shell like nanostructure over TiO₂, and the

Pd dispersion first increased and then decreased with Au amount. At a similar metal deposition amount, the bimetallic catalyst presented much higher activity than the monometallic ones due to more accessible active sites. The catalytic activity first increased and then decreased with Au content and Pd-Au(1.0)/TiO₂ had the highest activity. In addition, TOF of bromate reduction exhibited a volcano-type activity with Au content, which can be explained by the changeable of H₂ activation ability and the adsorption interaction between the reactant and the surface of Pd nanoparticles. The electronic repulsion between the catalyst surface and bromate was enhanced with the reaction solution pH and the catalytic reduction of bromate can be well described by the Langmuir-Hinshelwood model, reflecting an adsorption controlled mechanism.

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Tables and Figures

Figure captions:

- Figure 1: Surface charge densities (ζ) of TiO₂, Pd(1.0)/TiO₂ and Pd-Au(1.0)/TiO₂ as a function of solution pH.
- Figure 2: UV-vis diffuse reflectance spectra of Pd/TiO₂, Au(1.0)/TiO₂ and Pd-Au(1.0)/TiO₂,
- Figure 3: (a) TEM images and (b) histograms of metal particle size distributions of the catalysts.
- Figure 4: (a) HR-TEM image of a Pd-Au particle on Pd-Au(1.0)/TiO₂ and the corresponding EDS elemental mapping of (b) Ti element (red), (c)O element (green), (d) Au element (pink), (e) Pd element (blue), (f) the overlapping of Pd and Au elements.

Figure 5: XPS profiles of Pd/TiO₂ and Pd-Au/TiO₂ with varied Au contents in Pd 3d region.

- Figure 6: Catalytic hydrogenation reduction of bromate over Pd/TiO₂, Au(1.0)/TiO₂, and Pd-Au(1.0)/TiO₂. Reaction conditions: pH 5.6. Catalyst dosage: 0.1 g l⁻¹, bromate concentration: 0.4 mM.
- Figure 7: (a) The catalytic hydrogenation reduction of bromate over Pd-Au/TiO₂ with varied Au contents. (b) TOF dependence on Au core size. Reaction conditions: pH 5.6. Catalyst dosage: 0.1 g l⁻¹.
- Figure 8: (a) The catalytic hydrogenation reduction of bromate at different initial bromate concentrations and (b) linear plot of 1/r₀ versus 1/C₀. Reaction conditions: pH 5.6. Catalyst: Pd-Au(1.0)/TiO₂. Catalyst dosage: 0.1 g l⁻¹. Line represents the fitting curve using the Langmuir–Hinshelwood model.
- **Figure 9**: Initial activity of Pd-Au(1.0)/TiO₂ catalyst versus pH. Reaction condition: initial bromate concentration 0.4 mM, catalyst dosage: 0.1 g l⁻¹.

H۰ H۰ Pd BrO₃-Pd H_2 H٠ H٠ Pd Pd Au $Br^{-} + H_2O$ TiO₂ $BrO_3^- + 3H_2 \xrightarrow[1 \text{ atm, } 25 \text{ °C}]{} Br^- + 3H_2O$

Scheme 1. Reaction pathway of the catalytic hydrogenation reduction of BrO₃⁻

Figure 1:





Figure 3:

(a)





Figure 4:



Figure 5:







Figure 7:







Figure 9:



Samples	BET (m ² g ⁻¹)	Pd content (%)	Au ^a content ^a (%)	Particle size ^b (nm)	Pd dispersion ⁽ (%)	H ₂ adsorption amount (μmol g ⁻¹)
Au(1.0)/TiO ₂	40.7	-	1.0	8.4	-	0
Pd/TiO ₂	40.9	0.99	-	4.7	17.1	7.9
Pd-Au(0.5)/TiO ₂	40.9	1.0	0.5	6.0	20.5	9.63
Pd-Au(1.0)/TiO ₂	40.6	1.0	1.0	8.2	25.8	12.1
Pd-Au(2.1)/TiO ₂	40.0	0.99	2.1	9.4	17.5	8.23
Pd-Au(4.3)/TiO ₂	41.1	0.98	4.3	10.1	17.2	7.96

Table 1. Properties of the monometallic and bimetallic catalysts ^{*a*}Determined by ICP.

^bCalculated from TEM.

^cCalculated from H₂ chemisorption.

Table 2. Parameters of XPS spectra of the catalysts

Samples	Pd 3d _{3/2}	Au 4f _{7/2}	Pd/Au bul	kPd/Au su	urface Surface concentration	atomic ion
			ratios	ratios	Pd (%)	Au (%)
Au(1.0)/TiO ₂	-	83.7	0	0		0.11
Pd/TiO ₂	340.7	-	- >	-	0.17	-
Pd-Au(0.5)/TiO ₂	340.7		2.0	2.6	0.21	0.08
Pd-Au(1.0)/TiO ₂	340.4	83.4	1.0	2.78	0.25	0.09
Pd-Au(2.1)/TiO ₂	340.2	83.5	0.48	1.36	0.19	0.14
Pd-Au(4.3)/TiO ₂	340.0	83.6	0.23	1.19	0.32	0.27