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# Formation of monometallic Au and Pd and bimetallic Au–Pd nanoparticles confined in mesopores via Ar glow-discharge plasma reduction and their catalytic applications in aerobic oxidation of benzyl alcohol

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# 1. Introduction

#### ABSTRACT

Successfully prepared via Ar glow-discharge plasma reduction, Au–Pd bimetallic nanoparticles were highly active in the selective oxidation of benzyl alcohol, showing a rate constant of  $0.50 h^{-1}$ , which was 12.5 and  $2\times$  that of Au and Pd monometallic catalysts, respectively. Characterization analyses attributed the enhancement in both activity and selectivity to a Pd-rich shell/Au-rich core structure with abundant surface-coordination-unsaturated Pd atoms of those effectively confined and well-dispersed Au–Pd nanoparticles. As a green, efficient, and safe protocol, plasma reduction outperformed conventional H<sub>2</sub> thermal reduction due to the different particle nucleation and growth mechanism, which afforded modified morphology and surface chemistry of metal nanoparticles. Further oxidation and re-reduction of plasma-reduced Au–Pd catalyst resulted in the atomic rearrangement of nanoparticles, leading to inferior catalytic performance.

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Tremendous efforts have been devoted to developing heterogeneous noble metal catalysts from the viewpoints of atomic efficiency and environmentally benign processes. Supported gold (Au) and palladium (Pd) nanoparticle catalysts have been investigated intensively [1-4] since the first successful CO oxidation over Au and the application of Pd in catalyzing aerobic oxidation of alcohols reported by Haruta et al. [5] and Blackburn and Schwartz [6], respectively. Bimetallic nanoparticles are of greater interest than monometallic ones for improving the catalytic properties due to synergetic effects between two elements. Recently, several research groups have examined supported Au-Pd bimetallic catalysts, which have remarkably enhanced catalytic activity and product selectivity in various alcohol oxidation reactions. Enache et al. reported an extraordinarily high TOF (269,000 h<sup>-1</sup>) of Au-Pd/TiO<sub>2</sub> in 1-phenylethanol selective oxidation, showing that the combination of gold and palladium in an alloyed nanoparticle configuration led to a 25-fold improvement in catalytic activity [7]. The advantage of bimetallic catalysts is attributed not only to electronic interaction between the two metals but also to the complex structure of bimetallic nanoparticles. Several studies tested different bimetallic nanoparticle structures, such as core-shell structure [8], clusterin-cluster structure [9], and single-alloy structure [10]. Our group reported on Au–Pd bimetallic nanoparticles with a Pd-cluster-on-Au-cluster structure confined in a supercage of SBA-16 mesoporous materials, which exhibited excellent catalytic activity for benzyl alcohol oxidation [3].

Different preparation procedures may result in variation in the particle size, morphology, structure, and electronic properties of bimetallic nanoparticle catalysts, which significantly affect the metal–support interaction and consequently the catalytic performance. The pretreatment step, for example, reduction, is essential to obtain uniform and well-dispersed metallic active species. Conventionally, the catalysts are reduced by flowing hydrogen (H<sub>2</sub>) at elevated temperatures or by chemical reactants, such as formalde-hyde and hydrazine. Nonetheless, H<sub>2</sub> requires special care in production, transportation, storage, and use, while most chemical reducing agents currently employed in catalyst preparation are hazardous to both the human body and the environment. Our group previously reported a facile microwave-assisted polyol reduction (MAPR) method, in which ethylene glycol served as both solvent



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and reducing agent [4]; nonetheless, high temperatures and microwave radiation are required. Recently, a green, rapid, facile, and energy-efficient glow-discharge plasma reduction route for reducing supported metal catalysts using inert gas (Ar) as the plasma-forming gas has been reported [11–13]. This novel plasma reduction is carried out at ambient temperature, which significantly reduces the energy consumption and cost as well as emission of the toxic and hazardous materials.

Here, Ar glow-discharge plasma reduction was employed to synthesize monometallic Au and Pd and bimetallic Au–Pd nanoparticles confined in mesochannels of SBA-15 silicas. In view of the importance of alcohol dehydrogenation to ketone and aldehyde, which are valuable intermediates/products for the pharmaceuticals, agrochemicals, and perfumery industries [14–16], the solvent-free aerobic oxidation of benzyl alcohol to benzaldehyde is chosen as a model reaction to test the catalytic performance of plasma-reduced noble metal nanoparticle catalysts. The effects of plasma treatment on the structure/configuration and catalytic activity of nanoparticle catalysts were carefully examined and benchmarked against conventional  $H_2$  thermal reduction. Post-treatments (oxidation and re-reduction) were carried out to further reveal the stability of plasma-reduced bimetallic nanoparticles.

# 2. Experimental

# 2.1. Catalyst synthesis

SBA-15 mesoporous silica was purchased from the laboratory of Professor D. Y. Zhao (Department of Chemistry, Fudan University, People's Republic of China,  $S_{\text{BET}} \approx 600 \text{ m}^2/\text{g}$ ,  $d_{100} \approx 10 \text{ nm}$ ) [17] and calcined in air at 500 °C for 3 h to remove the adsorbed water prior to use. The monometallic Au and Pd and bimetallic Au-Pd catalysts confined in SBA-15 were prepared via conventional incipient-wetness impregnation with aqueous solutions of tetrachloroauratetrihydrate (HAuCl<sub>4</sub>:3H<sub>2</sub>O) and/or palladium nitrate dihydrate  $(Pd(NO_3)_2 \cdot 2H_2O)$ . The nominal metal loadings are 2 wt.% for monometallic Au or Pd catalyst and 2 wt.% Au-2 wt.% Pd for Au-Pd bimetallic catalyst. The plasma was applied to reduce the metal precursors, following the glow-discharge plasma setup and plasma reduction protocol previously reported [18,19]. Typically, the sample (0.4 g) was loaded onto a quartz boat and placed in a quartz tube (i.d. 35 mm) with two stainless steel electrodes (o.d. 30 mm). When the discharge tube was evacuated to 100 Pa, the glow-discharge plasma was generated by applying 1000 V to the electrodes using a high-voltage amplifier (Trek, 20/20B). The signal input for the high-voltage amplifier was supplied by a function/arbitrary waveform generator (Hewlett-Packard, Model 33120A) with a 100-Hz square wave. Ultrahigh-pure-grade argon (>99.999%) was used as the plasma-forming gas. The plasma reduction was operated for 10 min per cycle (eight cycles in total), with manual mixing of the sample at intervals between the treatments to ensure even exposure to the plasma. The bulk temperature of the plasma (measured by infrared imaging, Ircon modes 100PHT) was close to room temperature, indicating the negligible heating effect of the glow discharge. The obtained catalysts were denoted as Au/S15-p, Pd/S15-p, and AuPd/S15-p. For comparison, the impregnated AuPd/S15 catalyst was reduced in a H<sub>2</sub> flow (purified H<sub>2</sub>) of 20 mL min<sup>-1</sup> at 400 °C for 2 h and designated as AuPd/S15-H. To study the effect of posttreatment, AuPd/S15-p was subjected to reoxidation in an O<sub>2</sub> flow of 30 mL min  $^{-1}$  at 500 °C for 3 h, followed by re-reduction in a  $\rm H_2$ flow (5 vol.%  $H_2/He$  ) of 60 mL min  $^{-1}$  at 500  $^\circ C$  for 4 h, and designated as AuPd/S15-pO and AuPd/S15-pR, respectively. The same posttreatment procedures were also applied to AuPd/S15-H, which is denoted as AuPd/S15-HR. A diagram of the preparation procedure and sample denotation is presented in Scheme 1.

#### 2.2. Catalyst characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Man-2500 V/Pc diffractometer under ambient conditions using a filtered CuK $\alpha$  radiation source ( $\lambda = 1.54056$  Å) operated at 40 kV and 20 mA. Diffraction data were collected from 20° to 80° (2 $\theta$ ) at a scanning speed of 4°/min. Prior to the test, samples were dried overnight at 100 °C.

Transmission electron microscopy (TEM) measurements were taken on a Philips Tecnai G2 F20 system operated at 200 kV. The samples were suspended in ethanol and dispersed on a holey carbon-coated Cu grid. The mean particle diameter was calculated from the mean frequency distribution by counting ca. 200 particles according to  $d = \sum_{n_i}^{n_i \cdot d_i}$ , where  $\sum$  is the sum of *i* over the entire sample, and  $n_i$  is the number of particles with particle diameter of  $d_i$  in a certain range. The corresponding root-mean-square error  $\sigma$  was determined using the statistical expression  $\sigma(d) = \sqrt{\sum_{n_i=1}^{n_i(d-d_i)^2}}$ . Scanning transmission electron microscopy-energy-dispersive X-ray spectroscopy (STEM-EDX) was also conducted using the same equipment combined with a Sirion200 field emission scanning electron microscope. High-resolution TEM (HRTEM) was performed on a JEOL JEM-2010 operated at 200 kV, following the same sample preparation procedure as described above.

X-ray photoelectron spectroscopy (XPS) was performed on a VG Escalab 250 spectrometer equipped with an Al anode (Al  $K\alpha$  = 1486.6 eV). The background pressure in the analysis chamber was lower than  $1 \times 10^{-7}$  Pa. Measurements were taken using 20-eV pass energy, 0.1-eV step and 0.15-min dwelling time. The correction of the binding energy (BE) employed the C1s peak of adventitious C at 284.6 eV. The background contribution caused by an inelastic process was obtained by the Shirley method and subtracted. The curve-fitting was done with a Gaussian–Lorentzian function to deconvolute the overlapped peaks. The atomic ratios of the different elements were estimated using the ratio of the normalized peak intensities corrected with the atomic sensitivity factors (5.240 for Au4*f*, 4.462 for Pd3*d*, 0.711 for O1s and 0.283 for Si2*p*).

Diffuse reflectance Fourier transform infrared (DRIFT) spectra of adsorbed CO were obtained on a Tensor 27 spectrometer (Bruker) equipped with a liquid-nitrogen-cooled mercury–cadmium–tellurium (MCT) detector, a diffuse reflectance accessory, and a high-temperature reaction chamber (Praying Mantis, Harrick). The powder (7 mg) was loaded into the reflectance cell and purged with flowing helium (20 mL min<sup>-1</sup>) at 300 °C for 1 h to remove gas phase and weakly bound water. CO adsorption was carried out in 1.11 vol.% CO/He (20 mL min<sup>-1</sup>) for 30 min at 25 °C, followed by purging with He (20 mL min<sup>-1</sup>) for another 30 min at the same temperature. The in situ DRIFT spectra were recorded for 64 scans at a 4 cm<sup>-1</sup> resolution and illustrated using Kubelka–Munk (K–M) units.

## 2.3. Catalytic activity

The solvent-free aerobic oxidation of benzyl alcohol using molecular  $O_2$  was carried out in a batch-type reactor operated under atmospheric conditions. Experiments were conducted using a three-necked glass flask (capacity 25 mL) precharged with benzyl alcohol and catalyst (benzyl alcohol/metal = 250/1 mmol/mg). The mixture was stirred using a magnetic stirrer and heated in a silicon oil bath. The system was equipped with a thermocouple to control the temperature and a reflux condenser. In each reaction run, the mixture was heated to 160 °C under vigorous stirring (stirring rate 1000 rpm). Oxygen was bubbled into the mixture at a constant flow rate of 20 mL min<sup>-1</sup> to initiate the reaction. After the allowed reaction time, the catalyst powder was filtered off and the liquid



Scheme 1. Sketch diagram of preparation procedures for Au, Pd, and Au–Pd catalysts with their corresponding structures.

organic products were analyzed using an Agilent 6890 gas chromatograph equipped with an HP-5 capillary column (30 m long and 0.32 mm in diameter, packed with silica-based SUPELCOSIL). Dodecane was used as an internal standard to calculate benzyl alcohol conversion and benzaldehyde selectivity. The conversion, selectivity, and quasi-turnover frequency (qTOF) are defined as follows: [Comp: Set the following three equations entirely roman]

conversion(%) =	moles of reactant converted
	moles of reactant in feed
selectivity(%) =	moles of product formed $\times 100\%$
	moles of reactant converted ^ 10070
$qTOF(h^{-1}) = \frac{1}{mol}$	moles of reactant converted
	es of total active sites × reaction time

# 3. Results

# 3.1. Monometallic Au/S15-p and Pd/S15-p and bimetallic AuPd/S15-p catalysts

During the plasma reduction, distinct color changes were observed for the samples: from pastel yellow to brown purple for Au/S15-p and from earth yellow to light gray for both Pd/S15-p and AuPd/S15-p, implying the formation of metallic nanostructures over SBA-15 support.

The wide-angle XRD patterns of these samples are shown in Fig. 1. A broad diffraction peak at ca. 22.4° is observed for all the samples and ascribed to the amorphous silica framework of SBA-15. Au/S15-p exhibits four diffraction peaks at 38.16°, 44.30°, 64.58°, and 77.54°, indexed to (111), (200), (220), and (311) reflections, respectively, for the face-centered cubic (FCC) lattice structure of Au (PDF# 65-2870). The peaks are sharp and intense, indicating good crystallinity of metallic Au. Pd/S15-p shows only one diffraction peak at 39.72°, assigned to Pd(111) reflection (PDF# 46-1043) that is weak and broad, indicating poor crystallinity with structural defects. The average particle size based on the (111) reflection using the Scherrer formula is 5.8 and 1.6 nm for Au/S15-P and Pd/S15-p, respectively. For bimetallic AuPd/S15-p, reflections assigned to both metallic Au and Pd are clearly seen individually, which rules out the possibility of a single-phase homogeneous Au-Pd alloy. Besides the predominant presence of Au-Pd bimetallic nanoparticles, the probability of sporadically dispersed Au and Pd monometallic nanocrystallites should also



Fig. 1. XRD patterns of representative Au, Pd, and Au-Pd catalysts.

be taken into consideration. The diffraction peaks of metal oxides are undetectable, suggesting that the Ar glow-discharge plasma can effectively reduce the metal cation to the metallic phase at room temperature [11].

The TEM micrographs of Au/S15-p. Pd/S15-p. and AuPd/S15-p. and their corresponding particle size distributions are depicted in Fig. 2. The highly ordered mesoporous structure of SBA-15 is well preserved after precursor impregnation and glow-discharge plasma reduction. For Au/S15-p (Fig. 2a), Au nanorods are formed along the channels of SBA-15, which are uniform in shape with a diameter of ca. 5.9 nm and an aspect ratio of around 4. Spherical Pd nanoparticles are highly dispersed and confined in the SBA-15 channels for Pd/S15-p. The average particle size is determined to be  $5.3 \pm 0.6$  nm, dramatically larger than the average size of single Pd crystalline particles calculated by XRD (1.6 nm), which can be ascribed to the fact that powder XRD is sensitive to the size of coherent domains, which can differ significantly from the particle size in the case of multiple crystals composed of smaller primary nanoparticles [20]. The different morphologies of nanostructures (nanorods for Au versus nanoparticles for Pd) obtained after reduction in glow-discharge plasma have been reported by Wang et al. and attributed to the intrinsic properties of different metals, such as surface energy and redox potential [12]. Bimetallic AuPd/S15-p also shows a spherical morphology with a narrow particle size distribution centered at 5.7 nm.



Fig. 2. TEM results for mono- and bimetallic catalysts: (a) Au/S15-p; (b) Pd/S15-p; (c) AuPd/S15-p; (d) AuPd/S15-H. 1, Low-resolution TEM image; 2, HRTEM image; 3, corresponding size distribution.

The HRTEM images are also depicted in Fig. 2. Au nanorods consist of multiple crystals, showing clear lattice fringes with d = 0.236 and 0.205 nm assigned to the (111) and (200) planes of Au, respectively (Fig. 2a-2), which is in good agreement with XRD results. Pd/S15-p exhibits a fringe distance of 0.227 nm (Fig. 2b-2), corresponding to the Pd(111) plane. Fig. 2c-2 shows that the bimetallic nanoparticles in AuPd/S15-p retain the FCC lattice structure without the structural incoherence assignable to separate monometallic phases. A subtle phase contrast at the fringe is observed, and the calculated lattice fringes of d = 0.235 and  $0.203 \ nm$  correspond to Au(111) and Au(200) facets, respectively. Surprisingly, no lattice facets assigned to Pd can be determined. The line-scan EDX analysis was carried out in the STEM model to further confirm the local composition and element distribution of the bimetallic nanoparticles. The EDX profiles of Au  $L\alpha$  and Pd  $L\alpha$ X-rays are plotted in Fig. 3a along the line for a representative individual nanoparticle (inset of Fig. 3a). The particle is ca. 6 nm in diameter, and both Au and Pd are detected, confirming the successful preparation of Au-Pd bimetallic nanoparticles. Different intensity profiles are shown: a volcano-like distribution with the maximum at the center for Au and a uniform distribution throughout the scanning track for Pd. The intensity of each element is assumed to be proportional to the atomic densities. A similar EDX result was obtained in our previously reported Au–Pd bimetallic catalysts and denoted as a structure of Pd clusters on an Au-rich core [3].

In addition to the bulk morphology and structure, additional information about the surface components of Au–Pd bimetallic nanoparticles was further derived by XPS measurements. The XPS spectra of Au4*f*, Pd3*d*, O1*s*, and Si2*p* core levels are shown in Fig. 4, and the surface compositions are summarized in Table 1. For AuPd/S15-p, BEs at 87.3 ( $4f_{5/2}$ ) and 83.5 ( $4f_{7/2}$ ) eV are characteristic of metallic Au, while two symmetric peaks at 340.6 ( $3d_{3/2}$ ) and 335.5 ( $3d_{5/2}$ ) eV are assigned to metallic Pd, suggesting the complete reduction of Au and Pd by Ar glow-discharge plasma. The expected Au/Pd molar ratio in bulk is 0.54. Nevertheless, AuPd/S15-p shows a significantly decreased ratio of 0.21, implying that the plasma-reduced Au–Pd bimetallic nanoparticles are surface-enriched in Pd. Hutchings and co-workers have attributed this Pd surface enrichment to the formation of a Pd(shell)–Au(core)



**Fig. 3.** The line-scan EDX intensity profiles of a single bimetallic particle of (a) AuPd/S15-p and (b) AuPd/S15-pR along the line. The inset is the corresponding STEM image.

structure [8]. The characteristic peaks for O1s and Si2p exhibit BEs consistent with SiO<sub>2</sub>. The surface O/Si atomic ratio is 2.69, which is higher than the bulk stoichiometric ratio of 2.0 due to the coverage of surface hydroxyl groups [21].

To summarize these XRD, TEM, HRTEM, EDX, and XPS analyses, a Pd-rich shell/Au-rich core structure can be proposed for AuPd/S15p catalysts. The so-called geared step-cycled reduction mechanism due to the different redox potentials of Au and Pd may explain the formation of such structures [3,22]: during the plasma reduction of Pd and Au cations, the preferential reduction of Au is favored via an electron transfer from Pd to Au because of the higher electronegativity of Au. Pd<sup>2+</sup> precursor acts as an electron-mediate and accelerates the reduction of Au cations. After the coalescence and growth of Au clusters, Pd cations are adsorbed onto Au surface and further reduced, creating a Pd shell/Au core structure. In addition, a reasonable explanation for the expansion of Pd facets is the pseudomorphically epitaxial growth of Pd on Au-rich cores, which has been suggested by Hori and co-workers [23].

Fig. 5 shows CO-adsorbed infrared spectra at room temperature on various catalysts. For Au/S15-p, a doublet at 2172 and 2119 cm<sup>-1</sup> due to gas-phase CO is observed upon introducing CO. CO linearly bonded to low-coordinated metallic Au sites (step sites over the Au surfaces and step sites at the interface of Au and the support) should show a characteristic peak at ca. 2100 cm<sup>-1</sup> [24]; and the residual Cl<sup>-</sup> after impregnation may change the electronic properties of Au and shift this adsorption peak to a higher frequency [25]. Here, the band at 2119 cm<sup>-1</sup> will be ascribed to a combination of gaseous CO and CO linearly adsorbed onto step sites of metallic Au<sup>0</sup> [24]. After gas-phase CO is removed, this absorbance is red-shifted to 2117 cm<sup>-1</sup>, with a substantial asymmetric tailing in the high-frequency region, suggesting a wide distribution of CO sites with different adsorption strengths [26].

Three distinct bands are clearly observed for Pd/S15-p after exposure to CO: (1) a band at  $2089 \text{ cm}^{-1}$  attributed to linear carbonyls on the (111) facet of Pd particles (designated as L); (2) a band at 1990 cm<sup>-1</sup> assigned to twofold bridged carbonyls on the (100) facet of Pd particles (designated as  $B_1$ ); and (3) a broad band at  $1948 \text{ cm}^{-1}$  corresponding to twofold bridged carbonyls on the (111) facet of Pd particles (designated as B<sub>2</sub>). The intensities of these absorbencies significantly increase at higher CO coverage. After 20 min of CO exposure, the intensities of the three bands no longer change, indicating the saturation of CO adsorption on Pd particles. Upon purging under He, the characteristic peaks assigned to gaseous CO completely disappear after 5 min. The intensities of other bands also decrease and red-shift to lower frequencies due to the decreased CO coverage. After purging with He for 30 min, only the features of L and B<sub>2</sub> remain, suggesting preferential and more stable carbonyl adsorption on Pd(111) facets than on Pd(100) facets. Furthermore, no band for Pd<sup>2+</sup> (between 2160 and  $2116 \text{ cm}^{-1}$ ) or Pd<sup>+</sup> (between 2114 and 2140 cm<sup>-1</sup>) can be seen, confirming the exclusive presence of surface metallic Pd species in Pd/ S15 [27].

AuPd/S15-p exhibits CO-DRIFT spectra characteristic of Pd, implying that Au may be covered (at least partially) by Pd in the bimetallic nanoparticles, which further suggests the possibility of a Pd-rich shell/Au-rich core structure. After purging under He for 30 min, L and B<sub>1</sub> CO bands red-shift from 2090 to 2085 and from 1944 to  $1939\,cm^{-1}$ , respectively, compared to monometallic Pd/ S15-p, which can be attributed to either a geometric or an electronic effect [28]. First, Pd crystallites form small islands and rough surfaces in the presence of Au cores, leading to weaker lateral interaction between adsorbed CO molecules (i.e., decreased dipole-dipole coupling in the adlayer). Second, due to the higher electronegativity of Au than of Pd, Pd donates electrons to Au and becomes electron-deficient, which is compensated for via increased back donation in the  $2\pi^*$  antibonding orbitals of adsorbed CO molecules. Therefore, not only has the Pd ensemble size been affected, but also the electronic properties of Pd have been modified in the presence of Au. The synergistic effect between Au and Pd on the local structure and active site distribution of bimetallic nanoparticles can also be semiguantitatively reflected by the intensity of bridge CO relative to linear CO  $((B_1 + B_2)/L)$  [19]. To exclude the interference of gaseous CO, the CO-DRIFT spectra of COdesorption after 30 min of He purging were employed to analyze the peaks. Outgassing at room temperature completely depletes the  $B_1$  band, and only the area ratio of  $B_2/L$  is calculated, showing 1.65 and 1.43 for Pd/S15-p and AuPd/S15-p, respectively. CO is preferentially bound linearly (L) on low-coordinated Pd atoms and the B/L ratio decreases for small particles due to the larger fraction of low-coordinated surface atoms [29]. In this study, although it shows a slightly larger particle size than Pd/S15-p (5.3 and 5.7 nm for Pd/S15-p and AuPd/S15-p, respectively), AuPd/S5-p possesses more exposed Pd atoms of low coordination (edge/corner sites), suggesting that the Pd nanocrystallites undergo a major restructuring, leading to large exposure of coordinationunsaturated Pd atoms.

The selective oxidation of benzyl alcohol with molecular O<sub>2</sub> was employed as a chemical probe reaction to examine catalytic performance of the plasma-reduced mono- and bimetallic catalysts. In the absence of catalysts, only 7.5% of benzyl alcohol converts due to noncatalytic oxidation. The SBA-15 support does not show any catalytic activity (8.1% conversion). The evolution of the catalytic performance with reaction time was studied and the results are illustrated in Fig. 6, and the yield of benzaldehyde is shown in Fig. S2. Monometallic Au catalyst possesses poor activity and quickly deactivates after 4 h, while both Pd/S15-p and AuPd/S15-p catalysts show monotonically increased benzyl alcohol conversions. After 8 h, only 25.7% conversion is achieved over Au/S15-p, and Pd/S15-p can convert 83.6% of



Fig. 4. XPS spectra of AuPd/S15-p, AuPd/S15-H, and AuPd/S15-pR: (a) Au4f; (b) Pd3d; (c) O1s; (d) Si2p.

# Table 1

Surface compositions calculated from XPS results of representative samples.

Sample	Surface atoms percentage (at.%) <sup>a</sup>				Surface Au/Pd ratio (at.%)	Surface O/Si ratio (at.%)	Relative abundance of Pd <sup>0</sup> and Pd <sup>2+</sup> (at.%)	
	Au	Pd	0	Si			Pd <sup>o</sup>	Pd <sup>2+</sup>
AuPd/S15-p	0.060 (0.56)	0.27 (1.47)	72.67	27.00	0.21	2.69	100.00	0
AuPd/S15-H	0.10 (1.01)	0.19 (1.03)	73.18	26.53	0.53	2.76	100.00	0
AuPd/S15-pR	0.10 (1.05)	0.29 (1.56)	73.01	26.59	0.36	2.75	59.29	40.71

<sup>a</sup> Values in parentheses are wt.%.



Fig. 5. DRIFT spectra of CO adsorbed at 25 °C on Au/S15-p, Pd/S15-p, AuPd/S15-p, and AuPd/S15-H. Sample exposed to 1.1 kPa CO for (a) 1 min, (b) 5 min, (c) 10 min, (d) 20 min, and (e) 30 min and purged with He for (f) 1 min, (g) 5 min, (h) 10 min, (i) 20 min, and (j) 30 min.

benzyl alcohol. AuPd/S15-p exhibits excellent catalytic activity, showing 100% conversion of benzyl alcohol. The plots in Fig. 6a are fitted with first-order reaction kinetics, and the rate constants are listed in Table 2. AuPd/S15-p shows a rate constant k of  $0.50 \pm 0.05 h^{-1}$ , which is  $12.5 \times$  that of Au/S15-p ( $0.04 \pm 0.01$ ) and  $2 \times$  that of Pd/S15-p ( $0.28 \pm 0.02$ ). The catalytic activity is also represented using qTOF (Fig. 6c). After the first 0.5 h of reaction, AuPd/S15-p shows a qTOF of ca. 27,000 h<sup>-1</sup>, which is more than twice that of monometallic Pd and Au catalysts. Therefore, besides excellent long-term stability, AuPd/S15-p also shows high catalytic activity.

The selectivity toward benzaldehyde differs remarkably among these catalysts (Fig. 6b). Benzaldehyde is produced dominantly (selectivity > 98%) over Au/S15-p during the first 3 h, followed by slightly decreased selectivity due to the overoxidation of benzaldehyde to benzoic acid, which occurs independent of the intervention of catalyst [30]. Pd/S15-p shows a low benzaldehyde selectivity of 59.0% after the first 0.5 h of reaction, with tremendous amounts of toluene as by-product. The selectivity increases with the reaction time, reaches its maximum at 3 h, and further deteriorates due to formation of benzoic acid. After 8 h of reaction, only 53.2% benzaldehyde selectivity remains, accompanied by the large quantity of benzoic acid due to overoxidation. AuPd/S15-p shows a good selectivity profile in between monometallic Au and Pd catalysts, which can be well maintained at high conversion up to 8 h.

The effect of reaction temperature from 120 to 160 °C was also examined for these catalysts. In general, an elevated temperature leads to an increased reaction rate. The Arrhenius plot is shown in Fig. S1. The determined preexponential factors are  $1.44 \times 10^5$ ,  $5.95 \times 10^7$ , and  $2.87 \times 10^1$  for Au/S15-p, Pd/S15-p, and AuPd/S15p, respectively. The frequency factor A reflects the total number of collisions per unit time, while the rate constant k is the number of collisions that result in a reaction. Therefore, the ratio of k to A (k|A) is approximately the number of effective active sites for reactions. As shown in Table 2, A is large while k is rather small for Au/ S15-p, implying that most collisions cannot initiate the reaction due to insufficient effective active sites. In contrast, Pd/S15-p shows the highest k/A ratio due to the abundance of effective active sites. AuPd/S15-p possesses a moderate number of active sites. The information derived from the k/A ratio complements the true activation energy  $E_a$  measured according to the rate constant k (as listed in Table 2). Au/S15-p exhibits a remarkably high  $E_a$  of 75.7 ± 2.9 kJ/mol, demanding a high-energy input to initiate the reaction, which is consistent with its low catalytic activity. In contrast, the  $E_a$  for Pd/S15-P is extremely low (16.7 ± 0.7 kJ/mol), suggesting an easily initiated reaction. Nonetheless, mass-transport limitation and reactant diffusion resistance may be concerned when the surface reaction occurs much faster than reactant adsorption and/or product desorption [3]. The calculated  $E_a$  for AuPd/S15-p (45.1 ± 4.2 kJ/mol) is moderate to readily initiate the reaction as well as to obtain an optimal reaction–diffusion balance. Additionally, this  $E_a$  is remarkably higher than that of SBA-16-supported Au–Pd catalyst (16.7 kJ/mol) in our previous report [3], indicating that the ordered arrangement of mesochannels of SBA-15 exhibits less resistance for electric charge and ion diffusion than that of SBA-16.

To clarify the origin of toluene and the reaction mechanism, we studied the catalytic performance in 1 h of reaction time over these three catalysts in a N<sub>2</sub> atmosphere. The results are depicted in Fig. 6d-f. When benzyl alcohol was exposed to the anaerobic conditions, benzaldehyde and toluene were both produced, implying a dehydrogenation mechanism in which benzaldehyde formation occurs in the absence of oxidant. Au catalyst shows the highest selectivity (>65%). For Pd/S15-p, 43.4% benzaldehyde and 56.6% toluene are produced after first 10 min. Benzaldehyde is generated as a subordinate component until 50 min of reaction, accompanied by a large amount of toluene. Mixing Au with Pd can remarkably suppress the formation of toluene over Pd catalyst, implying that toluene is generated via either a hydrogen transfer or an oxygen transfer mediated by surface-enriched Pd over AuPd/S15-p with a Pd-rich shell/Au-rich core structure [30]. Fig. 6f shows that toluene and benzaldehyde are generated in almost equimolar amounts in the initial stage of reaction over AuPd/S15-p, implying that the disproportionation of benzyl alcohol occurs even at very low conversions. The initial rates, which are determined from the slopes of the conversion curves at zero conversions under aerobic (O<sub>2</sub>) and anaerobic (N<sub>2</sub>) conditions, are summarized in Table 2. It is noteworthy that for these three catalysts, the initial rates are one order of magnitude higher under O2 than under N2, indicating the essential role of  $O_2$  in benzyl alcohol oxidation. Pd itself shows  $r_0$  comparable to that of Au-Pd bimetallic catalyst under N<sub>2</sub>, further suggesting that Pd is dominantly responsible for the reaction over AuPd/S15-p. After O<sub>2</sub> is introduced, Au-Pd bimetallic nanoparticles remarkably enhance the initial rate, showing an increasing rate of benzyl alcohol disappearance and benzaldehyde appearance.



**Fig. 6.** The time–activity profile for selective benzyl alcohol oxidation under aerobic conditions for (a) benzyl alcohol conversion; (b) benzaldehyde selectivity; (c) and qTOF and under anaerobic conditions for (d) Pd/S15-p; (e) Au/S15-p; and (f) AuPd/S15-p. Reaction conditions: benzyl alcohol/metal = 250/1 mmol/mg; O<sub>2</sub>(N<sub>2</sub>), 20 mL min<sup>-1</sup>; temperature, 160 °C.

Table	2
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The average particle size and kinetic parameters of benzyl alcohol oxidation under anaerobic and aerobic conditions.<sup>a</sup>

Catalyst	Particle size (nm) <sup>b</sup>	$E_{\rm a}  (\rm kJ/mol)^{\rm c}$	$A (h^{-1})^{c}$	Rate constant $k$ $(h^{-1})^d$	Initial rate $r_0$ (mol/h)	
					Anaerobic	Aerobic
Au/S15-p	5.9(D)	75.7	5.95E7	0.04	0.0009	0.010
Pd/S15-p	5.3	16.7	2.87E1	0.28	0.0027	0.022
AuPd/S15-p	5.7	45.1	1.44E5	0.50	0.0042	0.039
AuPd/S15-H	5.8	e		0.36	-	0.025
AuPd/S15-pO	13.9	-		0.28	0.0024	0.028
AuPd/S15-pR	6.7	_		0.33	0.0021	0.033

<sup>a</sup> Reaction conditions: benzyl alcohol/metal = 250/1 mmol/mg; O<sub>2</sub>(N<sub>2</sub>), 20 mL min<sup>-1</sup>; temperature, 160 °C.

<sup>b</sup> Determined from TEM results.

<sup>c</sup> Determined from Arrhenius plots  $\ln k = -\frac{E_a}{RT} + \ln A$ .

 $d^{d}$  k is determined for reaction under aerobic conditions.

e Not determined.

#### 3.2. Plasma reduction vs. H<sub>2</sub> thermal reduction

Au–Pd bimetallic catalyst was also prepared by conventional thermal reduction under hydrogen and was denoted as AuPd/S15-H. The XRD pattern of AuPd/S15-H catalyst, as depicted in Fig. 1, is similar to that of AuPd/S15-p. The (111), (200), (220), and (311) reflections of Au and the (111) reflection of Pd are clearly identified, suggesting the FCC lattice structure of AuPd/S15-H. However, the peak intensity of AuPd/S15-H is much lower than that of the plasma-reduced sample, implying unsatisfactory crystallinity after  $H_2$  reduction. No characteristic peaks of PdO can be observed.

The morphology of AuPd/S15-H bimetallic nanoparticles is more directly shown in the TEM micrograph in Fig. 2d-1. Spherical nanoparticles are highly dispersed on SBA-15, and the average particle diameter of AuPd/S15-H (ca. 5.8 nm) is similar to that of AuPd/S15-p. Nonetheless, the particle size distribution is remarkably broad. A noticeable fraction of particles are smaller than 2 nm, and many particles are larger than 12 nm (Fig. 2d-3). HRTEM results show that the particle exhibits a decahedral multiply twinned structure for AuPd/S15-H, and each twinned part maintains the FCC structure. Fig. 2d-2 presents two twinned boundaries of a multiply twinned particle, which is distinctly different from the Pd-rich shell/Au-rich core structure of AuPd/S15-p. The lattice fringe assigned to the Au(111) facet is determined as 0.236 nm, which is consistent with the value derived from the XRD pattern.

The surface compositions of AuPd/S15-H were also examined by XPS measurements. As depicted in Fig. 4, AuPd/S15-H exhibits XPS spectra of Au4*f*, Pd3*d*, O1*s*, and Si2*p* core levels similar to those of AuPd/S15-p. The bimetallic nanoparticles after H<sub>2</sub> thermal reduction consist exclusively of metallic Au<sup>0</sup> and Pd<sup>0</sup> species. The surface Au/Pd ratio of AuPd/S15-H is determined as 0.53, which is almost identical to the nominal bulk ratio (0.54), suggesting the absence of preferential enrichment of Au or Pd on the surface. We speculate that there is a possibility of aggregated bimetallic nanoparticles with irregular Au–Pd distribution. The surface O/Si atomic ratio is 2.76, which is also contributed to by the surface coverage of hydroxyl groups [21].

CO-adsorbed DRIFT results are illustrated in Fig. 5. Despite similarity to the CO-DRIFT spectra of AuPd/S15-p, the IR bands of AuPd/S15-H are sharper, implying stronger adsorption of CO, which can be attributed to either smaller particle size or weaker metal-support interaction [13]. Upon introducing CO, both linear-(L) and bridge-bound (B<sub>1</sub> and B<sub>2</sub>) CO bands appear. After 30-min He purging, B<sub>1</sub> disappears, indicating unstable carbonyl adsorption on the Pd (100) facet. The L band is centered at 2089 cm<sup>-1</sup>, which is in accordance with AuPd/S15-p. Nonetheless, B<sub>2</sub> shows a higher frequency (1946 cm<sup>-1</sup>) than AuPd/S15-p, which is attributed to a geometric or electronic effect. The intensity of bridge-bound CO relative to linear-bound CO ((B<sub>1</sub> + B<sub>2</sub>)/L) of AuPd/S15-H is determined as 0.8, suggesting the high abundance of low-coordinated Pd atoms due to the noticeable fraction of small particles that contribute dominantly to the linearly binding CO.

The catalytic behavior of AuPd/S15-H was examined for the selective oxidation of benzyl alcohol under aerobic conditions, as shown in Fig. 7. Although AuPd/S15-H possesses a similar average particle size, the catalytic activity is poorer than that of AuPd/S15-p. The rate constant and the initial rate are determined as  $0.36 \pm 0.04$  h<sup>-1</sup> and 0.025 mol/h, respectively (Table 2). Wang and co-workers have proposed that benzyl alcohol molecule is adsorbed via such a conformation that the benzene ring is parallel to the terrace sites, while the  $\beta$ -H is attached to the edge/corner sites; that is, the adsorption needs terrace atoms, while the  $\beta$ -H cleavage requires the edge/corner sites. Thus, a balance of terrace to edge/corner atoms is critical, which favors both adsorption of benzyl alcohol and subsequent  $\beta$ -H cleavage [31]. It is noteworthy



**Fig. 7.** The activity profile for selective benzyl alcohol oxidation using molecular  $O_2$  over AuPd/S15-p and AuPd/S15-H: (a) benzyl alcohol conversion; (b) benzaldehyde selectivity. Reaction conditions: benzyl alcohol/metal = 250/1 mmol/mg;  $O_2$ , 20 mL min<sup>-1</sup>; temperature, 160 °C.

that the selectivity toward benzaldehyde is also poor over AuPd/ S15-H and the best selectivity obtained at 3 h (82.4%) is ca. 15% lower than over AuPd/S15-p. A large amount of benzoic acid is produced and only 16% selectivity toward benzaldehyde remains after 8 h. It was proposed that only selected sites allow the desorption of benzaldehyde, implying that the benzaldehyde selectivity is dependent on the particle size as well as the active site distribution [32]. AuPd/S15-H has a large number of particles small in diameter, which shows high oxygen heat of adsorption, that is, strong affinity for oxygen, and is prone to oxygen poisoning. According to the oxidative dehydrogenation reaction mechanism, the metal surfaces will be covered with dehydrogenation products, such as organic substrates/intermediates, oxygen, and hydrogen. As the reaction proceeds, the concentration of benzyl alcohol decreases and excess amounts of oxygen occupy the metal surfaces, leading to the overoxidation of benzyl alcohol to benzoic acid and thereby the sharply decreased selectivity.

# 3.3. Effect of post-treatment of AuPd/S15-p

These results have verified the superiority of Ar glow-discharge plasma treatment to conventional H<sub>2</sub> thermal reduction. To further understand the nature of bimetallic nanoparticles formed under plasma reduction, we introduced the post-treatment of the assynthesized AuPd/S15-p, that is, O<sub>2</sub> calcination of AuPd/S15-p (AuPd/S15-pO) followed by H<sub>2</sub> thermal reduction at 500 °C for 4 h (AuPd/S15-pR). The effect of post-treatment was examined by the following characterizations and catalytic tests.

The wide-angle XRD patterns of AuPd/S15-pO and AuPd/S15-pR are depicted in Fig. 1. In both samples, Au exists as a metallic phase

with a slight shift toward high angle for the characteristic peaks, implying a shrunken lattice constant and possible lattice contraction. For AuPd/S15-pO, the peaks assigned to metallic Pd<sup>0</sup> completely disappear. An intense peak at 33.76° and four weak diffraction peaks at 41.92°, 54.58°, 60.16°, and 71.48° appear, which are indexed to (101), (110), (112), (103), and (211) reflections of the tetragonal PdO lattice (PDF # 41-1107). Therefore, PdO is the predominant phase after reoxidation under O<sub>2</sub>. The diffraction peaks are sharp and intense, suggesting the aggregation of PdO particles to a certain extent during the oxidative thermal treatment. For AuPd/S15-pR, a shoulder peak at 39.5° assigned to the Pd(111) plane appears. Surprisingly, the diffraction peaks of PdO only become weak and broad rather than disappearing, implying the incomplete reduction of PdO. This is in contrast to the exclusive presence of the metallic Pd<sup>0</sup> phase for monometallic Pd/S15 synthesized via the same preparation procedure in the previous report [11] and can be attributed to the synergistic interaction between Pd and Au. Introducing Au may effectively hinder the decomposition of PdO to Pd at high temperatures [33]. Doping Au with Pd is also suggested to "protect" TiO<sub>2</sub> support under reducing atmosphere [34]. From the XRD pattern, we suggest that the structure of the nanoparticles in AuPd/S15-pR (Au, Pd, and PdO) is ill defined; nonetheless, the presence of a homogeneous phase of Au-Pd alloy can be ruled out due to the individual peaks for Au and Pd.

The nanoparticle morphology and structure of AuPd/S15-pO and AuPd/S15-pR, as well as their corresponding size distributions, are directly shown in Fig. 8. Only large particles exist for AuPd/S15-pO (13.9  $\pm$  3.3 nm), suggesting the substantial aggregation of Au and/or PdO nanoclusters. The HRTEM image in Fig. 8b-2 shows the lattice constants *d* = 0.235 and 0.266 nm, corresponding to the Au(111)

and PdO(101) planes, respectively. After H<sub>2</sub> re-reduction, AuPd/ S15-pR shows an improved particle size distribution. Lattice facets corresponding to Au(111) (d = 0.233 nm) and Pd(111) (d = 0.225nm) can be observed in Fig. 8c-2. Fig. 3b shows the EDX profiles of Au L $\alpha$  and Pd L $\alpha$  X-rays plotted along the line for a representative individual nanoparticle over AuPd/S15-pR. In contrast to AuPd/S15p, Pd in AuPd/S15-pR displays a profile similar to that of Au, and the intensity along the entire line scans is strong. Therefore, Au and Pd should coexist in bimetallic nanoparticles, with Pd/PdO clusters covering on the small Au core.

AuPd/S15-pR shows XPS spectra of Au4f, O1s, and Si2p core levels similar to those of AuPd/S15-p, as depicted in Fig. 4. The Pd3d spectrum consists of two asymmetric peaks attributed to  $Pd3d_{3/2}$ and  $Pd3d_{5/2}$  core levels (Fig. 4b). In addition to the characteristic peaks assigned to metallic Pd<sup>0</sup>, two small peaks around 341.3 and 336.4 eV corresponding to Pd<sup>2+</sup> species appear after deconvolution. The calculated abundance of surface Pd<sup>2+</sup> is 40.71%. The Au4f spectrum shows that Au remains in the metallic phase. The peaks of both metallic Au<sup>0</sup> and Pd<sup>0</sup> shift to lower BEs due to the increased number of Au-Pd bonds as the Au core becomes smaller, which is consistent with the EDX results. After H<sub>2</sub> re-reduction, the residual oxide species on the topmost Pd layer may induce the inner Pd atoms at the Au-Pd interface to become partially positively charged, which significantly affects the Au-Pd bonding strength and thereby imposes a strong impact on the bimetallic synergistic interaction. The surface Au/Pd atomic ratio of AuPd/ S15-pR (0.36) is higher than that of AuPd/S15-p (0.21), which corresponds to a Pd surface enrichment with larger abundance of surface Au<sup>0</sup> species.

CO-adsorbed DRIFT spectra of AuPd/S15-pO and AuPd/S15-pR are illustrated in Fig. 9. For AuPd/S15-pO, besides the gaseous CO



Fig. 8. TEM results for different bimetallic Au-Pd catalysts: (a) AuPd/S15-p (for comparison); (b) AuPd/S15-pO; (c) AuPd/S15-pR. 1, Low-resolution TEM image; 2, HRTEM image; 3, corresponding size distribution.

band at 2172 cm<sup>-1</sup>, only two adsorption bands at 2113 and 1956 cm<sup>-1</sup> appear. The higher-wavenumber band can be assigned to CO adsorbed onto  $Pd^{2+}$  sites and the lower-frequency band is due to Pd<sup>+</sup>-CO-Pd<sup>+</sup> species [35]. Both bands show a remarkable red-shift to 2168 and 1948 cm<sup>-1</sup>, respectively, when purged under He for 5 min, which can be assigned to L and B<sub>2</sub> bands of CO adsorption on metallic Pd<sup>0</sup> sites formed by the slow reduction of PdO during CO adsorption and He outgasses (the peaks assigned to gaseous  $CO_2$  appear and are not shown here). Moreover, both bands undergo a slight blue-shift compared to AuPd/S15-p, which is contributed by the electronic effect associated with the weakened surface CO bond; that is, the compression of the CO adlayer by surface oxygen species (PdO) leads to higher frequencies. The band  $B_1$  is undetectable, implying the absence of exposed Pd(100) facets, which is consistent with the exclusive presence of PdO after O<sub>2</sub> reoxidation. The calculated intensity of bridgebound relative to linear-bound CO (B/L = 5.55) is higher than for AuPd/S15-p (1.43), indicating that the bimetallic nanoclusters in AuPd/S15-pO predominantly consist of close-packed planes with few low-coordinated atoms due to the large particles and poor dispersion (13.9 ± 3.3 nm). After re-reduction, AuPd/S15-pR shows CO-DRIFT spectra similar to those for AuPd/S15-p. Notably, the B<sub>1</sub> band appears when CO gas is introduced, which suggests the exposure of Pd(100) facets and confirms the atomic rearrangement after re-reduction. The B/L value of AuPd/S15-pR is 1.81, which is slightly higher than that of AuPd/S15-p due to the slight increase in particle size (6.7 ± 0.9 nm).

The catalytic activities of AuPd/S15-pO and AuPd/S15-pR are compared with that of AuPd/S15-p in Fig. 10. The conversion plots are fitted with first-order reaction kinetics, showing the rate constants k as 0.28 ± 0.04 and 0.34 ± 0.08 h<sup>-1</sup> for AuPd/S15-pO and AuPd/S15-pR, respectively. The initial rates  $r_0$  are 0.028 and 0.033 for these two samples, as listed in Table 2. Reoxidation and subsequent re-reduction show catalytic performances inferior to those of plasma-reduced AuPd/S15-p catalyst due to the modified morphology and surface chemistry of catalyst after post-treatments. O<sub>2</sub> reoxidation of AuPd/S15-p leads to an apparent deterioration of activity, particularly a depressed initial reaction rate. Metallic Pd<sup>0</sup>

is suggested to be more active than PdO and predominantly contributes to the high activity [36]. Our previous study also demonstrated that the initial reaction activity is intimately related to the surface Pd<sup>0</sup> concentration [4]. After reoxidation, AuPd/S15-pO consists exclusively of Au and PdO species. Consequently, an induction period is required to transform PdO into metallic Pd nanoparticles, which accounts for the low initial activity. The slightly higher selectivity toward benzaldehyde over AuPd/S15-pO is in accordance with the poor activity. Subsequent H<sub>2</sub> re-reduction can retrieve an initial activity comparable to that of AuPd/S15-p, implying the existence of surface Pd<sup>0</sup> species. However, the conversion reaches a plateau after 2 h, suggesting a rapid deactivation and declining stability, which is contributed by lower hydrogen uptake due to the higher abundance of surface Au on AuPd/S15-pR than on AuPd/S15-p. The  $\beta$ -H elimination producing carbonyl and surface hydride is known to be the rate-limiting step in the dehydrogenation of alcohols. Therefore, the weakened capability to adsorb surface metal hydride components may be responsible for the poor long-term stability. Nonetheless, the lower abundance of surface hydride species contributes to the high benzaldehyde selectivity by effectively suppressing the hydrogenolysis of benzyl alcohol to toluene, as shown in Fig. 10b.

The catalytic performances in N<sub>2</sub> over AuPd/S15-pO and AuPd/ S15-pR are recorded within 1-h reaction time, as depicted in Fig. 10c and d. A dehydrogenation mechanism is verified due to the formation of benzaldehyde in the absence of oxidant. As the solely detectable by-product over both catalysts, toluene is initially produced in a moderate amount rather than equimolar to benzaldehyde, suggesting that after post-treatments (reoxidation and/or re-reduction), the formation of toluene probably undergoes a hydrogenolysis step rather than disproportionation of benzyl alcohol, which is suppressed by smaller amounts of surface metal hydride. As listed in Table 1, the initial rates  $r_0$  over two catalysts under anaerobic conditions are similar (AuPd/S15-pO, 0.0024 mol/ h; AuPd/S15-pR, 0.0021 mol/h) and are only half of that of AuPd/ S15-p. The decreased exposure of Pd may account for the low initial activity, since Pd has been evidenced to be dominantly responsible in Au-Pd bimetallic catalyst.



Fig. 9. DRIFT spectra of CO adsorbed at 25 °C on AuPd/S15-pO and AuPd/S15-pR, with the results of AuPd/S15-p included for comparison. Sample exposed to 1.1 kPa CO for (a) 1 min, (b) 5 min, (c) 10 min, (d) 20 min, and (e) 30 min and purged with He for (f) 1 min, (g) 5 min, (h) 10 min, (i) 20 min, and (j) 30 min.



**Fig. 10.** The time–activity profile for selective benzyl alcohol oxidation under aerobic conditions for (a) benzyl alcohol conversion; (b) benzaldehyde selectivity and under anaerobic conditions for (c) AuPd/S15-pO; (d) AuPd/S15-pR. Reaction conditions: benzyl alcohol/metal = 250/1 mmol/mg;  $O_2(N_2)$ , 20 mL min<sup>-1</sup>; temperature, 160 °C.

# 4. Discussion

The structures of Au, Pd, and Au-Pd catalysts proposed previously are summarized in Scheme 1. AuPd/S15-p shows Pd-rich shell/Au-rich core structure with surface enrichment of coordination-unsaturated Pd atoms. The superior catalytic performance of AuPd/S15-p to monometallic Au and Pd catalysts can be addressed from the following two aspects. (i) The changed interatomic distance of Pd on the surface may have both geometric and electronic effects. Au can disperse/isolate Pd sites, preventing oxygen poisoning of Pd in the liquid-phase oxidation [10]. Au, with higher electronegativity, also withdraws electrons from Pd atoms, leading to an enhanced interaction of Pd atoms with the substrate and thereby improved activity and selectivity. Recently, it has also been reported that the presence of nanocontacts triggers electron transfer and localized charge redistribution in the contact region, which are highly attractive to charged organic molecules, resulting in the improvement of organic transformations [37]. (ii) As suggested by Mori et al., low coordination Pd surface sites (edges and/or corners) are more active than the highly coordinated terrace sites for  $\beta$ -H elimination, which is the rate-limiting step in the oxidative dehydrogenation of alcohols. In this study, AuPd/ S15-p with more surface-coordination-unsaturated Pd atoms, as evidenced by CO-DRIFT measurements, shows a strong positive effect toward  $\beta$ -H cleavage, thus leading to high activity.

Compared to AuPd/S15-p, both inferior structure and catalytic activity were observed over AuPd/S15-H prepared by conventional hydrogen thermal reduction (Scheme 1 and Fig. 7). The advantage of Ar glow-discharge plasma reduction over H<sub>2</sub> thermal reduction may be attributed to its plausible mechanism, involving two processes: (i) a direct process, in which the high-energy species

generated by the plasma, such as electrons and ions, directly reduce the metal ions through a recombination process; (ii) an indirect process involving the excitation (dissociation and ionization) of the chemisorbed water molecular to generate active species (e.g.,  $e_{aq}^-$ ) with strong reducibility, which is normally attributed to nonhydrogen glow-discharge treatment [38]. In both processes, metallic nanoparticles can be obtained with regular and uniform distributions.

Au-Pd bimetallic catalysts are speculated to undergo different atomic arrangements during Ar glow-discharge plasma treatment at room temperature and H<sub>2</sub> thermal reduction at elevated temperature. Meanwhile, we admit that the catalyst after plasma reduction may be unstable and undergo a subtle change once it is exposed to air. Due to the limitations of experimental conditions, we cannot follow the in situ plasma reduction process at this juncture and obtain real-time information on the catalyst. Therefore, we introduced post-treatment processes (further O2 reoxidation and H<sub>2</sub> re-reduction) on both AuPd/S15-p and AuPd/S15-H, and carried out control experiments for the corresponding Au-Pd catalysts. The structural information is illustrated in Fig. 1. AuPd/S15-H and AuPd/ S15-HR present similar XRD patterns, indicating the "stable" configuration of bimetallic nanoparticles formed by H<sub>2</sub> thermal reduction at high temperature. In contrast, the bimetallic Au-Pd nanoparticles in AuPd/S15-p experience a structural transformation from a Pd-rich shell/Au-rich core structure to a cluster-in-cluster structure. Their catalytic performances are also compared, as depicted in Fig. 11 and Fig. S3. As shown in Fig. 11a, the plots of conversion and selectivity almost coincide for AuPd/S15-H and AuPd/ S15-HR. Surprisingly, the plots in Fig. 11b exhibit the dramatic difference between AuPd/S15-p and AuPd/S15-pH. After post-treatment, the selectivity increases from 67.7% to 81.5% during the



**Fig. 11.** Catalytic performance of Au–Pd catalysts: (a) AuPd/S15-H and AuPd/S15-HR; (b) AuPd/S15-p and AuPd/S15-pR (solid, conversion; hollow, selectivity).

first 0.5 h, whereas the conversion decreases from 69.0% to 51.0% after 8 h. This evidence indirectly implies that during the Ar glow-discharge plasma reduction, the bimetallic nanoparticles undergo a different atomic arrangement of surface atoms, reaching a highly active but "unstable" structure that can be affected readily by post-treatment.

# 5. Conclusions

Bimetallic Au-Pd nanoparticles supported on SBA-15 mesoporous materials were prepared by Ar glow-discharge plasma reduction. The size of metal nanostructure (diameter of metal nanoparticles/nanorods) can be effectively controlled and tailored by the highly ordered mesopores of SBA-15 silica. Adding Au to Pd to form bimetallic Au-Pd nanocomposites well retains the morphology of spherical nanoparticles with a similar particle size distribution. As a green, efficient, and safe reduction method, plasma reduction outperformed conventional H<sub>2</sub> thermal reduction, showing uniform particle dispersions and size distributions. Characterization results suggested a Pd-rich shell/Au-rich core structure with abundant surface-coordination-unsaturated Pd atoms for the effectively reduced Au-Pd bimetallic nanoparticles, which accounted for the good catalytic activity in the selective oxidation of benzyl alcohol compared to Au and Pd monometallic catalysts. At 1 h of reaction, AuPd/S15-p shows a conversion of 47.4% and TOF of 16,375  $h^{-1}$ . We believe that the particle nucleation and growth mechanism in the plasma reduction process is different from H2 thermal reduction, affording modified morphology and surface chemistry of metal nanoparticles. Further oxidation and re-reduction of plasma-reduced Au–Pd catalyst resulted in the atomic rearrangement of nanoparticles, leading to inferior catalytic performance.

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