Chemical Nature of Microfluidically Synthesized AuPd Nanoalloys Supported on TiO$_2$

Ghazal Tofighi$^{1,4}$, Xiaojuan Yu$^{2,4}$, Henning Lichtenberg$^{1,3}$, Dmitry E. Doronkin$^{1,3}$, Wu Wang$^4$, Christoph Wölf$^1$, Yuemin Wang$^{2,*}$, and Jan-Dierk Grunwaldt$^{1,3,*}$

1 Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany
2 Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany
3 Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany
4 Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany

ABSTRACT: Metal oxide supported bimetallic AuPd nanoparticles (NPs) are known to exhibit significantly enhanced activity and selectivity in numerous reactions compared to their monometallic counterparts. An atomic-level understanding of the nature of AuPd nanoalloys is among the most important and challenging topics in catalysis and nanoscience. Here, colloidal monometallic Au and Pd as well as bimetallic Au$_x$Pd$_{1-x}$ NPs (~1 nm) with different Au:Pd ratios were synthesized in a continuous microfluidic reactor and then deposited on TiO$_2$. The structural, electronic and reactive properties of Au$_x$Pd$_{1-x}$/TiO$_2$ were first investigated by a multi-technique approach including scanning transmission electron microscopy, energy dispersive X-ray spectroscopy mapping, in situ X-ray absorption spectroscopy, FTIR spectroscopy, and X-ray photoelectron spectroscopy. Temperature-dependent IR spectroscopy using CO as a probe molecule provided deeper and solid evidence for the presence of a variety of active sites on the surface of monometallic Au and Pd NPs and Au$_x$Pd$_{1-x}$ nanoalloys. The results demonstrated consistently strong electronic interactions between Au and Pd upon alloying, leading to an interatomic charge transfer and electronic modifications in the d bands of Au and Pd. The Au$_x$Pd$_{1-x}$/TiO$_2$ sample with an Au:Pd ratio of 3:7 exhibited the highest catalytic activity in CO oxidation compared to the other alloys. This was attributed to a synergistic effect where the activation of dioxygen is facilitated at the Pd-enriched sites while both bimetallic Au and Pd sites chemisorb CO. Hence, the combination of microfluidic synthesis and advanced characterization including FTIR allowed deeper insights into the nature of AuPd nanoalloys for catalytic applications.

1. Introduction

For a long time, the most noble among all metals, gold, was not expected to exhibit significant catalytic activity. However, in the early 1990s Haruta et al. and then also other research groups demonstrated that small Au nanoparticles (NPs) with diameters of 1-5 nm, deposited on suitable support materials, are active in low temperature CO oxidation$^{6-8}$ and selective oxidation of propylene to propylene oxide in the presence of oxygen and hydrogen.$^9$ Since then, catalytic properties of Au NPs have attracted much attention with respect to many applications such as water-gas shift (WGS) reactions$^{10-12}$, reduction of nitrogen oxides$^{13,14}$, oxidation of alcohols$^{15,16}$, H$_2$O synthesis from H$_2$ and O$_2$,$^{17,18}$ aerobic oxidation of alcohol$^{19-21}$, selective hydrogenation of alkenes$^{22}$ etc. Particle size affects two essential factors for the catalytic activity of supported gold NPs: the number of low-coordination sites and the total length of perimeter sites at the metal-support interfaces. So far, it has been difficult to unambiguously distinguish these two effects, and unraveling the importance of the individual contributions to the synergistic catalytic performance remains to be a major challenge. Additionally, quantum size effects resulting from confining the metal electrons and strain effects reducing the lattice constant of small metal particles may contribute to the chemical activity of ultrasmall metal particles.$^1$ Alternatively, various catalytic properties can be obtained by combining different metals to synthesize intermetallic compounds and nanoalloys.$^{20,21}$ Alloing often leads to synergistic effects resulting in higher catalytic activity, and the variety of alloys with different compositions, structures and properties gives many degrees of freedom to design bi- or trimetallic catalysts for particular applications, especially in the field of structure-sensitive reactions.$^{3,22}$ Bimetallic AuPd catalysts have been extensively applied for synthesis of vinyl acetate$^{24-25}$, H$_2$O$_2$,$^{26,28}$ as well as alcohol and glucose oxidation.$^{29,30}$ Moreover, as Pd is already a key element in the well-established three-way catalyst due to its high CO oxidation activity at elevated
temperatures, addition of Pd to Au-based catalysts could be beneficial to improve the catalytic performance and durability of gold at high temperatures, while also inhibiting Au NP aggregation. With respect to CO oxidation, several publications reported that O\(_2\) dissociation, which in Au/TiO\(_2\) takes place at the interface of Au and TiO\(_2\), could be facilitated by the presence of Pd. In some cases, such bimetallic systems were found to exhibit improved stability and higher catalytic activity at low temperatures compared to monometallic Au and Pd catalysts. However, details of the involved mechanisms for charge transfer in small nanoalloys are still unclear. A deeper understanding requires a combination of well-defined homogenous nanoalloy materials and advanced characterization techniques.

The homogeneity of the alloy particles, or the extent of segregation, is strongly influenced by the synthesis procedure and post-synthetic treatment such as precursors, temperature and pressure, and also on the nanoalloy composition. Within the interdisciplinary field of colloidal chemistry, NPs with tailored physical and chemical properties determined by particle size and shape can be synthesized. Apart from conventional-stirred batch reactors, microfluidic reactors equipped with micromixers are able to achieve homogeneous and efficient mixing of the reactants at a short time scales (ms). These advantages have attracted considerable attention in recent years, and microfluidic systems are of pronounced interest as novel, powerful devices to produce monometallic and alloyed NPs in a profoundly controlled manner. This allows tailoring particle sizes, structures (e.g., homogeneous nanoalloys, core-(multi-) shell and segregated sub-cluster structures), and achieving narrow size distributions of the nanoalloys, a requirement for further tuning the desired catalytic properties.

Recently, we have studied the synthesis of Au and Pd NPs and also homogeneous Au\(_3\)Pd\(_4\) nanoalloys inside a novel microfluidic reactor. For the present study (note that this work was conducted in the frame of the PhD thesis by Ghazal Tofighii), such bimetallic NPs were deposited on TiO\(_2\) and the effects of alloying and Au-Pd interaction on surface properties. Next, the electronic structure and morphology were investigated using a multi-technique approach. Employing a novel ultrahigh-vacuum Fourier-transform infrared spectroscopy (UHV-FTIR) apparatus, a systematic in situ IR study using CO as probe molecule on Au/TiO\(_2\), Pd/TiO\(_2\), and Au-Pd/TiO\(_2\) at different temperatures was conducted on these well characterized systems. The temperature-dependent FTIRS data in conjunction with high-resolution XPS results provided new insights into the chemical nature of the Au-Pd interaction, allowing us to substantially advance the understanding of the mechanisms governing CO oxidation reactions on supported alloy particles.

2. Experimental Section

2.1 Materials

HAuCl\(_4\)·3H\(_2\)O (Roth, 99.5% purity), K\(_2\)PdCl\(_4\) (Alfa Aesar, 99.99% purity), polyvinylpyrrolidone (Sigma-Aldrich, average molecular weight 40 kDa), NaBH\(_4\) (Sigma-Aldrich, 99.99% purity), H\(_2\)SO\(_4\) (Sigma-Aldrich, 95% purity) and TiO\(_2\) (Evonik, commercially available Aeroxide P-25, anatase:rutile phase ratio of 80:20, surface area of 50 m\(^2\) g\(^{-1}\)) were used without further purification.

2.2. Microfluidic Reactor

In previous work, we have introduced a novel microfluidic setup providing a continuous flow of reactants at high flow rates which was successfully employed to synthesize highly monodisperse and ultrasmall Au, Pd and AuPd NPs. The setup shown in Figure 1 features a fluid delivery rack and a microfluidic chip consisting of 3 cyclone micromixers and a meandering microchannel. A nitrogen gas pressure of 13 bar acts as a driving force for the flow of reactants stored in corrosion-resistant stainless steel vessels. The vessel for the metal precursor solution is coated with polyethylene. For each reactant, a flow rate of 1.3 L h\(^{-1}\) was applied to approach turbulent mixing conditions for the reactant flow in the micromixers with a Reynolds number of 2400 (total flow rate 2.6 L h\(^{-1}\)). This provides efficient mixing in 2 ms which is essential for such rapid reduction reactions. The total residence time of the reactants in the microfluidic device amounts to 20 ms. The microfluidic chip consists of Si-bonded glass. Inlet and outlet ports and the cylinders for the cyclone micromixers were produced by laser drilling. The meandering channel (cross section: 300 x 300 \(\mu\)m\(^2\)) was produced by Si etching. The design of the microfluidic chip also allows in situ characterization of the NPs during synthesis using spectroscopic and scattering techniques.

Figure 1. Schematic of the microfluidic setup including reactant vessels and microfluidic chip for synthesis of the metal NPs and nanoalloys in continuous flow (F, T and P: Flowmeter, temperature sensor and pressure transducer). The microfluidic chip made of Si-glass bonded wafer is sandwiched between the stainless steel support parts.

2.3. Microfluidic Synthesis of Au, Pd and AuPd Nanoparticles

Monometallic Au and Pd NPs as well as AuPd nanoalloys were synthesized following a previously published procedure. In this colloidal route, the metal precursors are reduced under basic conditions (via NaBH\(_4\)) in the presence of PVP as a surfactant. Typically, an aqueous solution of mixed Au and Pd precursors (7.5 mM) with 666 mg PVP was prepared for all samples. The nominal molar Au:Pd ratio was 1:0, 7:3, 11:1, 37:1 and 61:1. A basic aqueous solution of NaBH\(_4\) (37.5 mM) with 666 mg PVP was prepared as the reducing agent. These two solutions were poured separately into the corresponding vessels of the
microfluidic setup. A total flow rate of 2.6 L h\(^{-1}\) (turbulent regime) at 13 bar N\(_2\) pressure (due to the high pressure drop) was used to push the reactants through the micro mixers and the microchannel. Afterwards, the nanoparticles were collected in a flask and magnetically stirred for 1 h in an ice/water bath.

2.4. Preparation of Au/TiO\(_2\), Pd/TiO\(_2\) and AuPd/TiO\(_2\) Catalysts

After dispersing 1 g TiO\(_2\) in 80 mL distilled water in an ultrasonic bath, the colloidal NPs obtained from the microfluidic reactor were added to the suspension at room temperature and stirred for 1 h. Before impregnating TiO\(_2\) with the NPs, the support was acidified with 0.1 M pure H\(_2\)SO\(_4\) solution (pH = 2). Subsequently, the suspension was centrifuged 4 times (4500 rpm, 5 min each) and washed with H\(_2\)O in between. Finally, the catalysts were dried at 353 K overnight and calcined at 673 K for 3 h in static air. This method was applied for preparing 2.4 wt.% Au/TiO\(_2\), Pd/TiO\(_2\) and AuPd/TiO\(_2\).

2.5. Characterization

2.5.1. Transmission Electron Microscopy

The catalyst powder samples were directly dispersed on Cu grids coated with holey carbon film. For colloidal samples, 5 μL of the diluted colloidal solution was dropped on a holey carbon Cu grid covered with 2 nm carbon film and then dried at room temperature. Microstructure and morphology of the sample materials were investigated by high resolution transmission electron microscopy (HRTEM) and high angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM). Composition was determined by energy dispersive X-ray spectroscopy (EDX) using an EDAX S-UTW EDX detector in a FEI Titan 80–300 microscope operating at 300 kV. Particle size statistics of the specimens were determined from the HAADF-STEM images by the ImageJ 1.49v software. Particle shaped were approximated with ellipsoids.\(^{45}\) STEM-EDX data were analyzed by the TEM Image & Analysis (TIA 4.7 SP3 version) software.

2.5.2. X-Ray Absorption Near Edge Structure (XANES)

XANES spectra of Pd/TiO\(_2\) and AuPd/TiO\(_2\) pellets at the Pd K-edge (24.350 keV) were acquired at room temperature in transmission mode at CAT-ACT\(^{46}\), a new wiggler beamline recently installed at the Karlsruhe Institute of Technology, using a Si (311) double crystal monochromator (beam size 1 × 1 mm\(^2\)) and ionization chambers. Higher harmonics were suppressed by a Rh-coated mirror downstream from the monochromator. Under the same conditions XANES data of the powder samples were acquired in situ (in quartz capillaries) under N\(_2\) flow (33 ml min\(^{-1}\) flow rate) during heating to 673 K at 5 K min\(^{-1}\). For raw data treatment the Athena program of the IFEFFIT software package\(^{47}\) was used.

2.5.3. FTIR Spectroscopy and X-Ray Photoelectron Spectroscopy (XPS)

The FTIRS and XPS measurements were performed with a sophisticated ultra-high vacuum (UHV) setup, combing a vacuum FTIR spectrometer (Bruker Vertex 80v) and a multi-chamber UHV system (Prevac). This apparatus allows both IR reflection-absorption spectroscopy (IRRAS) on model systems and IR transmission on powders.\(^{48-49}\) The AuPd/TiO\(_2\) powder samples were first pressed into an inert metal grid and then mounted on a sample holder specifically designed for temperature-dependent FTIR transmission measurements. Prior to the IR measurements, the samples were pre-treated by annealing at 673 K for 1 h under UHV conditions. Oxidation states were monitored using an XPS apparatus equipped with a VG Scienta 4000 electron energy analyzer before IR measurements. Al K\(_{α}\) (nonmonochromatic, 1486.6 eV) radiation was used as excitation source. The energy resolution was better than 1 eV with a pass energy of 200 eV. The binding energies were calibrated based on the C1s line at 284.8 eV as a reference. The XP spectra were deconvoluted using the Casa XPS program with a Gaussian-Lorentzian mix function, a Doniach-Sunjic function for metallic Pd\(^{50}\) species,\(^{50}\) and Shirley background subtraction. For a quantitative analysis of the relative surface concentration of Au and Pd, sensitivity factors of 9.58 for Au 4f\(_{7/2}\) and 9.48 for Pd 3d\(_{5/2}\) were used.\(^{50}\)

The TiO\(_2\)-supported metal particles were exposed to CO by using a leak-valve-based directional doser connected to a tube (inner diameter: 2 mm) terminating at a distance of 3 cm from the sample. IR spectra were recorded with a resolution of 4 cm\(^{-1}\) by using a spectrum of the clean sample as background reference. The temperature-dependent FTIR spectra were quantitatively analyzed by peak fittings in order to obtain normalized peak areas as a function of temperature.

2.5.4. CO Oxidation Test Procedure

CO oxidation was chosen as test reaction to assess the catalytic performance of the TiO\(_2\) supported metal NPs. CO oxidation experiments were performed two times after two different pre-treatment procedures: exposure to N\(_2\) at 673 K for 1 h and H\(_2\) pre-treatment (5% H\(_2\) in N\(_2\)) at 523 K for 1 h (10 K min\(^{-1}\) ramp rate in both cases). During the tests the catalysts were heated in a fixed-bed continuous-flow reactor (quartz tube, inner diameter 8 mm) in a temperature programmed mode from 303 K to 523 K at a ramp rate of 1 K min\(^{-1}\), 70 mg of 2.4 wt.% AuPd/TiO\(_2\) catalysts (sieve fraction 125–250 μm) were mixed with 930 mg SiO\(_2\) and then fixed between glass wool plugs in the tube (catalyst bed length ~15 mm, gas flow 600 ml min\(^{-1}\), gas hourly space velocity, GHSV: 48000 h\(^{-1}\)). The gas mixture contained 1000 ppm CO and 10% O\(_2\) in nitrogen (CO feed rate: 5.8 × 10\(^{-6}\) mol s\(^{-1}\) g\(^{-1}\)). The gas feed passed through a Messer Hydroisorb® cartridge to remove traces of water before reaching the reactor. Reaction products were analyzed using a UARAS 10E NDIR CO/CO\(_2\) analyzer. Each heating and cooling cycle was applied twice. Only the data acquired during the second cycle are shown in this paper. Turnover frequencies (TOFs) were calculated in the region between 3-17% CO conversion (for Au/TiO\(_2\) below 40% in the temperature range of 323-336 K) and based on the assumption that the reaction rate (r) did not depend on the CO concentration.\(^{8}\) For TOF calculations
the metal dispersion was estimated from mean NP diameters (determined by STEM).

3. Results and Discussion

3.1. Electron Microscopy and in situ XANES Spectroscopy under N₂ Flow

The different mono- and bimetallic NPs were all deposited on the same well-defined TiO₂ support in order to keep all parameters besides NP composition identical for comparability. STEM images allow characterizing particle shapes and sizes, as well as their aggregation, upon deposition and calcination. As an example, STEM images of colloidal Au₄Pd₃ NPs, supported/dried on TiO₂ and calcined sample with their corresponding histograms are shown in Figure S1. In this case, the average particle size increases from about 1 nm to 4 nm upon deposition on TiO₂ and further to 5 nm after calcination. A series of STEM images (Figure S2) shows the particle morphology and size distribution of NPs at different compositions deposited on TiO₂ after calcination at 673 K. The alloyed Au/Pd NPs, in particular the Au-rich alloys (Au₁Pd₉ and Au₅Pd₅) are notably smaller (5 and 6 nm) with narrower size distributions compared to Au/TiO₂ (11 nm). Due to low contrast in STEM image between oxidized Pd and the TiO₂ support in the calcined Pd/TiO₂ sample, the Pd NPs could not be unambiguously detected by electron microscopy. In case of Au₁Pd₅/TiO₂, precise determination of particle sizes is also difficult due to a segregated contiguous surface layer at the perimeter of the NPs on the support. STEM-EDX mapping (Figure 2) detected Pd in this segregated layer. Obviously, besides some Pd segregated out of the NPs, a certain amount of Pd is also located at the NP core together with Au, in accordance with the results of previous works. The HRTEM images of calcined Au/TiO₂, Au₅Pd₅/TiO₂ and Au₁Pd₉/TiO₂ catalysts in Figure S3 reveal the atomic structure of Au, Au₅Pd₅ and Au₁Pd₉ NPs. The measured d-spacing of the (111) lattice planes within Au₁Pd₅/TiO₂ and Au₅Pd₅/TiO₂ catalysts is slightly smaller compared to Au/TiO₂ (d-spacing (111)=2.33 Å) indicating a presence of alloy structure of Au₅Pd₅ NPs. In the Au-rich alloys, Au and Pd are distributed uniformly in the NPs. STEM images and elemental mapping indicate that, under the applied preparation conditions, alloying reduces NP agglomeration compared to monometallic Au and Pd NPs, and additionally keeps the Pd with Au in the nanoparticles, which could influence the catalytic performance.

In order to determine the initial oxidation state of Pd in calcined Pd/TiO₂ and AuPd/TiO₂ catalysts and to monitor changes in oxidation state during the annealing treatment (UHV, heating up to 673 K for 1 h and cooling down to room temperature), the samples were investigated by in situ XANES spectroscopy under N₂ gas flow during heating up to 673 K and cooling down to room temperature. Figure S4 shows selected spectra acquired during heating. The results indicate that oxidized palladium dominates in both samples at all temperatures. A comparable trend was also observed during cooling. Figure S4 shows that the spectra of the NP samples clearly differ from the absorption data of a Pd foil representing metallic Pd (i.e. oxidation state zero). The same applies to the ex situ Pd K-edge XANES data of pellet samples (see Figure S5a) which also show that with increasing Au content in the alloyed NPs, Pd gets more reduced (in accordance with FTIR results in section 3.3). The corresponding Au L₃-edge in Figure S5b shows a lower whiteline intensity for the alloyed AuPd compared to the Au NPs, in accordance with literature.

3.2. XPS Data

Figure 3 shows Au 4f and Pd 3d XP spectra of various AuₙPdₙ/TiO₂ samples (x:y = 1:0, 7:3, 1:1, 3:7, 0:1) pre-treated by annealing at 673 K for 1 h under UHV conditions. The monometallic Au/TiO₂ exhibits two spin–orbit components (4f½, and 4f¾) at 84.0 and 87.7 eV (Figure 3a), which are characteristic of the neutral Au⁰ species; the corresponding Au 4d⁵½ peak is located at 335.2 eV. For the pure Pd and all AuPd alloy samples, metallic Pd⁰ was identified as majority species based on the dominating doublet at 335.3 (Pd 3d⁵½) and 340.6 eV (Pd 3d⁷½, Figure 3b). Additionally, the monometallic Pd and Pd-rich (70%) alloy NPs show another doublet at 337.1 and 342.4 eV, revealing the presence of some minority Pd⁶⁺ species. It should be noted that in the core-level Pd 3d spectra, the relatively broad Au 4d⁴½ peak at 335.2 eV is clearly resolved for the gold-rich (50% and 70%) alloys although it overlaps with the Pd 3d⁴½ component.

On the basis of a quantitative analysis of the XPS data, the atomic ratios between Au and Pd were estimated. The results revealed a slightly higher Pd content for the
Au$_x$Pd$_y$/TiO$_2$ samples when compared to the initial synthesis ratio (Table 1), indicating an enrichment of all alloy surfaces with Pd, in line with the literature. The concentration of Pd$^{2+}$ was estimated as approx. 10% for monometallic Pd/TiO$_2$ and approx. 4.4% for Pd-enriched Au$_x$Pd$_y$/TiO$_2$. The Pd$^{2+}$ species presumably result from activation of dioxygen at the surface of pure Pd and at the Pd-enriched sites of Au$_x$Pd$_y$/TiO$_2$. Indeed, in case of Au-rich (Au$_x$Pd$_y$/TiO$_2$ and Au$_x$Pd$_y$/TiO$_2$) samples, where the Pd atoms are incorporated as Pd$^0$ in an AuPd alloy structure, Pd$^{2+}$ species were not observed. Allying Au with Pd tends to shift the electron density toward the element with the larger fraction of empty valence states. Figure 3a shows that for Au$_x$Pd$_y$/TiO$_2$ the Au 4f doublet shifts to lower binding energies (83.7 and 87.4 eV) upon alloying with Pd. This finding is attributed to the charge transfer from Pd to Au because Au is more electronegative. The electronic interaction between Au and Pd in the alloy is of complex nature. It has also been proposed that Au gains sp valence electrons and loses d electrons whereas Pd loses sp electrons and gains d electrons. According to Wang et al., Au obtains 6s conduction charge in AuPd bimetallics accompanied by a slight 5d charge depletion. The electronic perturbation in the d bands of Pd and Au was corroborated by the IR results shown below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Au (%)</th>
<th>Pd (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>0</td>
<td>100 (Pd$^0$: Pd$^{2+}$ = 90:10)</td>
</tr>
<tr>
<td>Au$_3$Pd$_7$</td>
<td>21.5</td>
<td>78.5 (Pd$^0$: Pd$^{2+}$ = 74.1:4.4)</td>
</tr>
<tr>
<td>Au$_5$Pd$_5$</td>
<td>36.6</td>
<td>63.4 (Pd$^0$)</td>
</tr>
<tr>
<td>Au$_7$Pd$_3$</td>
<td>56</td>
<td>44 (Pd$^0$)</td>
</tr>
<tr>
<td>Au</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 3. Deconvoluted X-ray photoelectron spectra of Au$_x$Pd$_y$/TiO$_2$ samples (x:y = 1:0, 7:3, 1:1, 3:7, 0:1): (a) Au 4f region and (b) Pd 3d region.
3.3. Temperature-dependent FTIR Spectroscopy with CO as Probe Molecule

The surface properties and chemical states of various Au$_x$Pd$_y$/TiO$_2$ samples were further characterized by FTIR spectroscopy using CO as a probe molecule (Figures 4 and 5). In contrast to XANES and XPS, the adsorbed CO species probe exclusively metal species (Ti, Au, Pd) present at the very surface of the samples. For all TiO$_2$-supported catalysts, CO adsorption at 110 K caused the appearance of a predominant IR band at about 2185 cm$^{-1}$, which is assigned to CO bound to surface five-fold coordinated Ti$^{4+}$ sites. The large blue-shift with respect to the gas-phase value (2143 cm$^{-1}$) is related to both electrostatic interactions (Stark effect and Pauli repulsion) and electron donation from CO 5σ orbitals to the surface Ti$^{4+}$ cations. Interestingly, the frequency typical for CO bound in the vicinity of O-vacancies on TiO$_2$ surfaces for both, single crystals and powder particles at 2178 cm$^{-1}$, was not observed, suggesting that the TiO$_2$ particles were fully oxidized, in line with the XPS observations (see Figure S6). Based on the temperature-dependent IR data and assuming a pre-exponential factor of $10^3$ s$^{-1}$, the binding energy of CO was estimated as ca. 40 kJ mol$^{-1}$, revealing a rather weak interaction between CO and Ti$^{4+}$. The attenuation of the 2185 cm$^{-1}$ band is accompanied by a slight blue-shift in frequency (from 2185 to 2200 cm$^{-1}$), which can be explained in terms of the reduced adsorbate-adsorbate interactions including both dynamic (dipole–dipole coupling) and substrate mediated static effects. Interestingly, a weak CO band appears at 2214 cm$^{-1}$ at elevated temperatures. This band shows a strongly enhanced thermal stability with regard to the CO species adsorbed on regular Ti$^{4+}$ sites (Figure 4a,d and 5a,d,g). This small band is tentatively assigned to a minority CO species coadsorbed with carbonates on the TiO$_2$ surfaces. Similar species have been reported in previous works for pure ZnO and Au/ZnO NPs. The existence of carbonate anions, formed probably via CO oxidation, increases the Lewis acidity of adjacent Ti$^{4+}$ cations. This effect accounts well for the unexpected enhancement of CO binding energy and the blue-shift of the ν(CO) band.

3.3.1. CO Adsorption on Monometallic Au and Pd NPs Supported on Titania

Upon CO adsorption on pure Au NPs supported on TiO$_2$ at 110 K (see Figure 4a-c), in addition to the intense TiO$_2$-related CO vibration at 2185 cm$^{-1}$, a second IR band was observed at 218 cm$^{-1}$ being characteristic for CO adsorbed on Au sites. The slight red-shift compared to the value of gas-phase CO (2143 cm$^{-1}$) is typical for CO bound to metals and is attributed to the electron back-donation
from Au to the empty CO $2\pi^*$ orbital. Temperature-dependent FTIR data provide direct spectroscopic evidence of the thermal stability of different adsorbed species. As shown in Figure 4b,c, the 2118 cm$^{-1}$ band increases first in intensity upon heating to 180 K. This could be related to (i) a restructuring process of the CO adlayer from an inhomogeneous distribution at low temperatures to a more uniform molecular environment and accordingly an increase in ordering and (ii) a thermal diffusion of CO adsorbed at Ti$^{4+}$ sites to more stable Au sites. Further rise of the temperature leads to a gradual attenuation of the Au-related CO band with a slight blue-shift in frequency from 2118 to 2129 cm$^{-1}$. According to previous works, the typical band of CO adsorbed on neu-

**Figure 5.** FTIR spectra recorded after exposing the Au$_5$Pd$_5$/TiO$_2$ (a-c), Au$_3$Pd$_7$/TiO$_2$ (d-f) and Au$_7$Pd$_3$/TiO$_2$ (g-i) samples to $4 \times 10^{-3}$ mbar CO at 110 K and then subsequent gradual heating; (a, d, g) CO-TiO$_2$ region, (b, e, h) CO-AuPd region and (c, f, i) normalized band intensity of the CO bound to different surface adsorption sites as a function of sample temperature.
tral Au⁰ sites appears at ~2100-2110 cm⁻¹. The observed blue-shift for CO on Au/TiO₂ indicates an electronic modification of surface Au species which is probably caused by the strong interactions between Au atoms and the TiO₂ support at the interfacial sites. We propose that CO adsorbs preferentially at the low-coordinated Au sites at Au/TiO₂ interfaces. This CO species desorbs completely only after increasing the temperature to 260 K, in agreement with published studies.

The corresponding FTIR results obtained for Pd/TiO₂ are displayed in Figure 4d-f. CO adsorption at 110 K leads to the appearance of a new IR band at 2161 cm⁻¹, which is assigned to CO bound to positively charged Pd²⁺. In fact, palladium is mostly oxidized as evidenced by in situ XANES and XPS results (cf. section 3.1 and 3.2, Figure S4a and Figure 3b). Upon temperature increase to 200 K (Figure 4e,f), the 2161 cm⁻¹ band gains intensity in parallel to the desorption of CO on Ti⁴⁺ due to the same reasons as discussed above. The CO-Pd²⁺ species disappear as the temperature raises further. Interestingly, a weak IR signal at 2100 cm⁻¹ appears and grows at temperatures above 300 K. It is known that CO molecules bound to specific surface Pd⁰ sites show different vibrational frequencies: typically 2100-2070 cm⁻¹ for linearly (on-top) bonded CO, 2000-1900 cm⁻¹ for 2-fold bridging CO, and 1900-1800 cm⁻¹ for CO adsorbed on 3-fold hollow sites. Here, the band observed at 2100 cm⁻¹ is characteristic for CO bound to Pd²⁺ atop sites. The intensity of this band reaches a maximum at 420 K, while at the same time the CO-Pd²⁺ species disappears. This observation suggests that the metallic Pd⁰ is formed by the reduction of surface Pd²⁺ species via reaction with the CO, i.e. oxidizing the CO to CO₂ by consuming adjacent oxygen species.

3.3.2. CO Adsorption on Bimetallic AuₚPdₚ (x:y = 7:3, 11:1, 37:1) NPs Supported on TiO₂

Figure 5a-c presents FTIR data obtained after CO adsorption on the bimetallic AuₚPdₚ/TiO₂ NPs at 110 K and then subsequently heating to higher temperatures. After exposure to CO at 110 K, one major IR band was observed at 2110 cm⁻¹ in the Au-Pd region apart from the typical bands on titania, as already described above. As the sample temperature increased, the IR band at 2110 cm⁻¹ was split into two components at 2121 and 2102 cm⁻¹, which are attributed to CO bound to Au⁰ next to Pd in an on-top configuration and Au⁰-enriched (contiguous) sites, respectively. Both CO species desorbed completely upon heating to ~280 K, in line with the thermal stability of Au-bonded CO molecules. The Pd species coordinated to Au atoms can also be detected, they give rise to the IR feature at 2086 cm⁻¹. This frequency is attributed to CO adsorbed on-top of Pd⁰ species. The 2086 cm⁻¹ band disappeared only after heating to about 420 K, revealing that CO adsorbs stronger to Pd atoms than to Au. Furthermore, this band shifts to 2072 cm⁻¹ with increasing temperature, i.e., with decreasing CO coverage (Figure 5b). The coverage-dependent frequency shift predominantly results from the adsorbate dipole-dipole coupling interactions, typically accompanying CO adsorption on metal surfaces. The present IR data demonstrated that the AuₚPdₚ/TiO₂ surface was dominated by the bimetallic Pd⁰ and Au⁰ atoms whereas no CO-Pd²⁺ species was observed, in good agreement with the XPS results (see Table 1). Interestingly, on the surface of pure Pd NPs supported on TiO₂ only the CO frequency characteristic for positively charged Pd²⁺ was observed (Figure 4e). These findings suggest that on pure Pd NPs O₂ readily dissociates to form PdO₂, which is apparently absent on the alloy NPs. In addition, Figure 5b displays a weak and broad feature centered at 1940-1950 cm⁻¹, which is assigned to CO adsorbed on bridge Pd sites, indicating the presence of a small amount of contiguous Pd ensembles on the surface.

As discussed in the XPS section, a net Pd to Au charge transfer is anticipated to occur upon alloying according to Pauling's electronegativity scale. However, this intermetallic charge transfer is partially compensated by the enrichment of Pd d-electrons and the depletion of Au d-electrons. Our IR data provides indirect information about modifications in the electronic structure of the bimetallic Au and Pd species. A lower Au d charge weakens the electron back-donation from Au into the CO 2π⁺ orbital and consequently strengthens the C–O vibration. In contrast, a red-shift of the CO-Pd⁰ band takes place due to the charge transfer into the d bands of Pd. Indeed, the IR band of CO adsorbed on-top of bimetallic Pd sites was detected at 2086-2072 cm⁻¹ (Figure 5b), which is obviously shifted to lower frequencies compared to that of CO bound to monometallic Pd atop sites (2100 cm⁻¹, Figure 4e). On the other hand, a blue-shift was observed for bimetallic Au-bonded CO (~2120 cm⁻¹) with respect to CO adsorbed at Au-enriched sites (2102 cm⁻¹, Figure 5b).

The IR spectra obtained after exposing AuₚPdₚ/TiO₂ to CO at 110 K show a broad band centered at ~2109 cm⁻¹ in the Au-Pd region (Figure 5e), which is ascribed to mixed CO species adsorbed on bimetallic Au⁰ and Pd⁰ sites. Again, the intensity of this band reached the maximum at about 200 K and then gradually decreased with rising temperature, as observed for other samples (Figure 5e,f). At temperatures above 300 K, the CO band was red-shifted to 2086 cm⁻¹ and disappeared at 420 K, corresponding to the more stable CO-Pd⁰ species on the bimetallic surface. Additionally, compared with pure Pd (Figure 4e) and Aurich alloy NPs (Figure 5b), the CO bound to Pd bridge sites becomes a dominating species as evidenced by the intense band at 1950-1925 cm⁻¹. This finding reveals the enrichment of the AuₚPdₚ/TiO₂ surface with Pd giving rise to contiguous Pd sites, where CO prefers to bind in a bridging configuration with a higher binding energy (Figure 5f). For this sample, the CO-Pd²⁺ species was observed only as a minority species, in line with the XPS results.

The FTIR data of CO adsorption on Pd-rich AuₚPdₚ/TiO₂ are presented in Figure 5g-i. In addition to the Ti⁴⁺-related CO vibration, three intense bands at 2612, 2105 and 1950 cm⁻¹ were observed after exposure to CO at 110 K (Figure 5h). They are attributed to CO adsorbed on positively charged Pd²⁺, on-top of bimetallic Au⁰ and Pd⁰ sites, as well as bridging on Pd⁰ sites in the Pd-enriched sample, respectively. These assignments are further supported by the thermal stability of various CO species, which is
demonstrated by the temperature-dependent IR experiments (Figure 5i). The attenuation of the CO band at \(-2100\) cm\(^{-1}\) at temperatures below 300 K originates predominantly from the desorption of CO-Au species because of a relatively weak bonding of CO to Au. Interestingly, this band shows a second maximum at 380 K, which is accompanied by a complete depletion of the CO-Pd\(^{2+}\) species (2161-2152 cm\(^{-1}\)), revealing the transformation of Pd\(^{2+}\) to Pd\(^{0}\) via CO oxidation (see above). As shown in Figure 5h, the corresponding IR band is located at \(-2100\) cm\(^{-1}\) being characteristic for CO bound in atop configuration on monometallic Pd\(^{0}\) sites, as observed for Pd/TiO\(_2\) (Figure 4e). These results suggest the coexistence of Pd-enriched and bimetallic Au and Pd sites, in good agreement with the STEM-EDX results showing a segregated contiguous Pd layer around the alloy NPs (Figure 2). The enrichment of the surface with Pd was further supported by the intense CO band at 1950-1970 cm\(^{-1}\) originating from CO adsorbed on Pd bridge sites. The catalytic experiments (for details see below) provided evidence that the Pd-rich Au\(_3\)Pd\(_7\)/TiO\(_2\) sample exhibited a higher CO oxidation activity compared to the other Au/Pd\(_{x}\)/TiO\(_2\) catalysts. This could be related to a synergistic effect: the Pd-enriched (contiguous) sites activate dioxygen while CO desorbs on both bimetallic Au and Pd sites. It should be noted that the bimetallic Au sites bind CO weaker than Pd, which is expected to facilitate CO oxidation at low temperature as the self-poisoning effect can be diminished.

3.4. CO Oxidation with and without Reductive Pre-treatment in H\(_2\)

Au/TiO\(_2\), Pd/TiO\(_2\) and AuPd/TiO\(_2\) catalysts were tested with respect to CO oxidation in order to assess their catalytic performance in the reactor and to correlate it to the characterization results discussed above. First pre-treatment in N\(_2\) up to 673 K for 1 h was applied in order to obtain conditions as close as possible to those during the FTIR measurements, and then the CO oxidation tests were performed. Afterwards, the samples were reduced in H\(_2\) at 523 K for 1 h, and the CO oxidation tests were repeated under the same reaction conditions. Figure 6 and S7 shows the test results and the corresponding reaction rates (r). Pd/TiO\(_2\) and AuPd/TiO\(_2\) started to show low activity above 373 K, whereas the CO conversion over Au/TiO\(_2\) was 30\% at this temperature. Following a moderate light-off curve, Au/TiO\(_2\) reached full CO conversion at around 500 K. Pd/TiO\(_2\) and AuPd/TiO\(_2\) catalysts showed a steeper rise in their activities and reached full conversion between 420-450 K (before Au/TiO\(_2\)). H\(_2\) pre-treatment did not alter the observed trends, although, it improved the performance of the catalysts. Among the bimetallic samples, Au\(_3\)Pd\(_7\)/TiO\(_2\) exhibited the best performance. This differ-
ence was more pronounced when only N₂ had been used for the pre-treatment. Reduction of oxidized metal nanoparticles with H₂ enhanced the activities of Au₃Pd₇/TiO₂, Au₇Pd₃/TiO₂ and Pd/TiO₂ more significantly compared to the Au₈Pd₂/TiO₂. The turnover frequencies (TOFs) calculated for the catalysts at 313 K (extrapolated from Arrhenius plots) and 393 K are given in Table 2. The TOFs disclose a gradual increase in the order of Au₈Pd₂/TiO₂ < Pd/TiO₂ ≤ Au₃Pd₇/TiO₂ < Au₇Pd₃/TiO₂ < Au/TiO₂. Apparent activation energies decreased in the order of Au₈Pd₂/TiO₂ > Au₇Pd₃/TiO₂ ≥ Pd/TiO₂ ≥ Au₃Pd₇/TiO₂ > Au/TiO₂. Reductive pretreatment increased the CO oxidation rate and decreased the activation energy Eₐ. This may be explained by O vacancies (Oₘ) created in the reducible titania support. Oₘ can have a two effects: on the one hand Oₘ facilitate dissociative adsorption of O₂, and, on the other hand, they can stronger bind adsorbed CO. It is well-known that CO oxidation to CO₂ on metallic clusters is governed by adsorption and dissociation of O₂ and the binding strength of CO. Since the activation energy of CO oxidation over Au₈Pd₂/TiO₂ and Au₇Pd₃/TiO₂ decreased after reductive pretreatment we believe that CO poisoning is also decreased (which would contradict stronger adsorption of CO on Oₘ of TiO₂), therefore dissociation of O₂ is rate limiting in this case, similar to the route proposed for Au/CeO₂. A lower degree of CO poisoning on AuPd alloys compared to pure Pd in the temperature range of interest is supported by the FTIR data (compare Figure 4f with Figure 5c,f,i) and first-principles calculations. The catalyst showing the highest synergistic effect of Au and Pd (both with and without reductive activation) is exactly the one which shows partial segregation of Pd. Even after the reductive pretreatments monometallic Pd⁸⁺ entities would be oxidized to PdO under CO and O₂ feed (which is net-oxidizing). Pd is known to be rapidly reoxidized in the presence of oxygen at intermediate temperatures, i.e. the reductive activation does not stabilize Pd⁸⁺ in the oxidizing atmosphere. Pd-enriched (contiguous) sites are highly active in dissociative adsorption of O₂ while bimetallic AuPd sites also present in the catalyst are responsible for adsorption of CO without being poisoned at the same time. The activation energies and turnover frequencies over Au₈Pd₂/TiO₂ are practically not influenced by the reductive activation. This indicates that O₂ activation in this sample occurs on Pd-enriched sites.

These results indicate synergistic effects in the AuPd bimetallic catalysts at higher temperatures, with Au₈Pd₂/TiO₂ exhibiting the highest CO oxidation activity due to AuPd alloyed NPs responsible for adsorption of CO without being poisoned and activation of O₂ molecules by the Pd²⁺ species. These results confirm the anticipation based on temperature-dependent FTIR data regarding the catalytic performance of such samples.

4. Conclusions

Ultrasmall AuₓPdᵧ (x:y = 1:0, 7:3, 11:3, 3:7 and 0:1) NPs with average diameters of ~1 nm were synthesized in a continuous turbulent flow using a microfluidic reactor. The AuPd NPs supported on TiO₂ (P=25) showed some level of aggregation upon deposition, drying and calcination. However, the alloyed AuₓPdᵧ/TiO₂ (especially the Au-rich alloys) showed a narrower size distribution with an average diameter of ca. 5 nm. STEM images and EDX mapping revealed a Pd segregated contiguous layer in the Pd-rich alloy (AuₓPdᵧ). Interestingly, this sample showed the highest synergistic effect in CO oxidation tests compared to the other bimetallic samples with a steep rise in their
activities surpassing Au/TiO₂. In situ XANES spectra of the Pd/TiO₂ and AuPd/TiO₂, proved the dominance of oxidized Pd at temperatures between 298 and 673 K under N₂ flow.

The different surface (active) sites (Ti⁺, Pd³⁺, Au⁴⁺, atop Pd sites) and bridge Pd sites) of monometallic and bimetallic AuPd NPs dispersed on TiO₂ powders were identified by temperature-dependent FTIR spectroscopy using CO as a probe molecule. The surfaces of pure Au and Pd particles mostly consists of neutral Au and positively charged Pd⁺, respectively. Upon alloying, the bimetallic Au⁺ and Pd⁺ sites become the major surface species while depending on the Au:Pd ratio, the Au-enriched and Pd-enriched components were also detected. The combined IR and XPS results demonstrated strong electronic interactions between Au and Pd, which likely result from an interatomic charge transfer and electronic modifications in the d bands of Au and Pd. A synergistic effect accounts for the higher activity of the AuPd/TiO₂ sample for CO oxidation to CO₂, in which the Pd-enriched sites are responsible for the activation of molecular oxygen while both bimetallic Au and Pd sites chemisorb CO. The interaction between metal NPs and support is known to play a crucial role in NP stabilization and the catalytic performance. The titania phase, surface crystallographic plane and defects are crucial parameters. The influence of TiO₂ support on the catalytic activity of AuPd nanoalloys would thus be an interesting topic for future studies.

AUTHOR INFORMATION

Corresponding Authors
* E-mail: yuemin.wang@kit.edu (Y.W.)
* E-mail: grunwaldt@kit.edu (J.-D.G.)
Tel.: +49 721 608-42120
Fax: +49 721 608-44820

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. F.(G.T.) and X.Y.) contributed equally.

Funding Sources
Virtual Institute VI-403 “In-situ Nano Imaging of Biological and Chemical Processes”;
BMBF (projects 05K10VK1, 05K13VK2);
“Science and Technology of Nanosystems” Programme (432202)
China Scholarship Council

ASSOCIATED CONTENT
Supporting Information. Nanoparticle aggregation during deposition on supports and calcination. STEM images and size distributions of AuPd/TiO₂. HRTEM images of supported nanoparticles on titania. In situ and ex situ XANES spectra, XPS data, CO oxidation tests.

ACKNOWLEDGMENTS

The Virtual Institute VI-403 “In-situ Nano Imaging of Biological and Chemical Processes”, the BMBF (projects 05K10VK1, 05K13VK2), “Science and Technology of Nanosystems” Programme (432202) and KIT are gratefully acknowledged for financial support. In addition, we would like to appreciate the Karlsruhe Nano Micro Facility (KNMF), a Helmholtz research infrastructure at KIT for providing STEM-EDX measurements. Xiaojuan Yu thanks the PhD fellowships sponsored by the China Scholarship Council. Finally, we thank the CAT-ACT beamline at the KIT synchrotron for providing beamtime, in particular Dr. Tim Prüßmann and Dr. Anna Zimina (IKFT) for their help and technical support during XAS experiments.

REFERENCES


Table of Contents artwork