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# Effect of reduction temperature on the characteristics and catalytic properties of $TiO_2$ supported AuPd alloy particles prepared by one-step flame spray pyrolysis in the selective hydrogenation of 1-heptyne

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## ABSTRACT

The bimetallic flame spray-synthesized $AuPd/TiO_2$ catalysts (Au:Pd weight ratio 1:1) were reduced for 2 h under $H_2$ at two different temperatures (40 °C and 500 °C) and tested in the liquid phase selective hydrogenation of 1-heptyne under mild conditions (30 °C and 4 bar $H_2$). Based on TEM-EDX analysis of individual nanoparticles, reduction at 500 °C tends to homogenize the composition of the individual AuPd nanoparticles without significant changes of their average particle size and bulk composition. Higher reaction rate (245 $\mu$mol $s^{-1}$ g cat.$^{-1}$) was obtained on the $AuPd/TiO_2$ R40 than on the $AuPd/TiO_2$ R500 (223 $\mu$mol $s^{-1}$ g cat.$^{-1}$). Upon reduction at 500 °C, the bimetallic $AuPd/TiO_2$ exhibited a similar degree of the strong-metal support interaction (SMSI) effect as the monometallic one. As revealed by XPS results, the ratios of Pd/Ti on both catalysts decreased by ca. 23%, due probably to the migration of $TiO_x$ species onto the metals. The highest yield of 1-heptene (~93%) was obtained over the bimetallic $AuPd/TiO_2$ reduced at 40 °C in 20 min reaction time under the reaction conditions used. The high temperature reduction is unnecessary for the improvement of catalyst performances when using supported bimetallic AuPd catalysts.

## 1. Introduction

Flame aerosol synthesis, especially flame spray pyrolysis (FSP) is one of the interesting methods of nanoparticle production and is also a beneficial catalyst synthesis technique because the catalysts can easily be prepared in one-step without post-treatment steps such as washing, drying, filtration, and calcination. FSP synthesis has been employed for the synthesis of $TiO_2$ supported monometallic Au and Pd catalysts [1–3]; meanwhile, bimetallic AuPd supported on $TiO_2$ nanoparticles were successfully synthesized by the single-step FSP in our recent study [4]. Formation of Au–Pd alloy bimetallic nanoparticles was evidenced for the $AuPd/TiO_2$ catalysts prepared by FSP. The alloy particles were more uniform than those prepared by co-deposition precipitation and co-impregnation methods [4]. The major drawback of the traditional preparations of supported AuPd catalyst is the lack of homogeneity in particle size, shape, and composition of AuPd catalysts [4].

The superior catalytic performance of Au–Pd nanoparticles compared to the individual Au and Pd (so-called the synergistic effect of AuPd alloy) is usually related to either ensemble or ligand modification [5]. The ensemble modification of Au-Pd system is mainly the diluting effect where Pd is diluted by Au [6–10]. As the surface ratio of Au–Pd increases, contiguous Pd ensembles disappear and Pd atoms are separated by Au forming isolated Pd ensembles [6,7]. This effect is shown to be responsible for the enhancement of activity and selectivity for certain reactions, e.g., vinyl acetate synthesis and direct $H_2O_2$ synthesis [11,12]. The ligand modification refers to a change in the local electronic structure due to charge transfer, orbital rehybridization, or other changes in electronic structure, which is responsible for the elimination of self-poisoning

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effect and the improvement in activity/selectivity, for examples, in hydrodesulfurization, CO oxidation, and acetylene trimerization [13–16].

The partial hydrogenation of unsaturated organic compounds for the synthesis of fine organic chemicals, e.g., selective hydrogenation of alkyne to the corresponding alkene is both of industrial and academic importance. Alkene products obtained via this reaction are useful in the synthesis of biological active compounds, the production of margarine, the lubricant industry, and the synthesis of important intermediates for fine chemical industries such as food (flavors), pharmaceutical (vitamins, sedatives), and cosmetics (fragrances) [17–19]. The selective hydrogenation of alkyne over monometallic Pd and bimetallic Pd–Au catalysts has been focused on both gas-phase and liquid-phase [1,4,20–25]. The dilution of Pd ensemble by Au atoms has shown to result in the improvement of hydrogenation activity [26,27]. A number of studies also reported the modification of activity and selectivity of supported Au–Pd catalysts due to electron transfer between Au and Pd [28–31]. For example, Chen and Lee [32] suggested that Pd could donate some electrons to Au, resulting in the hydrogen adsorption ability of Au, and as a consequence, the activity in the selective hydrogenation of *p*-chloronitrobenzene increased. Nevertheless, the degrees of AuPd alloying effect appeared to depend on several factors such as the molar ratio of Au to Pd, the preparation method, the particle morphology, the alloy particle size, and the metal-support interaction [24,25,33–35].

Despite the variety of supports being used for preparation of supported Au-Pd catalysts such as $\gamma$-$Al_2O_3$ [26,36], $SiO_2$ [29], $SiO_2$-$Al_2O_3$ [37], $CeO_2$ [38], carbon [39], and $TiO_2$ [4,25,36,40], only a few studies systematically reported the influence of support nature on the interaction of Au–Pd species and their corresponding catalytic behavior. Smolentseva et al. [38] showed that Pd–Au/$Al_2O_3$ exerted more pronounced interaction between gold and palladium species than Pd–Au/$CeO_2$ but the Pd–Au/$CeO_2$ manifested higher activity and selectivity in the selective oxidation of arabinose to arabinonic acid. The interaction of Au and Pd with reducible ceria coexisted with the mutual interaction between these metals. On the other hand, Kolli et al. [36] reported that the nature of supports between $Al_2O_3$ and $TiO_2$ had negligible effect on the composition of AuPd metal particles and did not participate in the selective hydrogenation of butadiene. In our recent study [40], the exertion of electronic modification by Au–Pd alloy was found to depend on the $TiO_2$ crystallite size in which the modification was more pronounced on the larger $TiO_2$ (15 nm) compared to the smaller one (9 nm), resulting in higher activity and lower selectivity in the selective hydrogenation of 1-heptyne.

High temperature reduction (i.e., at 500 °C) usually manifests the strong metal-support interaction (SMSI) of $TiO_2$ and group VIII transition metals (e.g., Pd, Pt, Ni, and Ir). The beneficial effect of SMSI on the catalyst performances has been reported for supported Pd/$TiO_2$ in the selective hydrogenation of acetylenic compounds [41–43]. However, the effect of reduction temperature on the characteristics and catalytic performances of AuPd alloy particles has not been investigated to much of a degree.

In the present work, the effect of reduction temperature on the catalytic performances of bimetallic Au-Pd/$TiO_2$ was investigated and compared to the monometallic Pd/$TiO_2$ in the liquid-phase selective hydrogenation of 1-heptyne under mild reaction conditions. Prior to the reaction tests, the catalysts were pretreated under hydrogen reduction temperature of 40 or 500 °C. The characteristics of catalysts were also investigated by X-ray diffraction (XRD), $N_2$ physisorption, temperature-programmed reduction ($H_2$-TPR), X-ray photoelectron spectroscopy (XPS), and transmission electron spectroscopy-energy dispersive X-ray spectroscopy (TEM-EDX).

## 2. Experimental

### 2.1. Catalyst preparation

The monometallic 1 wt.% Pd/$TiO_2$ and bimetallic 1 wt.% Au-1 wt.% Pd/$TiO_2$ catalysts were prepared by one-step FSP as described elsewhere [1,4]. Gold (III) chloride trihydrate (Sigma–Aldrich), palladium (II) acetylacetonate (Aldrich), and titanium (IV) butoxide (Aldrich) were chosen as Au, Pd, and $TiO_2$ precursors, respectively. The liquid precursor solution was prepared by dissolving all precursors into the mixture solution of xylene/acetonitrile (70/30 vol%) at total concentration of 0.5 M, then feeding into the flame reactor by using a syringe pump at a flow rate of 5 mL/min and dispersing with oxygen at a flow rate of 5 L/min to form the fine spray droplet after that. The pressure drop at the capillary tip was constantly adjusted at 1.5 bar by tuning the orifice gap area at the nozzle. To ignite the spray flame, oxygen and methane were provided as the supporting flame feed gases through a ring around the nozzle outlet at a flow rate of 3 and 1.5 L/min, respectively. The additional sheath oxygen was supplied through a sintered metal plate ring at flow rate of 25 L/min. A glass fiber filter with the aid of a vacuum pump was used to collect the product particles formed. The monometallic Pd/$TiO_2$ catalyst and $TiO_2$ support were also prepared by FSP method under similar conditions. The monometallic Pd/$TiO_2$ and bimetallic AuPd/$TiO_2$ catalysts were pretreated under hydrogen atmosphere (50 $cm^3$/min) at 40 and 500 °C for 2 h before being tested for catalytic performance. The monometallic Pd/$TiO_2$ and bimetallic AuPd/$TiO_2$ catalysts reduced at 40 and 500 °C are denoted as Pd/$TiO_2$ R40, Pd/$TiO_2$ R500, AuPd/$TiO_2$ R40, and AuPd/$TiO_2$ R500, respectively.

### 2.2. Catalyst characterization

The X-ray diffraction analysis was conducted on XRD D8 Advance of Bruker AXS with Ni-filter CuK$\alpha$ ($\lambda$ = 1.54056 A°) radiation from 20° to 80° $2\theta$ and step size of 0.020563 (step time = 88.5 s). The nitrogen physisorption technique was used to determine the BET specific surface area, pore volume, and pore diameter by using a Micromeritics ASAP 2020 automated system. The sample was degassed at 200 °C for 2 h (heating rate of 2.0 °C /min) under vacuum prior to $N_2$ adsorption analysis, which was carried out at liquid nitrogen temperature (−196 °C). XPS was performed using a Kratos Ultra DLD X-ray photoelectron spectrometer. The in situ high-energy XPS analysis was performed under reducing condition to ensure that the catalysts are in the active form. The C1s peak was used as reference at binding energy of 285.0 eV to calibrate for all XPS spectra. The TEM observations were performed in a JEOL JEM 2010 transmission electron microscope equipped with a $LaB_6$ electron beam source, a UHR polepiece (point resolution: 0.196 nm) and a Pentafet-Link Energy-Dispersive X-ray (EDX) spectrometer (and INCA software) from Oxford Instruments. The reducibility of catalyst as a function of temperature (TPR profile) was investigated by temperature programmed reduction technique using a MicromeriticsChemiSorb 2750 with ChemiSoftTPx software. Approximately 0.1 g of catalyst was pretreated under $N_2$ (25 mL/min) at 400 °C for 1 h before the TPR analysis in order to remove possible impurities contained in the samples. After cooling down to room temperature under $N_2$, the sample was exposed to mixture of 10% $H_2$ in Ar flowing at 25 mL/min with the temperature ramped of 10 °C/min from 35 °C to 700 °C. The temperature was held at 700 °C for 1 h and then cooled to room temperature. The actual amounts of Au and Pd were determined by the ICP-OES using the Optima 2100 DV spectrometer.