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Research Paper

Variability of particle configurations achievable by 2-nozzle flame syntheses of the Au-Pd-TiO$_2$ system and their catalytic behaviors in the selective hydrogenation of acetylene

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ABSTRACT

Catalysts with Au and Pd supported on TiO$_2$ (Au:Pd 1:1 wt/wt%) were prepared by 1- and 2-nozzle flame spray pyrolysis (FSP). The 2-nozzle configuration allowed to synthesize various particle configurations by separate or co-feeding of the metal precursor solutions to the two nozzles. For the Au-Pd/TiO$_2$ system, four different catalyst particle configurations were investigated: "TiO$_2$ + AuPd", "Pd/TiO$_2$ + Au", "Au/TiO$_2$ + Pd", and "Pd/TiO$_2$ + Au/TiO$_2$", where + separates the corresponding precursor solutions fed to the two nozzles. There were no significant differences in the specific surface areas and the average TiO$_2$ crystallite sizes of the catalysts (100 m^2/g and 16–17 nm, respectively) with the exception of "Pd/TiO$_2$ + Au/TiO$_2$", which exhibited larger surface area and smaller crystallite size (152 m^2/g, 12 nm) due to halving of the Ti precursor concentration in each nozzle. As revealed by CO chemisorption, XPS, and STEM-EDX results, the catalyst properties varied largely in terms of bimetallic AuPd particle compositions, the interaction between metal–metal and metal-support, and the location of Pd (or AuPd) on the TiO$_2$. Among the catalysts studied, "TiO$_2$ + AuPd" prepared with the 2-nozzle system exhibited the highest conversion of acetylene (~50%) at 40 °C with high selectivity to ethylene (> 95%). Co-feeding the noble metal precursors together with the Ti precursor afforded less active catalysts due to the formation of Ti-O species partially covering the most active bimetallic AuPd particles. Compared to the commercially available acetylene hydrogenation catalyst and the AuPd/TiO$_2$ prepared by conventional co-impregnation and deposition-precipitation, all the FSP-AuPd/TiO$_2$ catalysts showed superior performances under the reaction conditions used.

1. Introduction

During ethylene polymerization, the feed stream from thermal and/or steam cracking contains small quantities of acetylene ($<$ 2–3%) that poison the polymerization catalysts [1–3]. As a result, polyethylene products may not be properly vulcanized and become brittle [4]. In addition, acetylene can form metal acetylides, which are explosive contaminants [5]. Thus, the acetylene in ethylene feed should be eliminated or reduced to an acceptable level ($<$ 5 ppm) [4,6]. The most commonly used method for acetylene removal is the selective hydrogenation of acetylene using Al$_2$O$_3$ supported Pd-based catalysts [7–10]. However, at high acetylene conversion (100%), the catalysts show low ethylene selectivity (11%) [11]. An over-hydrogenation of ethylene to ethane can occur due to the strong adsorption of both reactants and products on the Pd sites [12]. One of the attractive techniques to control the contact of Pd with reactants and products is the addition of a second metal to form bimetallic catalysts. Gold has been used as such metal for the selective hydrogenation of acetylene [3,12–15].

The performance of AuPd catalysts in the selective acetylene hydrogenation was found to depend largely on the AuPd structure. For examples, Sárkány et al. [14] reported an activity decrease with increasing of Pd shell thickness of the Pd$_{shell}$-Au$_{core}$/SiO$_2$ catalysts.

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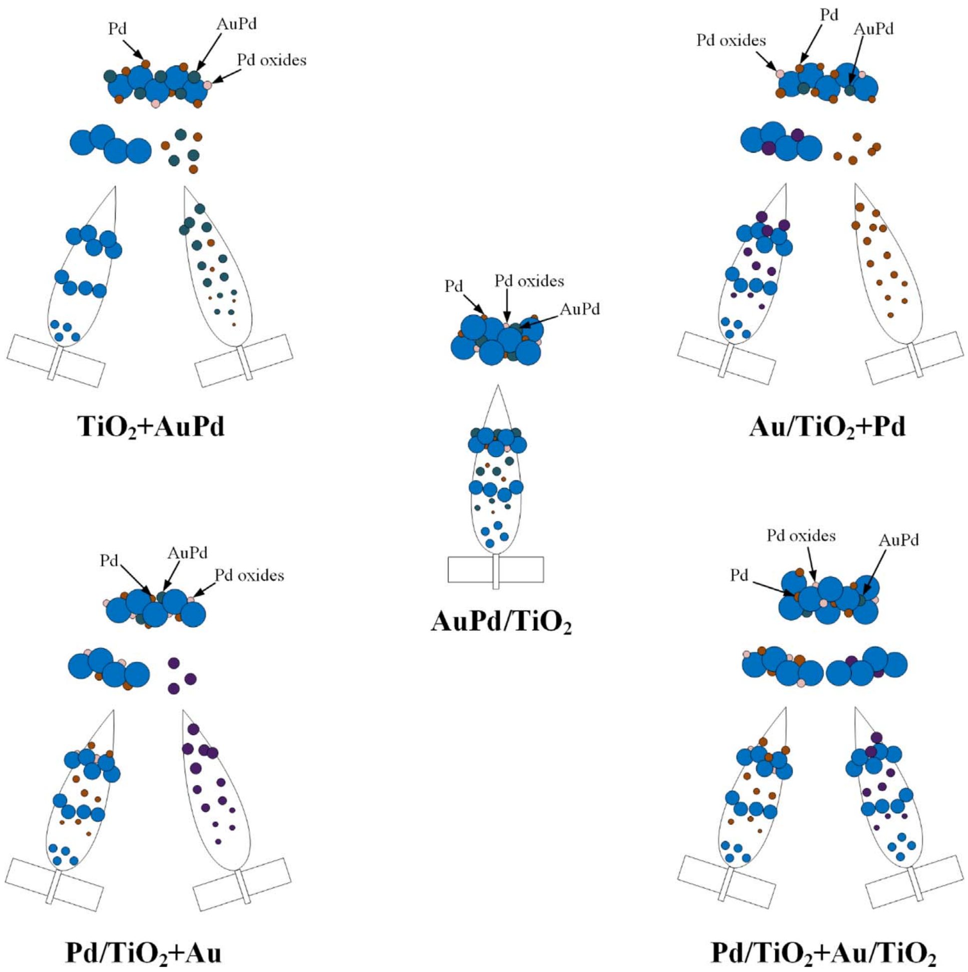

Fig. 1. Schematic of the 1-nozzle and 2-nozzle FSP for the preparation of AuPd supported on TiO_2.

Moreover, $AuPd/SiO_2$ with AuPd alloy structure exhibited better catalytic activity and selectivity than a core(Au)-shell(Pd) structure. Zhang et al. [3] synthesized $AuPd/SiO_2$ catalysts by electroless deposition with various surface coverage of Au on Pd and observed the formation of small ensembles of Pd sites at high Au surface coverage, which promoted the adsorption of acetylene as π-bonded species favoring hydrogenation to ethylene, whereas at low Au surface coverage larger contiguous Pd ensembles were formed resulting in ethane formation. The ethylene selectivity was also decreased due to the strong adsorption of acetylene as multi σ-bonded species [16]. Furthermore, alloying Pd with small Au nanoparticles (~3 nm) on a SiO_2 support with Pd/Au atomic ratios < 0.025 exhibited higher catalytic performance than the monometallic Pd or Au [12]. Pei et al. [12] proposed that Pd promoted acetylene conversion at lower reaction temperature, compared to Au, whereas the Au addition helped to isolate the Pd atoms and suppressed the hydrogenation of ethylene to ethane (improvement in selectivity). Additionally a weaker ethylene adsorption was observed for the $AuPd/SiO_2$ catalysts with Pd single-atom alloy structure in comparison to the monometallic Pd/SiO_2, thus leading to higher ethylene selectivity [12]. Zhang et al. [15] synthesized $AuPd/TiO_2$ catalyst (Au/Pd atomic ratio = 14) by deposition-precipitation of Au followed by impregnation with Pd. Large amount of surface Pd sites (both of isolated Pd atoms and contiguous Pd clusters) were formed, facilitating acetylene adsorption leading to the improvement of acetylene conversion.

Flame spray pyrolysis (FSP) technology has a great potential for rapid, flexible, and scalable synthesis of multi-component nanoparticles. The characteristics of such nanoparticles can be tuned by the FSP operating conditions such as precursor type [17,18], concentration [19–21], flow rate [19,21,22], type of solvent [23,24], dispersion gas type [19], dispersion gas flow rate [19,21], and other process conditions [20,21]. By varying these parameters, the combustion enthalpy change which affects the total net heating value of the spray flame. The metal precursor and solvent should be selected not only by their miscibility but also suitable combustion enthalpy for the FSP synthesis method.

The 2-nozzle FSP facilitates a better control of the mixing intensity of the individual components of the two flames [25]. Up to date, only a few catalyst systems have been reported using 2-nozzle FSP synthesis method (e.g., Al_2O_3 and $Ce_xZr_{1-x}O_2$ supported Pt-Ba catalysts [26,27] for NO_x storage, $CoMo/Al_2O_3$ [25] hydrotreating catalysts, Ba- and K-promoted Rh/Al_2O_3 [28] for CO_2 hydrogenation, and CO oxidation catalysts based on Pt-FeO_x/CeO_2 [29], MnO_x/Al_2O_3, and FeO_x/Al_2O_3 [30]). An important feature of the 2-nozzle FSP emerging from these previous studies is that the incorporation of the active phase into the oxide support could be prevented.

The 2-nozzle FSP allows designing multi-component nanoparticles by controlling the mixing of the individual components from the two flames. The present work reports the characteristics as well as the catalytic properties of the bimetallic $AuPd/TiO_2$ made by 2-nozzle FSP with different noble metal mixing. The degree of AuPd alloy formation, the interaction between metal–metal and metal-support, and the location of Pd (or AuPd) on the TiO_2 could be varied significantly. The catalysts were characterized by N_2 physisorption, X-ray diffraction (XRD), CO chemisorption, scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDXS), and X-ray photoelectron spectroscopy (XPS). Their catalytic performances were evaluated for low temperature (40 °C) gas-phase selective hydrogenation of acetylene in excess ethylene.