



Enhancement of palladium-catalyzed direct desulfurization by yttrium addition

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ABSTRACT

Bimetallic Pd-Y nanoparticles were synthesized by yttrium precursor reduction on the surface of colloidal Pd seeds catalyzed by palladium hydride. The addition of yttrium improved the thermal stability of the Pd nanoparticles to agglomeration. The nanoparticles before and/or after deposition on alumina were characterized by TEM, XPS, STEM with elemental mapping, temperature-programmed reduction, CO chemisorption and CO-DRIFT spectroscopy. The supported catalysts were evaluated in hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene at 350 °C and 1 MPa. Yttrium addition did not alter the overall HDS rate but increased the direct desulfurization selectivity from 71% to 84% and suppressed cracking twice as much as monometallic Pd catalyst did. The study demonstrates that PdY structures could be a promising candidate for low-pressure HDS of refractory sulfur compounds.

1. Introduction

Tuning product selectivity in complex reactions is of paramount importance in increasing the atom economy [1–3]. Selectivity control by operating parameters such as temperature, pressure, and residence time is not always feasible due to equipment, safety and economic limitations. Development of heterogeneous catalysts with desired active sites enables such technologies [1,4]. Increasingly stringent environmental regulations for the sulfur content in fuels pose significant technological challenges for refineries [5–7]. To achieve ultra-deep levels of sulfur, such as 10 ppmw S for transportation, the most refractory 4,6-dialkyldibenzothiophenes must be desulfurized [8–11] because they constitute around 20 wt% of total sulfur species in a conventionally pre-desulfurized fuel with 500 ppmw S [12]. The steric hindrance of alkyl groups prevents perpendicular σ -adsorption through sulfur atom for direct sulfur elimination, termed the direct desulfurization (DDS) pathway [8–10,12–15]. However, this hindrance can be reduced by changing the spatial configuration of the molecule through hydrogenation of flat π -adsorbed phenyl rings, known as the hydrogenation (HYD) pathway [10,14–16]. Accordingly, NEBULA catalysts rely on the HYD route, which requires elevated hydrogen pressure [17,18].

The DDS pathway requires lower operating pressure than the HYD route [19,20]. The aromaticity of desulfurized products via the DDS path is higher [20], giving the possibility of product quality control based on demand. On the other hand, low-pressure operations could

accelerate ring opening and cracking of naphthenic compounds, resulting in lower fuel quality and yield. This reveals the challenges to proper design and development of an active catalyst for low-pressure hydrodesulfurization (HDS).

Oyama et al. [20] reported 85% DDS selectivity (at 99% conversion) in HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) at 340 °C and 3 MPa over NiFeP/SiO₂ catalyst. However, the catalyst showed low volumetric activity, implying larger required reactor volume and increased energy consumption as compared to conventional HDS catalysts. Pt-group metals have also shown promising activity in HDS of refractory compounds in pre-desulfurized fuels due to their outstanding hydrogenation and hydrogenolysis properties [13,14,21–30]. Palladium and platinum and their bimetallic PtPd combinations promote the hydrogenation pathway in HDS of 4,6-DMDBT [14,23,30,31]. Pd is known for its high resistance to sulfur poisoning and high activity in HDS of 4,6-DMDBT [23,26,31]. In contrast to iridium, Pd does not significantly catalyze ring opening and cracking at low pressure [28] and thus represents a promising candidate for a low-pressure HDS. Since the DDS pathway proceeds via perpendicular σ -adsorption, the DDS selectivity can be promoted by decreasing the size of the Pd nanoparticles and thus increasing the fraction of low-coordinated active sites [20] (edges and corners of Pd nanoparticles) [24,32]. Higher DDS selectivity has been observed over smaller Pt [24], Ru [33], and Pd [34] nanoparticles. However, the thermal instability of smaller nanoparticles is a matter of significant concern [35–38], especially for sintering-prone metals such as palladium [39]. Nanoparticle growth deactivates

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catalysts and may alter selectivity. A promising strategy for constraining the sintering of metal nanoparticles is to create alloys with sintering-resistant elements such as iridium; however, this is a scarce and expensive metal [40].

It is desirable to use earth-abundant elements as a textural promoter. Yttrium provides the most thermally stable alloys; for example, Y stabilizes zirconia for high-temperature fuel cell applications [41]. An early study showed that yttrium significantly increased the mechanical stability and hydrogen permeability of Pd-based membranes [42]. In addition, nanostructured Pd-Y alloys prepared by ball-milling exhibited stability against grain growth up to 400 °C [43]. Palladium and yttrium can form various alloy structures at different Pd/Y ratios, from Pd₂Y to PdY₃, according to the Pd-Y phase diagram [44]. The palladium lattice is expanded upon alloying with yttrium due to the larger atomic size of yttrium than palladium [43,45], 1.82 Å vs. 1.37 Å [46], accompanied by a change in the filling and level of the Pd *d*-band [4,46,47]. Although the surface energies of Pd and Y are 2.050 J m⁻² and 1.125 J m⁻², respectively [48], an *ab initio* DFT study showed that Y tends to occupy the inner near-surface layers [46]. Depending on the distribution of Y atoms in the near-surface layers, the *d*-band center positions of surface atoms shift up- or downward [46]. The energy level of the *d*-band is known to affect the adsorption energies of surface species, leading to the changes in the reaction rates and selectivities [49–52].

The promising combination of yttrium and transition metals, especially noble metals, has been verified in a variety of catalytic applications, such as partial oxidation of methane [53], CO₂ and autothermal reforming of methane [54,55], oxygen reduction reaction (ORR) [46,56,57], and electrooxidation reaction [46,58]. The enhanced oxygen electroreduction activity and stability of platinum catalyst when alloyed with yttrium was also shown by density functional theory (DFT) calculations [58]. The higher ORR and ethanol electrooxidation activity of Pd₃Y alloy relative to monometallic Pd was attributed to the modified electronic structures of Pd by Y [46]. Yttrium was found to increase the surface area and dispersion of Ni₂P [59]. Adding Y to Pd/Al₂O₃ and Ni/Al₂O₃ catalysts for CO₂ and autothermal reforming of CH₄, respectively, enhanced the stability of the catalysts by suppressing particle sintering and coking [54,55]. This behavior was attributed to the formation of an intermediate surface compound between Ni and Y₂O₃ [55]. A similar explanation was provided for the enhanced stability of the Pt/Y₂O₃ system in partial oxidation of methane, which was that an intermetallic compound formed between the Pt and the yttria [53].

PdY catalysts have thus attracted our attention as promising catalysts that could potentially increase the direct desulfurization selectivity in 4,6-DMDBT HDS. The increased sintering resistance as compared to the monometallic Pd should provide a higher fraction of edge and corner Pd atoms and thus facilitate perpendicular 4,6-DMDBT adsorption for direct sulfur removal. The introduction of larger Y atoms into the Pd surface (or near-surface) layer should also alter the chemisorption strength of flat π -adsorbed species in the hydrogenation path. Increased DDS contribution is favorable for the development of low-pressure desulfurization technologies. The reported study herein thus provides an experimental validation of this hypothesis as relates to the hydrodesulfurization of 4,6-DMDBT at 350 °C and 1 MPa hydrogen pressure. As demonstrated below, compared to a monometallic Pd catalyst, the bimetallic PdY nanoparticles that were developed demonstrated enhanced DDS selectivity to the formation of 3,3'-dimethylbiphenyl while reducing the hydrogenation and hydrocracking selectivity. A control study conducted with Pd nanoparticles deposited on Y-impregnated Al₂O₃ revealed the crucial importance of the PdY alloy formation to achieve the desired catalytic performance. To the best of our knowledge, this is the first report on the catalytic performance of PdY bimetallic nanoparticles in an HDS reaction to demonstrate their superior selectivity to direct desulfurization of 4,6-DMDBT.

2. Experimental methods

2.1. Materials

Palladium(II) chloride solution (PdCl₂, 5 wt%), yttrium(III) nitrate hexahydrate (Y(NO₃)₃·6H₂O), gamma-alumina (Y-Al₂O₃, Mesh size 150, average pore diameter of 58 Å, BET surface area of 155 m²/g) and polyvinylpyrrolidone (PVP, average molecular weight of 29,000) were purchased from Sigma-Aldrich and used as received to prepare the catalysts. Milli-Q water, ethanol (95 vol.%, Fischer Scientific), and acetone ($\geq 99.7\%$, Fischer Scientific) were used for synthesis. Ultra-high purity (99.999%) hydrogen, nitrogen, helium, and argon were purchased from Praxair. A diesel model compound containing 720 ppmw sulfur as 4,6-dimethyldibenzothiophene (4,6-DMDBT, C₁₄H₁₂S, Sigma-Aldrich) dissolved in *n*-decane (Fischer Scientific) with 3.5 wt% *n*-dodecane (Fischer Scientific) as internal standard was used for the HDS reactions.

2.2. Catalyst preparation

Bimetallic palladium-yttrium nanoparticles were prepared using the hydrogen-sacrificial method as reported by Liu et al. [57]. This technique for bimetallic nanoparticle synthesis relies on the capability of the core metal to dissociate hydrogen to form metal hydride at a moderate temperature (50–200 °C), which is capable to reduce the reduction-resistant elements, such as yttrium, to form bimetallic structures [60,61]. In the present modification of the method, first, PVP-stabilized Pd nanoparticles were synthesized in a colloidal dispersion using the alcohol reduction method [62]. 500 μ l of Pd precursor was dissolved in 40 ml ethanol and then diluted with 60 ml milli-Q water containing 0.47 g of PVP (PVP-to-metal molar ratio of 30) in a 500-ml three-neck flask. The mixture was then stirred rigorously and refluxed for 1 h under nitrogen, followed by cooling to room temperature. Next, Pd seeds were hydrogenated by purging the colloidal solution with hydrogen gas for 2 h under stirring to create palladium hydride, so that it can reduce yttrium precursor on the surface of Pd nanoparticles. Then, a mixture of yttrium nitrate hexahydrate in 25 ml ethanol (at variable Pd/Y molar ratios) was added to this solution dropwise over the course of 2 h followed by an additional 2 h stirring under H₂. No precipitation was observed. The synthesized mono- and bimetallic nanoparticles were deposited on Y-Al₂O₃ by mixing the colloidal solution and the support with excess acetone, termed as acetone precipitation method, in which acetone fractionated the PVP-stabilized nanoparticles from the aqueous solution on Y-Al₂O₃. As a control catalyst, a Pd₂/Y-Al₂O₃ sample was prepared via incipient wetness impregnation of yttrium precursor on Y-Al₂O₃ followed by calcination at 400 °C to obtain Y-Al₂O₃. Pd nanoparticles prepared by the alcohol reduction method were then precipitated on Y-Al₂O₃ using acetone at a Pd-to-Y molar ratio of 2. All the catalysts were dried at room temperature for 2 h and then at 100 °C overnight with subsequent calcination at 400 °C for 4 h in a static air furnace to remove the organic stabilizer.

2.3. Catalyst characterization

Inductively coupled plasma mass spectrometry (ICP-MS) analysis was used to determine the palladium and yttrium contents of synthesized catalysts. Transmission electron microscopy (TEM) images were taken with JEOL JEM2100 operating at 200 kV. Scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDS) was conducted by a CM20FEG/STEM operated at 200 kV. The EDS spectra were obtained by an Oxford EDS detector. Particle size distributions (PSD) were measured by considering 500 particles.

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