

# Palladium Nanoparticle Size Effect in Hydrodesulfurization of 4,6-Dimethyldibenzothiophene (4,6-DMDBT)

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Pd nanoparticle size sensitivity of 4,6-dimethyldibenzothiophene (4,6-DMDBT) hydrodesulfurization was investigated by using 4, 8, 13, and 87 nm particles and was compared with the sulfur-free and sulfur-inhibited hydrogenation of 3,3-dimethylbiphenyl, which is a product of direct desulfurization of 4,6-DMDBT. The smallest 4 nm particles provided unprecedented (for Pd at 5 MPa and 300 °C) direct desulfurization selectivity of 20% at 40% conversion because of the reduced contribution of the hydrogenation path. The 4 nm particles were poisoned

# Introduction

Increasing demand for ultra-low sulfur fuels has reinvigorated academic and industrial interest in developing active catalysts and energy-conscious technologies that are able to bring the S content down to 10 ppm. The enormous body of knowledge that has accumulated in the field over many decades can deal with targets of 200-500 ppm. On pre-reduction of the S content in fuels to 500 ppm, 20 wt% of all S species belong to 4,6-dialkyldibenzothiophenes, which undergo the slowest desulfurization; that is why further S removal becomes such a difficult task.<sup>[1]</sup> The reason is steric hindrance: alkyl groups prevent the perpendicular adsorption required for C-S bond hydrogenolysis on a catalyst surface. The 4,6-dimethyldibenzothiophene (4,6-DMDBT) hydrodesulfurization (HDS) is known to occur through two reaction mechanisms (Scheme 1): perpendicular 4,6-DMDBT  $\sigma$ -adsorption through its sulfur atom leads to the direct desulfurization (DDS); and flat-lying  $\pi$ -adsorption through the aromatic rings results in hydrogenation (HYD) followed by sulfur extraction.<sup>[2]</sup> The DDS selectivity for dibenzothiophenes with alkyl groups in the 4 and 6 positions is very low with predominant HYD route for HDS. The saturation of the aromatic rings changes the spatial configuration of the sulfurous molecules, providing access of the sulfur atom to the catalyst surface.[3]

To promote the hydrogenation of the aromatic rings, highly active hydrogenation catalysts are required; that is why significant efforts have been made to research noble metals known for exceptional hydrogenation activity.<sup>[2,4]</sup> They may be used in

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lowest sulfur extraction from both 4,6-DMDBT and sulfurous intermediates as a result of the low availability of edge atoms for a perpendicular sigma-mode adsorption through the lone pair of the sulfur atom.

by the adsorbed sulfur to the greatest extent. The optimal size,

providing the highest Pd mass-based yield of the desulfurized

products, was found to be 8 nm. The catalyst with 87 nm parti-

cles was based on Pd nanocubes with the lowest edge/terrace

surface atom ratio and large terraces and this showed the



Scheme 1. Reaction pathways for HDS of 4,6-DMDBT at 300  $^\circ C$  and 5 MPa on a metal function (adapted from [6]).

the second reactor of a two-stage hydrotreating process: the sulfur amounts entering the second reactor may be low enough for the noble metals to maintain sufficient activity. A previous study has documented that the catalytic activity of noble metals decreases in the order  $Pd \approx Pt-Pd > Pt > Rh > Ru-Rh \gg Ru$  for 4,6-DMDBT hydrodesulfurization.<sup>[5]</sup>

Catalyst performance is often affected by the active nanoparticle size. As was shown for a FeNi phosphide catalyst, low coordination sites are particularly active in the direct desulfurization of 4,6-DMDBT,<sup>[6]</sup> which is in line with the DDS mechanisms: perpendicular adsorption onto the nanoparticle edges should provide better access of the otherwise hindered sulfur to the metal surface. The proportion of atoms on the edges and corners increases along with the particle dispersions. Thiophene conversion through the DDS pathway induced by the perpendicular adsorption mode was found to be greater on



smaller Pt clusters than on larger ones;<sup>[7]</sup> a similar trend was also observed with Ru dispersion changes.<sup>[8]</sup> Thiophene binds to the metallic active sites by  $\sigma$ -bonding through a lone pair on the sulfur atom  $(\eta^1)$  or  $\pi$ -bonding of the aromatic ring  $(\eta^4)$ .<sup>[7]</sup> Coordinatively unsaturated corner and edge atoms, abundant on small metal clusters, bind sulfur stronger than the less-unsaturated terrace atoms that are prevalent on the larger clusters. These interactions control the available metal vacancies necessary for hydrogen and thiophene adsorption. For Ru, for example, the size decrease from 6 to 1 nm led to the four-fold increase in DDS/HYD turnover rates in thiophene hydrodesulfurization.<sup>[8]</sup> Higher turnover frequencies in both pathways during thiophene HDS were observed on Pt nanoparticles than on Ru and were related to the relatively weak sulfur binding on Pt surfaces.<sup>[7,8]</sup> A different conclusion on the available metal centers on sulfided Pt and Pd clusters was drawn in ref. [9] where the 2 nm particles show the highest sulfur tolerance, which decreases with increasing size, and the decrease was more dramatic for Pd than for Pt. Overall, sulfur poisoning is known to affect product distribution, such as by enhancing dehydrogenation over hydrogenolysis<sup>[10]</sup> or boosting selectivity to methanol in syngas conversion.<sup>[11]</sup> A vigorous investigation of platinum catalysts supported on a variety of supports (alumina, silica, and molybdena) revealed that the observed support effect on the Pt sulfur poisoning could be ascribed to surface topography and linked to particle size rather than to a direct support effect.<sup>[12]</sup> A recent study on the sizedependent sulfur poisoning of Pt hydrogenation catalysts showed that the sulfur-free structure-insensitive hydrogenation becomes size-dependent upon thiophene addition to the feed; in the presence of S, the turnover frequency increased approximately four-fold upon 2 to 7 nm particle size increase.<sup>[13]</sup>

The current study aims to investigate the size effect of palladium nanoparticles on hydrodesulfurization of 4,6-DMDBT and understand the contribution of hydrogenation sites through 3,3'-dimethylbiphenyl (3,3'-DMBP) hydrogenation with and without sulfur addition. To verify the hypothesis of the nanoparticle edge contribution to the enhancement of the direct desulfurization pathway, we also compared nearly spherical particles with nanocubes that have the lowest edge/terrace atom ratio among the different structures.<sup>[14]</sup> To exclude the influence of extremely small particles that may be co-present with large agglomerates in traditional catalysts prepared by support impregnation with a metal precursor, we pre-formed Pd nanoparticles in a colloidal solution by using polymeric stabilizers, followed by deposition on a support. Such an approach yields narrower size distribution as opposed to the conventional catalysts and allows us to study anisotropic and larger particle sizes that otherwise would require very high metal loading in traditionally prepared catalysts. The feed amount of 4,6-DMDBT corresponds to approximately 800 ppmw of sulfur (hydrogen-free) to simulate the conditions of a potential second-stage hydrotreater for refractory sulfur compound removal. The study demonstrates how the relative DDS and HYD contributions in HDS of a refractory molecule may be controlled by the Pd nanoparticle size and structure and, for the first time, reports the optimal nanoparticle size for enhanced sulfur extraction from 4,6-DMDBT.

# **Results and Discussion**

Figure 1 depicts images and size distribution histograms for as-synthesized Pd nanoparticles of different sizes and shapes before deposition on the catalyst support. The particles have a high degree of size and shape uniformity. However, Pd is known for low sintering resistance, especially at the catalytic application temperature (300 °C). Indeed, significant sintering occurred during the reaction, accompanied not only by size increase for the spherical particles, but also the loss of the defined shape for some cubic nanoparticles (Figure 2 and Supporting Information).

To estimate the number of available surface palladium after the high-temperature treatment, CO chemisorption was performed. The results are presented in Table 1, and they are in line with the TEM images of the used catalysts.  $Pd_{rsr}$  and  $Pd_{rMr}$ catalysts were prepared with different polymeric stabilizers; as nanoparticle sizes estimated by CO chemisorption and by TEM are nearly identical, efficient surface purification from the sta-



Figure 1. TEM images of as-synthesized Pd- $_{S^{-}}$  (a), Pd- $_{M^{-}}$  (b), Pd- $_{L^{+}}$  (c), and Pd- $_{XL^{+}}$  (d) nanoparticles and corresponding size-distribution histograms.

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Figure 2. TEM images and size-distribution histograms of the catalysts after 18 h on stream.

Table 1. Nanoparticle sizes from CO chemisorption analyses of the supported catalysts after the high-temperature treatment.			
Catalyst	Nanoparticle size <sup>[a]</sup> [nm]	Dispersion <sup>[a]</sup> [%]	
Pd <sub>"s"</sub>	4.1	28.5	
Pd <sub>"M"</sub>	8.0	15.2	
Pd <sub>"L"</sub>	12.8	8.7	
Pd <sub>"XL"</sub>	86.9	1.3	
[a] Based on the molar adsorbed CO/surface Pd ratio of $0.6^{[15]}$			

[a] Based on the molar adsorbed

bilizers was achieved by pretreatment in air at 350°C and hydrogen at 300 °C. The same pretreatment was used for all the catalytic reactions.

The catalytic behavior of the four synthesized samples in 4,6-DMDBT HDS was dramatically different. Figures 3 and 4 report the catalyst activity and selectivity at the similar 4,6-DMDBT conversions (ca. 40%). The dispersion and particle sizes refer to the data of Table 1 (catalysts after the high-temperature treatment). The DMDBT consumption rate per total amount of Pd in the reactor (Figure 3a) increases from the Pd<sub>"XL"</sub> to Pd<sub>"M"</sub> sample, which is expected with the metal dispersion increase. However, the  $Pd_{s'}$  sample with ~25-fold higher dispersion compared with the  $\mathsf{Pd}_{^*\!\mathsf{XL}'}$  catalyst shows the same low activity per total gram of palladium, which results in the volcano plot. If only surface Pd amount is taken into consideration (Figure 3b), the activity of the largest particles and the smallest ones differ by an order of magnitude.

The activity behavior trend is in line with product selectivities (Figure 4a) and product formation rates (Figure 4b): the largest nanocube-derived particles Pd<sub>\*XL"</sub> have the highest hydrogenation activity, resulting in the highest formation of the hydrogenated intermediates. They provide the highest conversion of the 4,6- DMDBT, but at the same time they are the least active for sulfur extraction, both in HYD and DDS routes. The large terraces and very low edge/terrace ratio for the nanocube-derived large Pd<sub>"x1"</sub> sample likely facilitate the hydrogenations, which are often reported as structure-sensitive reac-

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Figure 3. Catalyst performance in HDS of 4,6-DMDBT at 300 °C, 50 bar H<sub>2</sub>: (a) 4,6-DMDBT consumption rate per total mass of Pd; (b) the consumption rates per mole of surface Pd as found in Table 1. The results are at similar 4,6-DMDBT conversions (ca. 40%).



Figure 4. Catalyst performance in HDS of 4,6-DMDBT at 300 °C, 50 bar H<sub>2</sub>: (a) selectivities and (b) product formation rates per gram of total Pd. The dispersion refers to the data of Table 1. The results are at similar 4,6-DMDBT conversions (ca. 40%).



tions,<sup>[16]</sup> with the preference for larger nanoparticles providing enough terrace surface for the flat reactant adsorption.<sup>[17]</sup>

The lack of edges compared with other samples corroborates with the hypothesis of facilitated direct desulfurization on low-coordination active sites. As the size decreases from  $Pd_{xL'}$  to  $Pd_{M'}$ , the DMDBT conversion increases, but the efficiently formed hydrogenated intermediates convert more easily to the sulfur-free products because of the increased edge/terrace proportion; the direct desulfurization activity also increases. The above changes occur for average particle sizes in the range 87 to 8 nm. The most active particles (on a total mass basis, Figure 3a and Figure 4b) for the DMDBT conversion and sulfur-free product formation are the 8 nm particles because of the seemingly optimal terrace/edge proportions and high metal dispersion.

The smallest 4 nm particles, Pd<sub>"S"</sub>, were the least active in the overall DMDBT conversion, both based on the total and surface Pd amounts, and higher Pd loading in the reactor had to be used to ensure similar DMDBT conversion for a fair selectivity comparison. The observed ~20% DDS selectivity is unprecedented, to the best of our knowledge, for 4,6-DMDBT HDS on monometallic Pd catalysts. However, it does not indicate improved direct desulfurization activity, but rather that the hydrogenation rates are reduced to a greater extent than the drop in desulfurization activity with the particle size decreasing to Pd<sub>"S"</sub>. As Figure 4b shows, the DDS rates for Pd<sub>"M"</sub> and Pd<sub>"s"</sub> catalysts per total gram of Pd are practically the same, but the metal dispersion is twice as high for Pd<sub>"5"</sub>, indicating that the surface Pd DDS activity on the smaller particles is twice as low, with hydrogenation rates reduced almost by an order of magnitude. This gives rise to the observed apparent DDS selectivity improvement. Overall, per total gram of Pd, the Pd<sub>"s"</sub> catalyst with 4 nm particles behaves very similarly in 4,6-DMDBT HDS as the largest 87 nm nanocube-derived particles. The only difference is that the latter shows the lowest DDS selectivity because of the lowest edge/terrace ratio on the nanocube-derived sample compared with all other cuboctahedral particles. The smallest particles, thus, possess the lowest HYD and DDS activity, with HYD suppressed to a greater extent than the DDS compared with the larger particles.

Hydrodesulfurization rates and product distribution can also be affected by the catalyst support acidity, as was shown for 4,6-DMDBT HDS over zeolite- and alumina-supported Pd and Pt catalysts.<sup>[4e]</sup> For palladium, with a strong hydrogenation ability, no products of acid-catalyzed isomerization were observed even for the strongly acidic zeolite.<sup>[4e]</sup> The four-fold increased HDS conversion for Pd/MNZ-5 versus Pd/\gamma-Al<sub>2</sub>O<sub>3</sub> was ascribed to the surface acidity; however, the Pd particle size changed from 3.8 to 1.3 nm, which according to our current findings could also affect the reaction rate. We used  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a support for the  $Pd_{"M"}$ ,  $Pd_{"L"}$ , and  $Pd_{"XL"}$  catalysts, and  $MgAl_2O_4$  spinel for the Pd<sub>"s"</sub> particles for improved sintering resistance.<sup>[18]</sup> The spinel is known to possess similar acidity as Al<sub>2</sub>O<sub>3</sub> with an isoelectric point value of 8.4.<sup>[19]</sup> In the current work, no acid-catalyzed isomers were observed, and the most dramatic changes in the contributions to hydrogenation and sulfur extraction were found for the three catalysts deposited on the same  $Al_2O_3$  support (Figure 4a for dispersions of 1%, 9%, and 15%). Thus, the support effect in terms of its acidity may be considered negligible for the present size-effect study, although not completely excluded for the catalyst with the highest dispersion.

The observed trend for the selectivity and surface activity change for Pd<sub>-S'</sub>, Pd<sub>-M'</sub>, and Pd<sub>-L</sub> catalysts cannot be directly explained by the change in the number of edge/corner and terrace atoms: as known from surface crystal statistics, at such Pd particle sizes (> 4 nm), no significant changes in the relative proportion of different surface atoms are expected for near-spherical (cuboctahedral) particles.<sup>[14b]</sup> The dramatic difference between the reactivities of the 13 and 87 nm particles could be a result of their structure: the cuboctahedral 13 nm particles possess mostly (111) terraces with some contribution from (100) surfaces, whereas the nanocubes used to prepare the 87 nm particles display only (100) terraces. The cubes also possess a larger terrace/edge ratio than cuboctahedral particles.

Thus, there is another size-dependent factor that affects the number of available atoms for HYD and DDS routes, which is suggested to be structure-sensitive sulfur poisoning. The  $p(H_2S)/p(H_2)$  ratio of  $10^{-4}$  used in this work suggests the thermodynamic stability of metallic Pd, which was shown to be stable at a  $H_2S/H_2$  ratio below 0.01 at 600 K.<sup>[4c]</sup> Sulfur compounds at such low concentrations, thus, compete with sulfurfree molecules for metallic active sites and are referred to as "labile sulfur" participating in the reaction.<sup>[4d]</sup> Sulfur association with Pd can been seen from the elemental mapping performed on the spent Pd<sub>-MT</sub> catalyst (Figure 5).



Figure 5. Pd and S elemental mapping of the spent  $Pd_{M'}$  catalyst.

To evaluate the hypothesis of structure-sensitive sulfur poisoning, we performed hydrogenation of 3,3'-DMBP for the Pd<sub>"5"</sub>, Pd<sub>"M"</sub>, and Pd<sub>"L"</sub> samples at the same conditions (300 °C, 5 MPa) in the presence and absence of 300 ppmw sulfur in the feed (as CS<sub>2</sub> based on the sulfur amount corresponding to 40% 4,6-DMDBT conversion in HDS, i.e., 40% of 800 ppmw). Conversions below 10% were ensured, which allowed us to calculate turnover frequencies (TOF) under the assumption of a differential reactor performance. As seen from Figure 6, in the sulfur-free feed, the hydrogenation TOF increased with the particle size increase, which is in line with our above discussion on the larger particle requirement for the flat reactant adsorption. A support effect on sulfur poisoning of Pt catalysts was





**Figure 6.** Turnover frequency of DMBP hydrogenation over  $Pd_{rs^*}$ ,  $Pd_{rM^*}$ , and  $Pd_{rt^*}$  catalysts, with and without 300 ppm of sulfur in the feed (CS<sub>2</sub> equivalent corresponding to 40% 4,6-DMDBT conversion in the HDS experiments with 800 ppm S).

suggested to be negligible, apart from providing different metal nanoparticle sizes.<sup>[12]</sup>

However, comparing Figure 3b and Figure 6, the activity per surface palladium during 4,6-DMDBT conversion changed more dramatically on going from Pd<sub>"S"</sub> to Pd<sub>"M"</sub> catalysts compared with the sulfur-free hydrogenation. On addition of sulfur (as CS<sub>2</sub>) to the 3,3'-DMBP feed, all three catalysts exhibited two orders of magnitude lower hydrogenation rates, but the smallest Pd<sub>"s"</sub> nanoparticles were poisoned to the largest extent and showed the lowest hydrogenation activity. The drop in DDS and HYD activity was also reported for thiophene hydrogenation on Pt and Ru for smaller particle sizes and was ascribed to the stronger metal-sulfur bonds and lower active vacancy concentration on corner and edge sites that are prevalent on the smaller clusters.<sup>[7,8]</sup> Our findings, thus, are in line with reported mechanisms and active site requirements for metal-catalyzed HDS and have established the most desirable Pd nanoparticle (8 nm) for enhanced sulfur extraction from a refractory 4,6-DMDBT molecule. Below this size, significant sulfur poisoning inhibits both hydrogenation and direct desulfurization rates.

# Conclusions

Among Pd clusters of average 4, 8, 13, and 87 nm particle size, the largest particles exhibited the highest surface activity in 4,6-DMDBT conversion, which, however, was a result of the formation of hydrogenated sulfurous intermediates with a low contribution from sulfur extraction. The smallest particles provided an unprecedented (for Pd at 5 MPa reaction pressure) direct desulfurization selectivity of 20% at 40% 4,6-DMDBT conversion because of the reduced contribution of the hydrogenation path, which requires a low edge/terrace atom ratio on the nanoparticle surface. The smallest particles were also found to be poisoned by adsorbed sulfur to a greater extent, as per kinetic studies of sulfur-free and sulfur-inhibited hydrogenation of 3,3'-dimethylbiphenyl. Among the studied catalysts, the optimal Pd nanoparticle size that ensures maximum sulfur extraction based on total Pd mass loading in the reactor was found to be 8 nm. Above this size, in spite of the surface activity increase, the size increase decreases the atom efficiency of the active metal.

# **Experimental Section**

#### Materials

Palladium(II) chloride solution (PdCl<sub>2</sub>, 5% w/v, Acros), sodium tetrachloropalladate(II) (Na2PdCl4, 98%, Sigma-Aldrich), poly(vinylpyrrolidone) (PVP) (MW = 40000, Sigma-Aldrich), generation 4 poly(amidoamine)-hydroxyl dendrimer (G4OH, 10 wt% in methanol, Dendritech Inc.), potassium bromide (KBr, >99%, Sigma-Aldrich), ethyl alcohol (denatured, Sigma-Aldrich), reagent alcohol (ethanol, 95 vol%, Fisher Scientific), ethylene glycol (EG, 99.8%, Sigma-Aldrich), ascorbic acid ( $\geq$  99%, Sigma–Aldrich), sodium borohydride (NaBH<sub>4</sub>, > 99%, Sigma–Aldrich), aluminum oxide ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 150 mesh, 58 Å pore size, Sigma-Aldrich), aluminum isopropoxide  $(Al(OCH(CH_3)_2)_3)_3)_3$ ,  $\geq$  98%, Sigma–Aldrich), magnesium nitrate hexahydrate  $(Mg(NO_3)_2 + 6H_2O_1) \ge 98\%$ , Sigma-Aldrich), and acetone (99.7%, Fisher Scientific) were used as received. The gases of ultrahigh purity (i.e., 99.999%) were purchased from Praxair. For catalytic reactions, n-decane (99.4%) from Fisher Scientific, n-dodecane (≥99%), and 4,6-DMDBT (97%), 3,3'-dimethylbiphenyl (99%), and carbon disulfide (99.5%) from Sigma-Aldrich were used as received. Milli-Q water was used throughout the work.

#### Catalyst preparation and characterization

Four samples of stabilized palladium nanoparticles with controlled size were prepared in colloidal solutions following methods available in the literature. The smallest nanoparticles  $(Pd_{"S"})$  with < 2 nmmean diameter were prepared by using a dendrimer-templating strategy, originally developed by Crooks and co-workers,<sup>[20]</sup> with some modifications. G4OH solution (10 mL of 0.25 mm) was prepared by diluting G4OH methanol solution (0.357 g of 10 wt%, 0.0025 mmol) in water. PdCl<sub>2</sub> methanol solution (100 mL of 1 mм) was prepared by adding PdCl<sub>2</sub> solution (0.356 mL, 5% w/v, 0.1 mmol) in methanol in a 250 mL round-bottom flask. Then, the G4OH solution was added into the reaction flask containing the  $PdCl_2$  methanol solution (molar ratio of G4OH to Pd = 1:40). After 1 h of complexation, NaBH<sub>4</sub> solution (2 mL of 1 м, 2 mmol; NaBH<sub>4</sub> to Pd molar ratio = 20:1; prepared and kept at  $0^{\circ}$ C) was added to the reaction mixture dropwise under vigorous stirring. The color of the Pd<sup>2+</sup>-G4OH solution changed from pale yellow to dark brown indicating the reduction of Pd ions to metallic Pd. The reaction was continued for 1 h for complete reduction.

Medium-size particles of ~3 nm (Pd<sub>"M"</sub>) were prepared by using Teranishi and Miyake's one-step alcohol reduction method in the presence of PVP,<sup>[21]</sup> with minor modifications.<sup>[22]</sup> A mixture containing PdCl<sub>2</sub> (0.2 mmol), ethanol/water solution (170 mL, 41 vol% ethanol), and PVP (0.4 mmol, PVP to metal molar ratio=20:1) was stirred and heated at reflux for 3 h under air. Transparent darkbrown colloidal solutions of monometallic Pd nanoparticles were obtained without any precipitate.

Larger nanoparticles of ~7 nm diameter (Pd-L-) were prepared by the ethylene glycol reduction method in the presence of PVP.<sup>[22,23]</sup> PdCl<sub>2</sub> (0.2 mmol) and PVP (4 mmol, PVP to Pd molar ratio = 20:1) were well dissolved in ethylene glycol (200 mL) at room temperature. Then, the PVP-Pd<sup>2+</sup>-EG solution was stirred and heated at reflux under air for 3 h for complete reduction.



Pd nanocubes with an average edge length of 16 nm (Pd<sub>-xL</sub>-) were prepared by using slow reduction by ascorbic acid in the presence of PVP and KBr, following the synthetic procedure described by Xia and co-workers<sup>[24]</sup> with some modifications. PVP (1 mmol), KBr (5.2 mmol), and ascorbic acid (0.2 mmol) were dissolved in water (20 mL) at 80 °C. Then, an aqueous solution (5 mL) containing NaPdCl<sub>4</sub> (0.2 mmol) was added to the reaction solution while stirring. The molar ratios of PVP, KBr, and ascorbic acid to Pd were 5:1, 2:1, and 26:1, respectively. The color of the reaction solution changed from yellow to dark brown, indicating the reduction of Pd<sup>2+</sup> to metallic Pd. The reaction was continued for 3 h at 80 °C for complete reduction.

The colloidal solutions were used to deposit the nanoparticles on a solid support with a target loading of 0.3 wt%. The freshly prepared  $Pd_{*M''}$ ,  $Pd_{*L''}$ , and  $Pd_{*XL''}$  particles were deposited on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which was pre-calcined in air at 500  $^\circ C$  for 2 h.  $Pd_{"M"}$  particles were deposited on  $\gamma\text{-Al}_2O_3$  by incipient impregnation.  $\text{Pd}_{"L"}$  and  $\text{Pd}_{"XL"}$ particles were precipitated with acetone and deposited on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by wet impregnation. Pd<sub>"s"</sub> particles were precipitated with acetone and deposited on MgAl<sub>2</sub>O<sub>4</sub> spinel support by wet impregnation. The support was prepared by a known procedure:<sup>[18]</sup> in a 1000 mL Pyrex bottle (autoclavable),  $Al(OCH(CH_3)_2)_3$  (0.1 mol) and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.05 mol) were dissolved in denatured ethanol (300 mL) under stirring until complete dissolution (at least 1 h). The reaction vessel was sealed, and the reaction mixture was heated to 150°C (hot plate digital display) for 12 h. The solvent, denatured ethanol, was evaporated at 100 °C under stirring, and the resulting gel was then dried in an oven at 90 °C overnight. To obtain the MgAl<sub>2</sub>O<sub>4</sub> spinel material, the dry powder was calcined in a furnace under static air at 800 °C for 12 h. The deposited Pd catalysts were calcined in air at 350 °C for 2 h, followed by reduction in a hydrogen flow at 300 °C for 1 h for the stabilizing polymer removal. The final Pd loadings were determined by neutron activation analysis (Becquerel Laboratories, Maxxam Company, Canada) and found to be 0.200 wt%, 0.240 wt%, 0.240 wt%, and 0.210 wt% for the Pd<sub>"S"</sub>, Pd<sub>"M"</sub>, Pd<sub>"L"</sub>, and Pd<sub>"XL"</sub> catalysts, respectively. Transmission electron microscopy (TEM) and CO chemisorption of the nanoparticles and/or supported catalysts were performed as described previously.<sup>[22]</sup> For the TEM analysis, 100–200 nanoparticles per sample were counted from TEM images by using ImageJ software. The reported sizes are based on the linear distribution. Prior to CO chemisorption, the catalysts were calcined at 350 °C for 2 h in air, which was followed by in situ reduction in 10%  $H_2/Ar$  at 300 °C for 1 h.

### Hydrodesulfurization of 4,6-DMDBT

Hydrodesulfurization of 4,6-DMDBT was performed at 300 °C and 50 bar with a hydrogen flow rate of 100 mLmin<sup>-1</sup> (STP) in a packed bed reactor (22" long stainless steel tube with an inner diameter of 1/2"), according to the pioneering works published by Prins's group<sup>[2,4]</sup> with some modifications by our group.<sup>[25]</sup> The calcined catalysts (0.09-0.54 g, diluted in 150 mesh SiC, total of 4 g) were packed in the reactor and then reduced in situ at 300 °C and 50 bar for 1 h under a hydrogen flow (100 mLmin<sup>-1</sup>). The catalyst amounts were different to ensure similar conversions for fair selectivity comparison. The 4,6-DMDBT was fed into the catalytic system by pumping a solution of 0.5 wt% 4,6-DMDBT (750 ppmw of sulfur) and 3.5 wt% dodecane (internal standard) balanced in decane (solvent) with a flow rate of  $87 \times 10^{-6}$  mol min<sup>-1</sup>. The catalytic performances were assessed after 16 h stabilization. Prior to sampling, the condenser was emptied after the 16-hour stabilization; liquid samples were then collected after 2 h (at 18 h time-onstream). The absence of external and internal mass transfer limitations was verified experimentally for the most active Pd<sub>"M"</sub> catalyst. The results can be found in the Supporting Information. Liquid samples were analyzed offline by using a Varian 430 gas chromatogram (GC) equipped with a flame ionization detector (FID). The GC capillary column was a CP-Sil 8 CB column, 50 m length×0.25 mm inner diameter. Initially, the oven temperature was stabilized at 50°C for 1 min and then increased to 300°C with a rate of 10°Cmin<sup>-1</sup>. The observed products were identified by GC-MS and found to be in agreement with the reaction mechanism in Scheme 1. The mass balance was closed within 94-99%. No acidcatalyzed isomerization products<sup>[4e]</sup> were observed. The reported selectivity is an integral selectivity (reported on molar basis; produced H<sub>2</sub>S not included) that was determined as the amount of each HDS product formed divided by the total amount of HDS products (except H<sub>2</sub>S). In the Results section, the selectivity to DDS is the selectivity to 3,3'-dimethylbiphenyl (DMBP); the selectivity to S-free products by HYD is the summation of the selectivities to 3,3'-dimethylcyclohexylbenzene (3,3'-DMCHB) and 3,3'-dimethylbicyclohexyl (3,3'-DMBCH); the selectivity to S-containing intermediates by the HYD route is the summation of selectivities to 4,6-dimethyltetrahydrodibenzothiophene (4,6-DMTHDBT), 4,6-dimethylhexahydrodibenzothiophene (4,6-DMHHDBT), and 4,6-dimethylperhydrodibenzothiophene (4,6-DMPHDBT); the selectivity to the total HYD route is (100%-selectivity to DDS), as per Scheme 1.

#### Hydrogenation of 3,3'-DMBP

DMBP hydrogenation to DMBCH and DMCHB was studied by using the same HDS setup at 300 °C and 50 bar with a hydrogen flow rate of 100 mLmin<sup>-1</sup>, which simulated the experimental conditions of HDS. The DMBP was fed into the catalytic system by pumping a solution containing 1 wt% DMBP and 3.5 wt% dodecane (internal standard) balanced in decane; the corresponding DMBP flow rate was  $1.96 \times 10^{-6}$  mol min<sup>-1</sup>. Pd catalyst (0.005 g) was pre-mixed with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0.2 g) to avoid bypassing and then packed into the reactor according to the procedure for the HDS reactions. The catalytic performances in DMBP hydrogenation were analyzed and reported at 18 h time-on-stream. DMBP hydrogenation was also performed with the presence of 300 ppmw sulfur in the feed solution (in the form of  $CS_2$ ) to simulate the amount of  $H_2S$  produced at about 40% DMDBT conversion during HDS reactions. Owing to the strong S-poisoning effect, DMBP hydrogenation with sulfur was tested at a lower space velocity; 0.2, 0.05, and 0.1 g of Pd<sub>"S"</sub>, Pd<sub>"M"</sub>, and Pd<sub>"1"</sub> catalysts were packed in the reactor, respectively.

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**Keywords:** desulfurization • nanoparticles • size control • structure sensitivity • supported catalysts

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