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Palladium islands on iron oxide nanoparticles for hydrodesulfurization catalysis

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A four-fold increase in palladium (Pd) mass-based hydrodesulfurization (HDS) activity was achieved by depositing Pd species as nanosized islands on 12-nm colloidal iron oxide (FeO<sub>x</sub>) nanoparticles via galvanic exchange reaction. The highest palladium dispersion was obtained for an optimal Pd/Fe molar ratio of 0.2, which decreased with the ratio increase. The improved dispersion was responsible for the enhanced catalytic activity per the total Pd amount in HDS of 4,6-dimethyldibenzothiophene at 623 K and 3 MPa as compared to the iron-free Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. The lattice strain and modified electronic properties of Pd islands suppressed deep hydrogenation to dimethylbicyclohexyl and changed hydrocracking products distribution. Pd nanoparticles deposited on commercial  $Fe_2O_3$  did not provide such activity enhancement and catalyzed significant cracking. This study demonstrates that  $FeO_x@Pd$  structures are a possible alternative to monometallic Pd catalysts with enhanced noble metal atom efficiency for ultradeep HDS catalysis and points to their great potential to reduce the catalyst cost and move towards more earth-abundant catalytic materials.

# 1. Introduction

Platinum group-based heterogeneous catalysts are known for their outstanding catalytic properties among other transition metals, but they occur at very low levels of abundance in the earth crust. Since catalytic activity depends on the surface fraction of metal nanoparticle atoms<sup>1,2</sup> enhancing the utilization of the noble metal atoms has been a scientific and technological matter of paramount importance.<sup>1,3,4</sup> Accordingly, vast efforts have been invested to increase the number of surface active atoms by downsizing nanoparticles (NPs) to subnanometers and single atoms <sup>1,5–11</sup>, introducing high-index crystallographic planes<sup>12–</sup> <sup>15</sup>, and structuring active metal as small particles (dumbbelllike)<sup>16,17</sup> or thin shell (core-shell)<sup>3,18-20</sup> over individual nanoparticles. The core-shell architecture is highly desirable due to the possibility of tailoring structural and chemical properties of multiple components at atomic levels within individual NPs.<sup>3,19–25</sup>A previous work by Hu et al.<sup>4</sup> showed the

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increased electrocatalytic activity of segregated Pd islands in bimetallic palladium-tungsten NPs suggesting the lack of necessity of a complete shell configuration for enhanced catalysis.

The surface availability of precious metals for catalysis can be remarkably increased by decorating them on low-cost nonnoble metal cores.<sup>3,4,26</sup> The exceptional reactivity of such structure was ascribed to the modification of electronic properties and the lattice strain of active metal atoms.<sup>26-28</sup> The electronic defects of reducible metal oxides provide anchoring sites for active metals<sup>29,30</sup>, where the degrees of their interactions control dispersion, morphology, and metal reactivity.<sup>29</sup> For example, Pt shell that formed on latticedefect-rich amorphous Fe NPs showed better catalytic performance than crystalline Fe NPs<sup>19</sup>, and in another study, the strong metal-support interactions stabilized more reactive Pt single atoms over iron oxide support.<sup>1</sup> The electronic impacts of core metal are limited to the first few layers and decline with layer thickness<sup>27</sup>, whereas the lattice strain effects remain for thicker layers<sup>26,27</sup> with the possibility of being tuned by altering the structural properties of core.<sup>28</sup> The lattice strain affects the *d*-band structure and hence the catalytic activity of heterostructured NPs by modifying the

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adsorption energy of reactants.<sup>26</sup> However, by increasing the layer thickness above a critical value, the overgrown layer dislocates to recover the strain-free prime-crystal structure, which can also change the morphology of NPs.<sup>31</sup> This explanation elucidates the fact that the activity is essentially maximized at a threshold layer thickness, which in some cases is hardly adjustable and/or stable under reaction conditions, especially for metals such as Pd that have a high tendency to thermal sintering. For instance, a core-shell structure of Fe@Pd has changed into FePd alloy after catalytic combustion of methane over 530 °C.<sup>32</sup>

Iron (Fe), as one of the utmost earth-abundant and environmentally benign elements, is a promising candidate as a core structure<sup>19,28,32–34</sup> that can also facilitate recovery of spent catalysts via magnetic separation.<sup>19,35–38</sup> The combinations of Fe with Pt-group metals have shown a superior performance in a variety of catalytic applications such as electrooxidation catalysis<sup>16,18,39</sup>, oxygen reduction reaction<sup>16,28,33,34,40</sup>, CO oxidation<sup>1,41</sup>, hydrodechlorination<sup>42</sup>, methane combustion<sup>32</sup>, and non-syngas-route methanol production.43 Even a mixture of Pd and iron oxide NPs exhibited higher activity than Pd NPs in hydrogenation of alkyne alcohols.<sup>36</sup> The Pd-Fe system is especially suitable for high-temperature applications requiring palladium because of the lower Pd surface energy and higher atomic diameter as compared to Fe, which causes large surface segregation of Pd and similar total surface-based activities of Pd and Pd-Fe systems in hydrogenations.<sup>44</sup> This promising combination has encouraged researchers to develop different hetero-Pd<sup>43,45</sup> configurations such as iron-oxide-supported dumbbells<sup>16,17</sup>, urchin-like NPs<sup>46</sup>, Pt single atoms on  $FeO_x^{1,8}$ , and cluster-in-cluster Pt-Fe<sub>x</sub>O<sub>y</sub> NPs<sup>47</sup> besides their alloys<sup>40,48-</sup> <sup>50</sup> and in different controlled shapes.<sup>51</sup>

Herein, we report the design of bimetallic FeO<sub>x</sub>@Pd nanoparticles using colloidal chemistry technique in which palladium atoms form islands on the surface of iron oxide nanoparticles. The synthesis uses a galvanic exchange reaction of  $Pd^{2+}$  reduction by  $Fe^{0}$  and/or  $Fe^{2+}$  on preformed iron oxide seeds.<sup>52,53</sup> The developed configuration allowed for the improved palladium dispersion and catalytic properties as compared to the monometallic Pd catalyst. The catalytic performance was evaluated in hydrodesulfurization (HDS) of a refractory sulfur compound, 4,6dimethyldibenzothiophene (4,6-DMDBT), as a model reaction in the production of fuels with ultra-low sulfur level for either transportation or fuel cell applications (Scheme 1).<sup>54–60</sup> When sulfur content in fuels has been pre-reduced to 500 ppm, 20 wt% of all sulfur species belong to 4,6-DMDBT.<sup>61–65</sup> Its desulfurization is hindered by the steric constrains from the alkyl groups, which can be lessened by partial hydrogenation of the aromatic rings (HYD path in Scheme 1). Pt-group metals attract considerable attention as potential catalysts for a second-stage ultra-deep desulfurization of fuels<sup>61,66–68</sup> because they are highly efficient hydrogenation catalysts. To the best of our knowledge, this is the first report to produce Pd islands on FeO<sub>x</sub> nanoparticles and demonstrate their performance in a high-temperature catalytic application. The optimized synthesized material can also be recommended for a variety of reactions catalyzed by Pt-group metals, where the efficiency of costly and scarce active metal is paramount.





# 2. Experimental 2.1. Materials

Palladium (II) chloride solution (PdCl<sub>2</sub>, 5 wt%), iron (III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), polyvinylpyrrolidone (PVP, average molecular weight of 29,000), sodium borohydrate (NaBH<sub>4</sub>), gamma-alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 150 mesh, 100 µm diameter, average pore diameter of 58 Å, BET=155 m<sup>2</sup>/g), and Fe<sub>2</sub>O<sub>3</sub> (<5 µm) all from Sigma–Aldrich were used for the catalyst preparation. Ethanol (95 vol.%, Fischer Scientific), Milli-Q water, ethylene glycol (≥99.7%, Fischer Scientific), and acetone (≥99.7%, Fischer Scientific) were used as received. 720 ppmw sulfur as 4,6dimethyldibenzothiophene (4,6-DMDBT, C<sub>14</sub>H<sub>12</sub>S, Sigma-Aldrich) was dissolved in *n*-decane (Fischer Scientific) as a

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solvent containing 3.5 wt% *n*-dodecane (Fischer Scientific) as the internal standard and was used as a model fuel for HDS reactions. Ultra-high purity (99.999%) argon and hydrogen gases were purchased from Praxair Canada.

# 2.2. Catalyst synthesis

Monometallic palladium and bimetallic iron-palladium nanoparticles (FeO<sub>x</sub>@Pd<sub>n</sub>, iron oxide as a core) were synthesized as colloidal dispersions in the presence of PVP as a stabilizer followed by deposition on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by acetone precipitation. An alcohol reduction method was used for the synthesis of Pd nanoparticles, as described in our previous work<sup>11</sup>. Briefly, 500 µl of the Pd precursor solution was dissolved in 40 ml ethanol and 60 ml Milli-Q water in the presence of PVP (PVP-to-Pd molar ratio of 30). The mixture was refluxed for 1 h and then cooled down to room temperature. For the synthesis of bimetallic FeO<sub>x</sub>@Pd<sub>n</sub> catalysts, 0.14 mmol of iron(III) chloride hexahydrate was dissolved in 100 ml of ethylene glycol containing 0.47 g of PVP. The mixture was stirred rigorously for 30 min at room temperature in a 500-ml three-neck flask while purging with ultra-high purity nitrogen. After obtaining a transparent yellowish solution, the temperature was gently increased to 413 K while purging with nitrogen. Excess amount of sodium borohydrate was added to the solution, changing the color to black first and then dark-green. The mixture was then refluxed for 2 h while purging with nitrogen. After cooling down to room tempeature, hydrogen was flown for 2 hours followed by drop-wise addition of palladium chloride in ethylene glycol (40 ml) within 1 h. The system was then purged with hydrogen for an additional 2 h. No precipitation was observed at the end of the synthesis procedure, and the obtained colloids were clear and macroscopycally homogeneous. All the synthesized nanoparticles were precipitated on dried  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> using acetone. For comparison, monometallic Pd nanoparticles were prepared with the same alcohol reduction method in the presence of PVP and were deposited on commercial  $Fe_2O_3$  (<5  $\mu$ m). All the synthesized catalysts were dried at room temperature for 2 h and then 373 K overnight with subsequent calcination at 673 K for 4 h to remove the polymer stabilizer. Prior to the HDS reaction, the catalysts were reduced in hydrogen at 623 K. Such a calcination-reduction treatment is known to remove the PVP stablizer from metal nanoparticles, as shown earlier<sup>72–74</sup>. The synthesis repeatability was verified for the most representative FeO<sub>x</sub>@Pd<sub>0.2</sub>/Al<sub>2</sub>O<sub>3</sub> and FeO<sub>x</sub>@Pd<sub>0.6</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, with identical characterization results for two different batches of each.

# 2.3. Catalyst characterization

The palladium and iron content of the calcined catalysts were determined using neutron activation analysis NAA (Becquerel Laboratories–Maxxam Company, Ontario, Canada). Gamma-ray spectrometer with a high resolution coaxial germanium detector was used to irradiate the samples. Transmission electron microscopy (TEM) images were recorded using a JEOL JEM2100 device operating at 200 kV. Scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDS) was performed using a field emission JEOL 2010F Transmission Electron Microscope operating at 200 kV. Particle size distributions (PDS) were measured by counting 200 particles.

X-ray diffraction (XRD) patterns of unsupported synthesized nanoparticles were recorded using Rigaku Ultima IV diffractometer equipped with a D/Tex detector, an Fe Filter, and Co K $\alpha$  radiation ( $\lambda$  = 1.78899 Å). The synthesized nanoparticles were first washed with Milli-Q water and were then dried at 333 K in air before XRD measurements. The diffraction patterns were collected over 5 to 90 degrees on continuous scan at 2 degrees 2 $\theta$  per minute with a step size of 0.02°. Data interpretation was done using JADE 9.6 with the 2016 ICDD and 2016 ICSD databases.

X-ray photoelectron spectroscopy (XPS) of the calcined and spent catalysts (after the HDS reaction for 18 h on stream) was performed using Kratos Axis 165 X-ray photoelectron spectrometer using Mono Al K $\alpha$  source operating at 14 kV and15 mA. Background subtraction and peaks fitting were performed using CasaXPS software package. All the XPS core–level spectra were corrected with C 1s at 284.8 eV.

Carbon monoxide (CO) chemisorption analyses were carried out using a Micromeritics Autochem II 2920 apparatus equipped with a TCD detector. About 300 mg of calcined catalysts were pretreated by hydrogen at the temperatures used for HDS reactions (623 K) for 1 h. This temperature is known to ensure various Pd species reduction on the supported catalysts<sup>75–77</sup>. The catalysts were then purged with helium (He) at the same temperature for 1 h. After cooling down to room temperature, 5 mol% CO in He was micropulsed to measure the amount of CO uptake. Temperature-programmed reduction (TPR) was performed using the same device. About 100 mg of the calcined catalysts were degassed by argon (Ar) at 473 K for 2 h. After cooling down to room temperature, TPR analysis was performed using a 10 ml/min of 10 mol% H<sub>2</sub>/Ar at the heating rate of 10 K/min from room temperature.

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#### 2.4. Catalytic experiments

Hydrodesulfurization of 4,6-dimethyldibenzothiophene (4,6-DMDBT) was studied under 3 MPa hydrogen pressure 623 K using a continuous-flow fixed bed reactor, as described in detail previously<sup>60</sup>. The calcined catalysts were diluted with silicon carbide (mesh 120, 22:1 weight ratio) and were then loaded in a stainless steel reactor (L=22", i.d.=0.5"). The dilution ensured the efficient heat conduction in the bed and negligble effect of axial dispersion. The effect of bed dilution on the conversion was found below the experimental error $^{78}$ . The corresponding calculations, along with the verification of the isothermal kinetic regime and near-ideal plug-flow behavior can be found in the Supporting Information<sup>79–81</sup>. The catalysts were reduced in situ for 1 h before the HDS reaction using 100 ml/min H<sub>2</sub> at the reaction temperature (623 K) and operating pressure of 3 MPa. A model liquid fuel containing 720 ppmw sulfur as 4,6-DMDBT with 3.5 wt% ndodecane as the internal standard in *n*-decane (solvent) was then introduced into the reactor at 0.05 ml/min downward continuous-flow using a Series II high-pressure pump. Before feeding to the reactor, the liquid feed was mixed with 100 ml/min hydrogen gas to reach the hydrogen-to-liquid molar ratio of 16. All the feed components were in the gas phase at the reaction conditions, as simulated by Aspen HYSYS (Version 9). The HDS experiments were performed for 18 h on stream including overnight catalyst stablization to reach steady-state conditions indicated by a maximum of 5% deviation in the conversions at 2 and 18 h on stream.

Indentification of the reaction products was carried out offline by a gas chromatography coupled with mass spectrometry (GC-MS) using a Thermo Scientific Trace GC Ultra, equipped with a Thermo Scientific TR-5 column (30 m, 0.25 mm, 0.25 µm film thickness). The quantitative analyses of 4,6-DMDBT and all of the reaction products were performed using a calibrated Agilent 7890A gas chromatograph equipped with a H-PONA Agilent capillary column (50 m, 0.25 mm, 0.25 µm film thickness) with high purity helium as the carrier gas and a flame ionization detector. The injector and detector temperatures were maintained at 573 K. The oven temperature was held at 313 K for 2 min, and then ramped up to 573 K at 10 K/min, and it remained at this temperature for 20 min. Examples of GC chromatograms can be found in the Supporting Information. According to the reaction mechanism in Scheme 1, the selectivity to the direct desulfurization (DDS) path was calculated based on the amount of dimethylbiphenyl (DMBP) divided by the amount of converted 4,6-DMDBT. Selectivity

to hydrogenation (HYD) path is the summation of selectivities to dimethylcyclohexylbenzene (DMCHB), dimethylbicyclohexyl (DMBCH), dimethylperhydrodibenzothiophene (DMPHDBT), dimethylhexahydrodibenzothiophene (DMHHDBT), and dimethyltetrahydrodibenzothiophene (DMTHDBT). Hydrocracking selectivity (HCK) includes benzene (BZ), toluene (TL), cyclohexane (CH), and methylcyclohexane (MCH). Yield of all sulfur-free products was calculated as a product of conversion by a sum of selectivities to each S-free bicyclic product and 50% of selectivities to each monocyclic product. The product amounts were identified with the aid of the internal standard in the feed. No solvent cracking products (lower alkanes) were found in the product by GC-MS. The internal standard/solvent peak ratio was 0.0375 for the feed and the reacted mixture.

In Scheme 1 the HCK products are shown to originate from the products of the hydrogenation path, not from 3,3'-DMBP. The reaction kinetics and the reaction pathways were not addressed in the current work but assumed based on literature that reported the formation of toluene and methylcyclohexane from the producs of the hydrogenation path in 4,6-DMDBT HDS.<sup>69,70,78</sup> Cracking of the DDS product can not excluded<sup>82</sup> but is less likely because of the very low observed selectivity to toluene as compared to methylcyclohexane.

The reported conversions are subject to 10% experimental error. Two standard deviations in selectivities are 3%. The carbon mass balance was above 95%.

# 3. Results and Discussion

#### 3.1. Catalysts characterization

Table 1 illustrates the physicochemical characteristics of monometallic Pd, Fe, and bimetallic FeO<sub>x</sub>@Pd<sub>n</sub> catalysts, where n is the molar ratio of Pd to Fe measured by neutron activation analysis (NAA). The bimetallic FeO<sub>x</sub>@Pd<sub>n</sub>/Al<sub>2</sub>O<sub>3</sub> structures exhibit higher CO uptakes than those of monometallic Pd catalysts (Pd/Al<sub>2</sub>O<sub>3</sub> and Pd<sub>0.2</sub>/Fe<sub>2</sub>O<sub>3</sub>), which also increase with the decreasing Pd concentration in the catalyst. The CO uptake of Pd<sub>0.2</sub>/Fe<sub>2</sub>O<sub>3</sub> catalyst, prepared by deposition of Pd NPs on commercial Fe<sub>2</sub>O<sub>3</sub>, was significantly lower than that of the synthesized FeO<sub>x</sub>@Pd<sub>0.2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. These results reveal the greater dispersion of Pd species in bimetallic FeO<sub>x</sub>@Pd<sub>n</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, which could not be achieved using commercial Fe<sub>2</sub>O<sub>3</sub> with the particle size <5  $\mu$ m.

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Figures 1a-c show TEM images of the colloidal FeO<sub>x</sub>, unsupported and Al<sub>2</sub>O<sub>3</sub>-supported FeO<sub>x</sub>@Pd nanoparticles. The image of the colloidal FeO<sub>x</sub>@Pd in Figure 1b shows the formation and deposition of ca. 2 nm Pd - nanoislands on the surface of FeO<sub>x</sub> particles of ca. 12 nm in size. The spatial association of Pd and Fe was also confirmed by EDS mapping (Figure 2). Remarkably, after the calcination at 673 K and an 18 h catalytic HDS reaction at 623 K, no agglomerates were observed for the supported FeO<sub>x</sub>@Pd catalyst (Figure 1c), while the FeO<sub>x</sub>-free Pd/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited sintered Pd nanoparticles up to 30 nm in size (Figure S2 in the Supporting Information). Thus, the colloidal FeO<sub>x</sub> serves as a highsurface area support for the Pd species, which prevents their sintering as opposed to Al<sub>2</sub>O<sub>3</sub> and commercial Fe<sub>2</sub>O<sub>3</sub> supports and explains the enhanced CO uptakes (Table 1). Highresolution TEM images of FeO<sub>x</sub>@Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, taken after the catalytic reaction, show different areas on the surface of a single nanoparticle suggesting the partial coverage of FeO<sub>x</sub> surface by Pd species (Figures 1d-f). The black Pd-containing areas exhibit fringes with spacing of 0.20-0.23 nm, which is different from the fringes on grey areas of 0.24–0.26 nm belonging to magnetite<sup>36,83</sup>, and the fringe of 0.35 nm to alumina.41 Monometallic Pd nanoparticles exhibited lattice spacing of 0.23 nm, which is characteristic of Pd(111) planes (Figure S2 in the Supporting Information). These lattice compression in bimetallic NPs, as compared to the monometallic Pd, are characteristic of surface Pd alloying with Fe<sup>32,50,84</sup> and/or smaller Pd nanoparticle size<sup>85</sup>.

The Pd lattice compression was also evidenced by XRD (Table 1 and Figure S3 in the Supporting Information). This lattice strain changes the filling and the energy level of Pd d-band<sup>86–</sup> <sup>88</sup>, which consequently tunes the surface free energy as well as chemisorption and catalytic properties of active sites.<sup>26,27,86</sup> For instance, a compressed Pt lattice downshifted the *d*-band center and thus reduced the adsorption energy of carbon monoxide.<sup>27</sup> The lattice compression of Pd in the  $FeO_x@Pd_{0.2}$  sample was greater than  $FeO_x@Pd_{0.6}$  suggesting smaller Pd nanoparticles and/or that more Pd atoms were involved in the interaction with FeO<sub>x</sub> probably by formation of thinner Pd islands. During synthesis, surface Fe<sup>0</sup> and/or  $Fe^{2+}$  on the iron oxide core may participate in the galvanic reaction of Pd<sup>2+</sup> reduction to Pd(0) that formed highlydispersed Pd islands.<sup>52,53</sup> The interaction between Pd and FeO<sub>x</sub>, as evidenced from lattice compression, prevented Pd sintering and maintained its dispersion even after high temperature treatment. This finding is in line with CO chemisorption uptakes (Table 1): 61% of Pd species are located on the surface in FeO<sub>x</sub>@Pd<sub>0.2</sub> vs. 18% for FeO<sub>x</sub>@Pd<sub>0.6</sub> and only 5% for the mono Pd. When the layer thickness increases above a critical value,<sup>31</sup> the overgrown layer recovers the strain-free prime-crystal structure. Thus, the metal dispersion is maximized at a threshold layer thickness. The highest dispersion in this work was found for Pd/Fe molar ratio of 0.2 as compared to 0.05, 0.6, 1.5, and mono Pd (Table 1).

Catalyst	Pd loading <sup>a</sup>	Fe loading <sup>a</sup>	CO up	otake	Pd lattice parameter <sup>c</sup> (Å)		
	(wt%)	(wt%)	µmol <sub>co</sub> /g <sub>cat</sub>	mol <sub>co</sub> /mol <sub>Pd</sub>			
$Pd/Al_2O_3$	0.410	0.0	2.03	0.053	3.893		
$FeO_x@Pd_{1.5}/Al_2O_3$	0.410	0.160	5.92	0.153	-		
$FeO_x@Pd_{0.6}/Al_2O_3$	0.180	0.160	3.02	0.179	3. 885		
$FeO_x@Pd_{0.2}/Al_2O_3$	0.060	0.160	3.43	0.608	3.826		
FeO <sub>x</sub> @Pd <sub>0.05</sub> /Al <sub>2</sub> O <sub>3</sub>	0.012	0.160	0.60	0.532	_		
$Pd_{0.2}/Fe_2O_3$	0.060	65.7	1.34 <sup>b</sup>	0.150	_		
FeO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	0.0	0.160	0.097	_	_		

Table 1. Phy	/sicochemical	properties of s	vnthesized	catalysts
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<sup>a</sup> measured by NAA; <sup>b</sup>CO uptake of commercial  $Fe_2O_3$  is 0.44  $\mu$ mol<sub>cO</sub>/g<sub>cat</sub>; <sup>c</sup> calculated from the Pd(111) peak position on the XRD profiles of as-prepared unsupported nanoparticles

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Figure 1. Electron microscopy images of fresh colloidal  $FeO_x$  (a) and  $FeO_x@Pd$  nanoparticles (b) and spent  $FeO_x@Pd_{0.6}/\gamma$ -Al<sub>2</sub>O<sub>3</sub> after HDS reactions at 623 K (c-f).



Figure 2. STEM-EDS mapping of spent FeO<sub>x</sub>@Pd<sub>0.6</sub>/Al<sub>2</sub>O<sub>3</sub>.

The TPR analyses (Figure 3) showed that the reduction of the commercial iron oxide proceeded in two steps: a low-temperature peak at ca. 700 K ( $Fe_2O_3$  to  $Fe_3O_4$ ) and a larger high-temperature peak at ca. 830 K ( $Fe_3O_4$  to FeO).<sup>89,90</sup> The first peak was shifted by 100 K to lower temperatures in the presence of Pd due to hydrogen spillover<sup>90</sup>. The synthesized  $FeO_x$  core nanoparticles deposited on  $Al_2O_3$  are reduced in a similar temperature range as the commercial  $Fe_2O_3$  but with a shift towards a lower temperatures. The XRD (Supporting Information) also revealed the presence of magnetite and hematite in the synthesized  $FeO_x@Pd$  materials. The TPR profile of the calcined  $Pd/Al_2O_3$  catalyst (Figure 3) shows a hydrogen evolution peak at ca. 350 K that can be ascribed to

the decomposition of Pd  $\beta$ -hydride formed at ambient temperature as a result of PdO reduction.<sup>68,91,92</sup> The peak intensity is known to be higher for the catalysts with lower Pd dispersion.<sup>68,91</sup> No  $\beta$ -hydride decomposition was observed for other Pd catalysts due to the higher Pd dispersion<sup>68,91</sup>, in agreement with CO chemisorption (Table 1).

XPS analyses were performed on the fresh catalysts after calcination in air and on the spent catalysts (after calcination, reduction, and HDS reaction at 623 K) (Table 2 and Figure S4 in Supporting Information). Iron oxide sulfidation is thermodynamically and kinetically favourable at the reaction temperature.<sup>85,93</sup> The sulfide detection by XPS is known to be masked by iron oxides at ca. Fe  $2p_{3/2}$  711 eV<sup>94</sup> but an observed positive shift in the Fe 2p<sub>3/2</sub> binding energies (BE) in the spent versus calcined samples and a sulfide peak at 163 eV (Figure S5 in the Supporting Information) are in line with the iron sulfide formation.95 Palladium sulfide was not expected to be formed because the HDS reaction was conducted at a  $p(H_2S)/p(H_2)$  ratio of  $10^{-4}$  while metallic Pd is thermodynamically stable at the ratio below  $10^{-2}$  at 600 K.<sup>93</sup> Indeed, the XPS of the spent catalysts (Table 2 and Figure S4 in Supporting Information) revealed metallic Pd with negligible presence of Pd sulfides at 337 eV<sup>96</sup>. The Pd BE in the FeO<sub>x</sub>@Pd samples shifted to higher values as compared to  $Pd/Al_2O_3$  sample, which is expected for the Pd nanoparticles with higher dispersion.<sup>85,97</sup> Similar Pd(0) species were found by XPS in an earlier reported FeO<sub>x</sub>@Pd system with highly dispersed Pd.<sup>53</sup>



Figure 3. TPR profiles of calcined supported catalysts. The inverted TCD signal reflects hydrogen consumption.

 Table 2. Binding energy values of Pd 3d and Fe 2p in the fresh

 (calcined) and spent catalysts.

				-									
Catalyst	Binding Energy (eV)												
	Pd 3	3d <sub>5/2</sub>	Pd 3	8d <sub>3/2</sub>	Fe	2p <sub>3/2</sub>	Fe 2p <sub>1/2</sub>						
	fresh	spent	fresh	spent	fresh spent		fresh	spent					
Pd/Al <sub>2</sub> O <sub>3</sub>	336.3	335.4	341.5	340.6	-	-	-	-					
FeO <sub>x</sub> @Pd <sub>0.2</sub> /Al <sub>2</sub> O <sub>3</sub>	336.7	335.7	341.9	340.9	710.9	711.1	724.0	724.1					
FeO <sub>x</sub> @Pd <sub>0.6</sub> /Al <sub>2</sub> O <sub>3</sub>	336.6	335.8	341.9	341.1	710.8	711.0	723.8	723.9					
FeO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	-	Ι	I	Ι	710.6	711.7	723.6	724.5					

Thus, the characterization results confirm the importance of the developed synthesis method as means to increase and Pd dispersion, which was maximized at Pd/Fe molar ratio of 0.2. The formation of Pd islands and increased Pd dispersion resulted in the lattice contraction. The following section explores how such modified electronic properties affected the catalytic function in HDS of 4,6-DMDBT at 623 K.

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# 3.2. Catalytic performance in HDS of 4,6-DMDBT

The catalytic activity and selectivity of the synthesized catalysts were assessed in the HDS of 4,6-DMDBT at 623 K and 3 MPa for 18 h on stream (Figure 4 and Table 3). The catalytic performance stabilized after 2 h on stream. Pd-free  $FeO_x/Al_2O_3$  sample did not show measurable activity in the reaction after the typical sulfidation procedure, which is expected for iron sulfides known for hydrogenation activity<sup>96</sup> but very low HDS activity<sup>98</sup>.

HDS of 4,6-DMDBT follows a pseudo-first-order kinetics, including on Pd catalysts.<sup>67,99,100</sup> Initial reaction rates in Figure 4 were calculated according to  $r = -[ln(1-X)]F_{Ao}/W$ equation in which X is 4,6-DMDBT conversion after 18 h on stream,  $F_{Ao}$  is entering 4,6-DMDBT molar flow rate, and W is the weight of Pd in the reactor. The catalytic activities of  $FeO_x@Pd_n/Al_2O_3$  samples depend on the Pd/Fe ratio in the catalysts and is maximized at the ratio of 0.2, which is in line with the maximized Pd lattice compression and Pd dispersion (Table 1). The high Pd dispersion leads to a greater metal atoms efficiency of the noble metal, and there is only a narrow window of Pd/Fe ratio (below 0.5) that allows for the dispersion and activity increase. The reaction rate per amount of Pd is 4-fold higher for the FeOx@Pd0.2/Al2O3 0.06 mol<sub>DMDBT</sub>/kg<sub>Pd</sub>/s, catalyst, compared to the monometallic Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. The reported activity for commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst (9 wt.% Mo) in HDS of 4,6-DMDBT at 613 K and 3 MPa was 5.07×10<sup>-3</sup> mol<sub>DMDBT</sub>/kg<sub>Mo</sub>/s.<sup>82</sup> When Pd was deposited on a commercial Fe<sub>2</sub>O<sub>3</sub> support (< 5 μm), initial rate of 4,6-DMDBT consumption per Pd amount was similar to the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst, which shows the necessity of the applied Pd deposition method on the nano-FeO<sub>x</sub> for the observed benefits.

Figure 4 also shows turnover frequencies (TOFs) as initial rates calculated based on the amount of surface Pd, as determined by CO chemisorption (Table 1) assuming CO:Pd stoichiometry of 1. Although the use of FeO<sub>x</sub>@Pd structures allowed for higher dispersion and 4-fold higher Pd mass-

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based catalyst activity, the modified electronic properties of Pd in  $FeO_x@Pd_n/Al_2O_3$  catalysts led to the decreased intrinsic site activity for 4,6-DMDBT conversion at 350 °C (Figure 4). Thiophene HDS at 400 °C was also inhibited when Pd was diluted with Fe, which was assigned to the formation of less active Fe-Pd alloy.<sup>101</sup>

The presence of nano-FeO<sub>x</sub> also affected the product distribution. As seen in the HDS reaction scheme (Scheme 1), detected reaction products include the direct the desulfurization product (DDS), hydrogenation products with and without extracted sulfur (HYD) and sulfur-free hydrocracking products with 6- membered rings (HCK). All Al<sub>2</sub>O<sub>3</sub>-supported catalysts yielded negligible amounts of hydrogenated sulfur-containing intermediates of 4,6-DMHHDBT and 4,6-DMPHDBT (Table 3), which is in line with the earlier findings by Prins and co-workers<sup>65</sup>. Pd/Al<sub>2</sub>O<sub>3</sub> and FeO<sub>x</sub>@Pd<sub>p</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts showed 27±3% selectivity to 3,3'-DMBP (direct desulfurization DDS product), 50±5% selectivity to hydrogenation (HYD) products (Scheme 1) and 20±5% selectivity to hydrocracking (HCK) products at similar ca. 33% 4,6-DMDBT conversion at 623 K. As compared to Pd/Al<sub>2</sub>O<sub>3</sub>, the  $FeO_x@Pd_n/Al_2O_3$  catalysts suppressed the complete hydrogenation to DMBCH with a larger remaining fraction of semi-hydrogenated DMCHB (Scheme 1), and also diminished the formation of cyclohexane (CH) in favor of the toluene (TL) and methylcyclohexane (MCH) (Table 3). Similarly, the formation of Pd-Fe alloy in SiO<sub>2</sub>-supported Fe-Pd nanoparticles, along with large bimetallic particle size,

suppressed phenylacetylene hydrogenation as compared to monometallic Pd catalyst.<sup>102</sup> The developed  $FeO_x@Pd_n/Al_2O_3$  catalysts allowed for the efficient sulfur removal, as seen from the S-free product yields (Table 1), at a three-fold lower Pd loading in the second-stage hydrotreater as compared to Pd/Al\_2O\_3, but they suppressed complete hydrogenation. This effect could be beneficial for deep desulfurization of ultraclean gasoline to minimize octane losses<sup>103</sup>, as opposed to the preferred cetane-boosting hydrogenation path in desulfurization of diesel fuels.<sup>104</sup>



**Figure 4.** Initial rate of 4,6-DMDBT HDS at 623 K and 3 MPa as a function of Pd/Fe molar ratio.

Catalyst g(cat)/mg(Pd) in the reactor	DMDBT conversion (%)	Selectivity (mol %)											Yield (%)	
		DDS	DS HYD						нск				Total	A.II. C
		DMBP	DM- CHB	DM- BCH	DM- THDBT	DM- HHDBT	DM- PHDBT	l otal HYD	СН	BZ	мсн	TL	нск	free
Pd/Al <sub>2</sub> O <sub>3</sub> 0.09/ 0.37	31	29	12	27	12	1	1	53	13	1	3	1	18	24
FeO <sub>x</sub> @Pd <sub>0.6</sub> /Al <sub>2</sub> O <sub>3</sub> 0.18 / 0.32	33	27	27	4	17	0	0	48	6	1	11	8	26	24
FeO <sub>x</sub> @Pd <sub>0.2</sub> /Al <sub>2</sub> O <sub>3</sub> 0.18 / 0.11	36	24	29	5	16	0	0	50	7	2	11	6	26	26
FeO <sub>x</sub> @Pd <sub>0.05</sub> /Al <sub>2</sub> O <sub>3</sub> 0.18 / 0.02	6	34	15	0	24	0	0	39	9	5	11	2	27	4
Pd <sub>0.2</sub> /Fe <sub>2</sub> O <sub>3</sub> 0.18 / 0.10	11	18	0	1	2	7	10	20	29	5	26	0	60	5

Table 3. Catalytic performance in HDS of 4,6-DMDBT at 623 K and 3 MPa at 18 h on stream.

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Remarkably, when Pd was deposited on the commercial  $Fe_2O_3$  support, the Pd/Fe<sub>2</sub>O<sub>3</sub> catalyst showed twice-higher hydrocracking selectivity of 60% even at 11% conversion vs. 26% HCK selectivity at ca. 40% conversions for all Al<sub>2</sub>O<sub>3</sub>-supported catalysts (Table 3). Iron catalysts are known for high cracking selectivity, as reported for thiophene HDS.<sup>101</sup> However, when the Pd islands were formed on the nano-FeO<sub>x</sub> in FeO<sub>x</sub>@Pd<sub>n</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, the excessive cracking selectivity was suppressed, which shows the necessity of the applied Pd deposition method on the nano-FeO<sub>x</sub> for the observed benefits.

# 4. Conclusions

 $FeO_x@Pd_n/Al_2O_3$  catalysts were developed via colloidal synthesis method for ultra-deep hydrodesulfurization (HDS) of refractory sulfur compounds. Palladium species preferentially reduced on the surface of FeO<sub>x</sub> nanoparticles as dispersed Pd(0) islands. The highest Pd dispersion and lattice strain was found for Pd/Fe molar ratio of 0.2 as compared to 0.05, 0.6, 1.5 and pure Pd. The  $FeO_x@Pd_{0.2}/Al_2O_3$  catalyst was found to be 4-fold more active in HDS of 4,6-DMDBT at 623 K and 3 MPa compared to monometallic Pd nanoparticles supported on either Al<sub>2</sub>O<sub>3</sub> (Pd/Al<sub>2</sub>O<sub>3</sub>) or commercial Fe<sub>2</sub>O<sub>3</sub> supports (Pd/Fe<sub>2</sub>O<sub>3</sub>). Such superior performance was attributed to the presence of highly dispersed Pd islands stabilized on the surface of FeO<sub>x</sub> nanoparticles. The lattice strain and thus modified electronic properties of Pd in the FeO<sub>x</sub>@Pd<sub>n</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts suppressed complete hydrogenation to DMBCH and changed the distribution of hydrocracking products. Pd/Fe<sub>2</sub>O<sub>3</sub> with the optimal Pd/Fe ratio of 0.2 did not provide such activity enhancement and led to significant cracking. This study demonstrates that FeO<sub>x</sub>@Pd structures could be a promising alternative to monometallic Pd catalyst for ultra-deep HDS catalysis, which delivered an enhanced activity with a significantly reduced noble metal usage in the catalyst formulation.

# **Conflicts of interest**

There are no conflicts to declare.

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