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Hydrothermally stable Pd/SiO₂@Zr Core@Shell catalysts for diesel oxidation applications

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► **To cite this version:**

Chih-Han Liu, Junjie Chen, Todd Toops, Jae-Soon Choi, Cyril Thomas, et al.. Hydrothermally stable Pd/SiO₂@Zr Core@Shell catalysts for diesel oxidation applications. Chemical Engineering Journal, 2021, 425, pp.130637. 10.1016/j.cej.2021.130637 . hal-03343231

HAL Id: hal-03343231

<https://hal.science/hal-03343231>

Submitted on 14 Sep 2021

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4 **Hydrothermally Stable Pd/SiO₂@Zr Core@Shell Catalysts for Diesel**
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7 **Oxidation Applications**
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4 **Abstract**
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7 Hydrothermally stable diesel oxidation catalysts (DOCs) with improved low-temperature activity
8 are desired for the abatement of emissions from diesel vehicles. Herein, novel
9 palladium(Pd)/SiO₂(core)@Zr(shell) structured DOCs were developed. SiO₂ was completely
10 covered by an 8.4 nm thickness Zr-based shell using a hard template method. The SiO₂@Zr
11 support was decorated by Pd and evaluated under a simulated diesel exhaust stream. Degreened
12 1 wt.% Pd/SiO₂@Zr achieved 90% CO and total hydrocarbon conversion at 178 and 372 °C,
13 respectively (feed: 6% CO₂, 12% O₂, 6% H₂O, 400 ppm H₂, 2000 ppm CO, 100 ppm NO, 1667
14 ppm C₂H₄, 1000 ppm C₃H₆, 333 ppm C₃H₈; HCs in C₁ basis and GHSV = 113,000 h⁻¹). After
15 hydrothermal aging, only a minor deactivation was observed, while the surface area of 1 wt.%
16 Pd/SiO₂@Zr was as high as 104 m²/g. The hydrothermal stability of 1 wt.% Pd/SiO₂@Zr was
17 attributed to the poor crystallinity of SiO₂@Zr, possibly due to the formation of Si-O-Zr bonds.
18 This work highlights the promising potential of utilizing durable Pd/SiO₂@Zr catalysts for diesel
19 oxidation applications.
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42 **Keywords:** diesel oxidation catalyst; heterogeneous catalysis; hydrothermal stability; oxidation;
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1. Introduction

Future aftertreatment systems will need to perform efficiently at increasingly low exhaust temperatures [1-3]: this so-called “150 °C challenge [4]” (i.e., achieve over 90% conversion below 150 °C) arises from continued improvements in engines efficiency and increasingly strict emission standards. An aftertreatment system normally consists of a diesel oxidation catalyst (DOC) for the oxidation of CO and hydrocarbons (HCs), a diesel particulate filter for the oxidation of particulate matter, and a selective catalytic reduction (SCR) catalyst for the reduction of NO_x to N₂ [5-7]. A DOC is required to survive hydrothermal aging at 800 °C/50 h under a feed of 10% O₂, 5% H₂O, 5% CO₂ that represents the in-use durability of a catalyst based on the low temperature aftertreatment protocol defined by U.S. DRIVE [8-10]. Under this severe aging condition, active metals tend to sinter resulting in loss of their catalytic activity [11-13]. Enhancing the metal-support interaction has shown to prevent active metal sintering [14-16]. For example, Kim et al. pretreated Pt-TiO₂ under a H₂ atmosphere at various reduction temperatures, and the results showed that pretreatment at 600 °C led to a higher CO conversion (100%) compared to a lower CO conversion (10%) achieved at room temperature when the catalyst was pretreated at 300 °C [16]. This behavior was attributed to the strong metal (Pt)-support (TiO₂) interaction (SMSI) occurring after pretreatment at temperatures > 500 °C, evidenced by the formation of smaller Pt particles (2.2-4.4 nm) compared to larger Pt particles (4.7-5.9 nm) formed after pretreatments at temperatures < 500 °C. ZrO₂ was reported to have SMSI with platinum group metals (PGMs), commonly used in DOCs [17-19]. SMSI between PGMs and ZrO₂ lead to high PGM dispersion and thus an improved DOC activity. Specifically, the T_{50,90}'s (temperature of 50 and 90% conversion) over 1 wt.% Pd/ZrO₂ were as low as 160, 180 °C for CO and 180, 195 °C for propylene (C₃H₆), respectively [20]. However, Pd/ZrO₂ suffers from a severe surface area loss from 93 m²/g

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4 (500 °C/2 h, 10% H₂/Ar) to 24 m²/g (hydrothermal aging, 800 °C/16 h, 10% O₂, 5% H₂O/Ar) due
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6 to the growth of the mean ZrO₂ crystallite size [20]. The ZrO₂ surface area loss can be prevented
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8 by incorporating oxides with higher crystallization temperature than ZrO₂ (~150 °C [21]), e.g.
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10 Al₂O₃ (850-900 °C [22]) or SiO₂ (1000-1400 °C [23, 24]) [25]. Specifically, Al₂O₃-ZrO₂ and ZrO₂-
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12 SiO₂ have a crystallization temperature of 700 and 800 °C, respectively [21, 26]. Thus, ZrO₂-SiO₂
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14 mixed oxide supports were utilized considering the exhaust temperature (500-700 °C) of diesel
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16 engines at 100% load [20, 27, 28]. Specifically, Kim et al. showed that hydrothermally aged
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18 (HTA) (800 °C/16 h) Pd/ZrO₂-SiO₂ had a T₅₀ and T₉₀ for CO at 280 and 320 °C and for C₃H₆ at
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20 307 and 332 °C, respectively [20]. Furthermore, incorporation of SiO₂, as an acidic support, is
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22 known to improve the sulfur tolerance of the catalyst compared to bare ZrO₂ [20]. However,
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24 uncontrolled synthesis of ZrO₂-SiO₂ by a sol-gel method resulted in segregation of SiO₂ and ZrO₂,
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26 leading to formation of large Pd particles on exposed SiO₂ surfaces due to weak Pd-SiO₂
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28 interaction. Specifically, the Pd particle size over Pd/ZrO₂, Pd/ZrO₂-SiO₂, Pd/SiO₂ increased from
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30 1.1 nm to 1.9 nm to 4.1 nm, respectively [20]. Therefore, a complete coverage of SiO₂ by a Zr-
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32 based shell is required to prevent Pd deposition on SiO₂ and thus enhance the diesel oxidation
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34 performance of Pd/ZrO₂-SiO₂ catalysts.
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43 Herein, SiO₂(core)@Zr(shell) supports were synthesized, where SiO₂ spheres were
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45 covered by a Zr-based shell. This was achieved by a hard template method as reported previously
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47 (Fig. 1) [3], where the SiO₂ core acted as a scaffold for the growth of the Zr-based shell layer. Pd
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49 was deposited on the SiO₂@Zr support by wet-impregnation resulting to 1, 2 and 4 wt.%
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51 Pd/SiO₂@Zr catalysts that were evaluated for their diesel oxidation activity and hydrothermal
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53 stability.
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56 57 58 59 **2. Experimental procedure** 60 61 62 63 64 65

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4 Reagents and materials, and characterizations are listed in the Supplementary material.
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8 *2.1. Catalysts preparation*

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10 The SiO₂@Zr core@shell support was synthesized, with some modifications, as reported
11 previously [3]. The synthesis schematic is shown in Fig. 1. Briefly, monodisperse silica spheres
12 were prepared following the Stöber process [29]. The SiO₂ spheres formed were dispersed in 100
13 g of ethanol and kept at 30 °C. Afterwards, 0.5 mL of Brij30 solution was added to the SiO₂
14 suspension and kept stirring for 1 h. Then, 1.8 mL Zr(BuO)₄ was added and the solution was
15 stirred overnight at 30 °C. The liquid phase of the colloid was then exchanged for 100 mL DI
16 water (4 times) and aged at room temperature for 3 days. Finally, the SiO₂@Zr spheres were
17 collected after centrifugation followed by drying at 110 °C overnight and calcination at 500 °C for
18 2 h (10 °C/min).
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32 The resulting SiO₂@Zr support was impregnated with 2.8, 5.6, 11.4 mL Pd(NH₃)₄(NO₃)₂
33 solution (0.0344 M) by wet-impregnation where the pH of the slurry was adjusted to 4 with 0.1 M
34 HNO₃, leading to Pd loadings of 1, 2, and 4 wt.%. The liquid phase of the slurry was then
35 evaporated at room temperature. After the impregnation, the catalyst was dried at 110 °C in air
36 and calcined at 500 °C for 2 h.
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45 *2.2 Catalyst evaluation*

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47 The performance of the as-synthesized catalysts was evaluated in a customized fixed-bed
48 U-shaped quartz reactor (I.D. = 8 mm) as reported previously [30]. The reactor was placed in a
49 cylindrical furnace surrounded by quartz wool to eliminate heat gradients. A K-type thermocouple
50 was attached outside the reactor, close to the top of the catalyst bed, to allow the PID temperature
51 controller control the furnace temperature. Catalyst powders were pressed and sieved and a final
52 pellet size range between 250 to 500 μm was used to avoid pressure effects during the reaction.
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4 100 mg of catalyst was loaded in the reactor stabilized by two loosely packed quartz wool plugs.
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7 Another K-type thermocouple was inserted through the reactor U-tube to the upper quartz wool
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9 plug for measuring the inlet gas temperature.
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11 The catalysts were first degreened (DG) (700 °C/4 h) under feed gas composition of 10%
12 O₂, 5% H₂O, 5% CO₂/Ar. Before evaluation, the catalysts were pretreated at 600 °C with 12% O₂,
13 6% H₂O, 6% CO₂/Ar for 20 min. Diesel oxidation evaluation experiments were performed using
14 the low temperature combustion of diesel (LTC-D) gas composition defined by U.S. DRIVE
15 (Table S1) [8]. The total flow rate was 333 sccm that corresponds to a gas hourly space velocity
16 (GHSV) of 113,000 h⁻¹. CO₂, O₂, H₂, CO, NO, C₂H₄, C₃H₆, C₃H₈ and Ar (UHP, Airgas) were
17 regulated by a set of MKS mass flow controllers. Water was supplied by a D-series pump
18 (Teledyne Isco), evaporated to steam in a tube furnace (200 °C) and carried by Ar to the reactor.
19 Light-off tests were conducted from 100 to 500 °C at a heating rate of 2 °C /min. The effluent gas
20 concentrations were analyzed by an MKS MultiGas 2030 FTIR gas analyzer with a gas cell at 191
21 °C. The reactor exhaust was diluted with 667 sccm Ar to reduce the response time of the gas
22 analyzer. To avoid water condensation, all the gas lines were heated to 170 °C. Hydrothermal
23 aging (HTA) treatment (800 °C /10 h) was conducted under feed gas composition of 10% O₂, 5%
24 H₂O, 5% CO₂/Ar. Pretreatment and evaluation of the HTA catalysts were performed under the
25 same conditions as the DG catalysts.
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19 **3. Results and Discussion**

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52 The high-angle annular dark-field scanning transmission electron microscopy (HAADF-
53 STEM) images and energy dispersive X-ray spectroscopy (EDS) elemental maps of fresh (calcined
54 at 500 °C/2 h) 1, 2 and 4 wt.% Pd/SiO₂@Zr catalysts are shown in Fig. 2. Moreover, a 3D
55 tomography video of 1 wt.% Pd/SiO₂@Zr is shown (Video S1). The 3D tomography suggests the

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4 complete coverage of SiO₂ core by Zr-based shell with Pd dispersed on the surface. A spherical
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6 structure was confirmed for all studied catalysts (Fig. 2). The EDS elemental maps of Si in Fig.
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8 2a.2, 2b.2 and 2c.2 reveal the successful synthesis of nano-spherical SiO₂ (diameter of about 150
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10 nm) as a support core. The higher density Zr presented as a shell layer (thickness: ~8.4 nm) (Fig.
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12 2a.3, 2b.3 and 2c.3) indicates the successful deposition of Zr species on the SiO₂ core. Palladium
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14 is well-dispersed over 1 wt.% Pd/SiO₂@Zr (Fig. 2a.4). However, as Pd loading increased to 2
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16 (Fig. 2b.4) and 4 wt.% (Fig. 2c.4), larger Pd clusters (~5 and 7 nm, respectively) can be observed,
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18 possibly due to Pd sintering.
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24 Fig. S1 shows the X-ray diffraction (XRD) patterns of fresh SiO₂@Zr, fresh and HTA (800
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26 °C/10 h, 10% O₂, 5% H₂O, 5% CO₂/Ar) 1 wt.% Pd/SiO₂@Zr. All samples display only one broad
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28 peak centered at ~23°, assigned to SiO₂ [31]. No peaks were detected for ZrO₂ over all analyzed
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30 samples, suggesting that the majority of Zr in SiO₂@Zr is not present in a ZrO₂ crystalline phase
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32 (monoclinic, tetragonal, cube). Moreover, presence of amorphous ZrO₂ is excluded since the
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34 samples analyzed by XRD are either fresh (calcined at 500 °C) or HTA (exposed to 800 °C/10 h)
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36 and amorphous ZrO₂ can readily crystallize at T > 300 °C [32]. Furthermore, no metallic Pd or
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38 PdO peaks were observed over fresh and HTA 1 wt.% Pd/SiO₂@Zr, which might be due to the
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40 low loading and the dispersed nature of Pd (Fig. 2a.4).
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46 The surface properties (Brunauer-Emmett-Teller (BET) surface areas and Barrett-Joyner-
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48 Halenda (BJH) pore volumes) of SiO₂ core, SiO₂@Zr, and 1 wt.% Pd/SiO₂@Zr are summarized
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50 in Table 1. The surface area of fresh SiO₂ core was as low as 2.3 m²/g. Fresh SiO₂@Zr and 1
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52 wt.% Pd/SiO₂@Zr had improved surface areas of 226.7 and 207.1 m²/g, respectively. Considering
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54 the low surface area of SiO₂ core, the improved surface areas of SiO₂@Zr and 1 wt.% Pd/SiO₂@Zr
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56 can be attributed to the Zr-based shell. Furthermore, the surface area loss after HTA was greater
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4 over 1 wt.% Pd/ZrO₂ (fresh: 93 m²/g, HTA (16 h): 24 m²/g) [20] than 1 wt.% Pd/SiO₂@Zr (fresh:
5 226.7 m²/g, HTA (16 h): 112 m²/g). The surface area of 1 wt.% Pd/SiO₂@Zr after 10 h of HTA
6 was 104 m²/g and it remained the same when the HTA time was extended to 16 h (112 m²/g). This
7 observation suggests that the surface area of Pd/SiO₂@Zr does not change after HTA for 10 h.
8 Moreover, the surface area of Pd/SiO₂@Zr is 4.5 times greater than the one of Pd/ZrO₂ after 16 h
9 of HTA. The significant surface area loss of 1 wt.% Pd/ZrO₂ when exposed to elevated
10 temperatures was attributed to the grain growth of crystalline ZrO₂ [33]. Therefore, the high
11 surface area of SiO₂@Zr and 1 wt.% Pd/SiO₂@Zr after HTA can be attributed to the non-
12 crystalline nature of the Zr-based shell (see XRD data (Fig. S1)). The N₂ adsorption-desorption
13 isotherms of fresh and HTA 1 wt.% Pd/SiO₂@Zr are shown in Fig. S2. Both samples have a type
14 IV isotherm, characteristic of mesoporous materials [34].

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31 Fig. 3 shows the catalytic evaluation results of degreened (DG) 1 wt.% Pd/SiO₂@Zr. 1
32 wt.% Pd/SiO₂@Zr can achieve 50 and 90% conversions at 168 and 178 °C for CO and 228 and
33 372 °C for total HCs (THCs), respectively (Fig. 3a). Moreover, 1 wt.% Pd/SiO₂@Zr can reach 50
34 and 90% conversions at 245 and 362 °C for C₂H₄ and at 192 and 216 °C for C₃H₆, respectively
35 (Fig. 3b). C₃H₈ was converted at a higher temperature (T₅₀= 376 °C, T₉₀= 428 °C) compared to
36 C₂H₄ and C₃H₆, attributed to its stable C-H bonds [35]. The negative conversion of C₃H₈ observed
37 between 180 and 340 °C (Fig. 3b) can be attributed to the desorption of C₃H₈ from PdO [36]. The
38 inflection in CO conversion at 190 °C (Fig. 3a) can be attributed to competition of CO and HCs
39 for active sites and mass transfer limitations [37]. Moreover, the inflection observed in C₂H₄
40 conversion (Fig. 3b) can be attributed to the adsorption of intermediates formed during C₂H₄
41 oxidation on Pd active sites (discussed later). These intermediate species can inhibit C₂H₄
42 adsorption and its further oxidation. Fig. 3c shows the concentrations of NO, NO₂ and N₂O and
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4 their total concentration ($= [\text{NO}] + [\text{NO}_2] + 2[\text{N}_2\text{O}]$) during the evaluation of DG 1 wt.%
5 Pd/SiO₂@Zr. The total concentration of NO, NO₂, and N₂O indicates that most N-containing
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7 species were in the form of NO, NO₂, and N₂O. The small negative peak observed at 165 °C can
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9 be attributed to N₂ formation (not detectable by the MKS IR). There are three NO consumption
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11 peaks at 165, 206 and 471 °C. NO consumed at 165 and 206 °C was converted to N₂ and N₂O,
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13 respectively, suggesting that a HC-SCR reaction took place [38]. The third broad NO consumption
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15 peak at temperature ~ 471 °C can be attributed to the catalytic NO oxidation over Pd [39] and
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17 homogeneous (gas phase) NO oxidation [30].
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24 A hydrothermal aging treatment (800 °C/10 h) was conducted to verify the durability of 1
25 wt.% Pd/SiO₂@Zr (Fig. 4). Compared to DG 1 wt.% Pd/SiO₂@Zr, HTA 1 wt.% Pd/SiO₂@Zr
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27 showed similar T₅₀ (168 °C) and T₉₀ (178 °C) for CO, while minor deactivation was observed for
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29 HC oxidation. Specifically, the T₅₀ (207 °C) and T₉₀ (372 °C) for THCs was increased by only 21
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31 and 9 °C, respectively, after hydrothermal aging of 1 wt.% Pd/SiO₂@ZrO₂. The ability of 1 wt.%
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33 Pd/SiO₂@Zr to achieve a similar performance under DG and HTA conditions highlights the
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35 hydrothermal stability of the catalyst. Similarly, the negative conversion of C₃H₈ observed
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37 between 180 and 340 °C (Fig. 4b) can be attributed to the desorption of C₃H₈ from PdO [36].
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39 Formaldehyde (CH₂O) was formed at the same temperature range that the inflection in C₂H₄
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41 conversion was observed (Figs. S3a, 4b). The inflection in C₂H₄ conversion was also observed
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43 when CO, NO, C₃H₆ and C₃H₈ were removed from the reactor feed (1667 ppm C₂H₄ (C₁ basis),
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45 6% CO₂, 6% H₂O, 12% O₂, and 400 ppm H₂) (Fig. S3b). This observation indicates that
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47 intermediates (e.g. CH₂O, CO) formed during C₂H₄ oxidation can be adsorbed on the Pd active
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49 sites. The adsorbed intermediates can inhibit C₂H₄ adsorption and thus its further oxidation.
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51 Similar NO conversion pattern was observed over both DG and HTA 1 wt.% Pd/SiO₂@Zr (Fig.
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4c). The decrease in the total concentration of NO, NO₂, and N₂O can be attributed to HC-SCR
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7 reactions [38], as discussed previously.
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10 The effect of Pd loading was investigated by comparing the catalytic performance of 1, 2,
11 and 4 wt.% Pd/SiO₂@Zr (Fig. 5). The CO T₅₀/T₉₀'s were similar at 168/178, 168/179 and 158/172
12 °C over DG 1, 2 and 4 wt.% Pd/SiO₂@Zr, respectively (Fig. 5a). However, the THC T_{50,90}'s
13 decreased as Pd loading increased. Specifically, the THC T₅₀/T₉₀'s decreased from 228/372 °C to
14 211/355 °C to 191/316 °C over DG 1, 2 and 4 wt.% Pd/SiO₂@Zr, respectively. After hydrothermal
15 aging the T₅₀/T₉₀'s for CO slightly decreased from 165/178 to 163/176 to 163/172 °C with
16 increasing Pd loading from 1 to 2 to 4 wt.% (Fig. 5b). Similarly, the T_{50,90}'s for THCs decreased
17 with increasing Pd loading from 1 to 2 to 4 wt.% as follows: 207/381 °C to 202/343 °C to 190/325
18 °C, respectively.
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31 Fourier transform infrared (FT-IR) spectra were collected over SiO₂ spheres and SiO₂@Zr
32 supports to investigate the support composition and thus the origin of the Pd/SiO₂@Zr thermal
33 stability (Fig. S4). Two peaks at 1101 and 802 cm⁻¹ were detected over both SiO₂ spheres and
34 SiO₂@Zr supports, attributed to Si-O-Si bonds [40]. The decrease observed in the transmittance
35 at 965 cm⁻¹ over SiO₂@Zr suggested the formation of Si-O-Zr bonds after Zr coating [41].
36 Moreover, Schüth et al. reported that the bulk and surface Zr/Si molar ratio of the core@shell
37 support was 0.2 and 1, respectively [42]. Si-O-Zr bond formation can hinder the crystallization of
38 the Zr-based shell [43]. Therefore, the improved hydrothermal stability of Pd/SiO₂@Zr can be
39 attributed to the presence of Si-O-Zr.
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53 NO_x-TPD provided an additional indication of the presence of Si-O-Zr bonds over
54 SiO₂@Zr supports. Law et al. showed that there is a linear relationship between NO_x uptake and
55 the accessible ZrO₂ surface area [44, 45]. Thus, NO_x-TPD was conducted to titrate the accessible
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4 surface area of ZrO₂ in SiO₂@Zr. The amount of desorbed NO_x was calculated to be 0.17 μmol
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6 NO_x/m²_{SiO₂@Zr} (Fig. 6), which is much lower than that of bare ZrO₂ (5.8 μmol NO_x/m²_{ZrO₂}) [44,
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8 45]. This result indicates that bare ZrO₂ presence on the SiO₂@Zr surface is minimal. This
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10 observation is consistent with the SiO₂@Zr XRD data (Fig. S1) where crystallized ZrO₂ was not
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12 detected. Moreover, SiO₂@Zr (Fig. 6) and ZrSiO₄ (Fig. S5), that contains Si-O-Zr bonds, showed
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14 similar NO_x desorption temperatures and NO_x uptake (0.43 μmol NO_x/m²_{ZrSiO₄}) indicating that the
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16 samples have a similar surface composition [46]. Therefore, the low NO_x uptake over SiO₂@Zr
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18 can be attributed to the formation of Si-O-Zr bonds on its surface.
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24 25 **4. Conclusions**

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27 In this work, a series of hydrothermal stable Pd-based DOCs on a novel SiO₂@Zr support
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29 were synthesized. Degreened 1 wt.% Pd/SiO₂@Zr was able to reach 90% CO and THC conversion
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31 at 178 and 372 °C, respectively (feed: 6% CO₂, 12% O₂, 6% H₂O, 400 ppm H₂, 2000 ppm CO,
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33 100 ppm NO, 1667 ppm C₂H₄, 1000 ppm C₃H₆, 333 ppm C₃H₈; HC in C₁ basis and
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35 GHSV=113,000 h⁻¹). Only a minor decrease in the THC conversion was observed after
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37 hydrothermal aging at 800 °C for 10 h (HTA). As the Pd loading increased from 1 to 2 to 4 wt.%,
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39 the T₉₀'s for THCs decreased from 372 to 346 to 316 °C, respectively. A similar trend was
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41 observed for Pd/SiO₂@Zr after HTA, where the THC T₉₀'s decreased from 381 to 343 to 325 °C
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43 with increasing Pd loading from 1 to 2 to 4 wt.% Pd/SiO₂@Zr. The high surface area of
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45 Pd/SiO₂@Zr compared to Pd/ZrO₂ before and after HTA was attributed to the poor crystallinity of
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47 SiO₂@Zr support. The poor crystallinity of SiO₂@Zr further contributes to the improved
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49 hydrothermal stability of Pd/SiO₂@Zr under conditions of low temperature combustion of diesel
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51 (LTC-D). Overall, this study revealed the potential of developing high surface area Pd/SiO₂@Zr
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4 catalysts with improved low temperature diesel oxidation performance and enhanced hydrothermal
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Table 1. BET surface areas and BJH pore volumes of SiO₂ core, SiO₂@Zr, and (fresh, HTA) 1 wt.% Pd/SiO₂@Zr.

	BET surface area (m ² /g)	BJH pore volume (cm ³ /g)
Fresh SiO ₂	2.3	0.009
Fresh SiO ₂ @Zr	226.7	0.170
Fresh 1 wt.% Pd/SiO ₂ @Zr	207.2	0.152
HTA 1 wt.% Pd/SiO ₂ @Zr	103.9	0.089

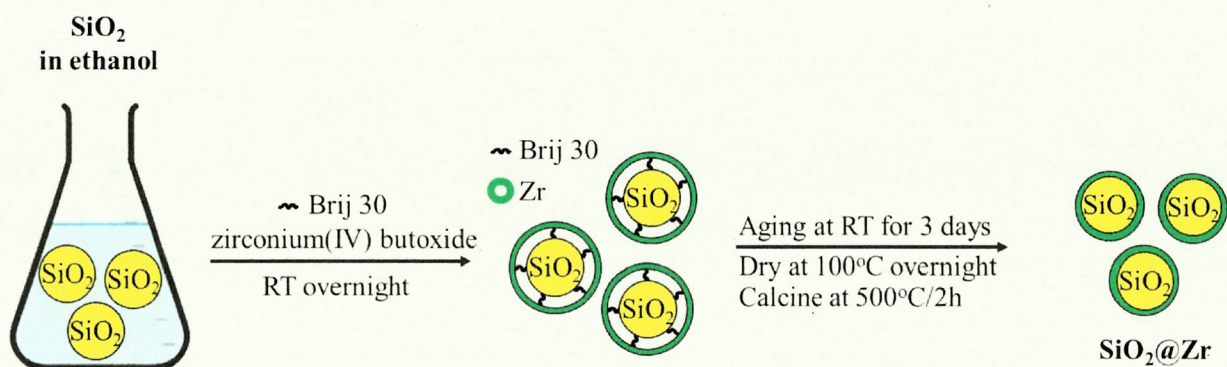


Fig. 1. Synthesis of $\text{SiO}_2@Zr$ core@shell support using a hard template method.

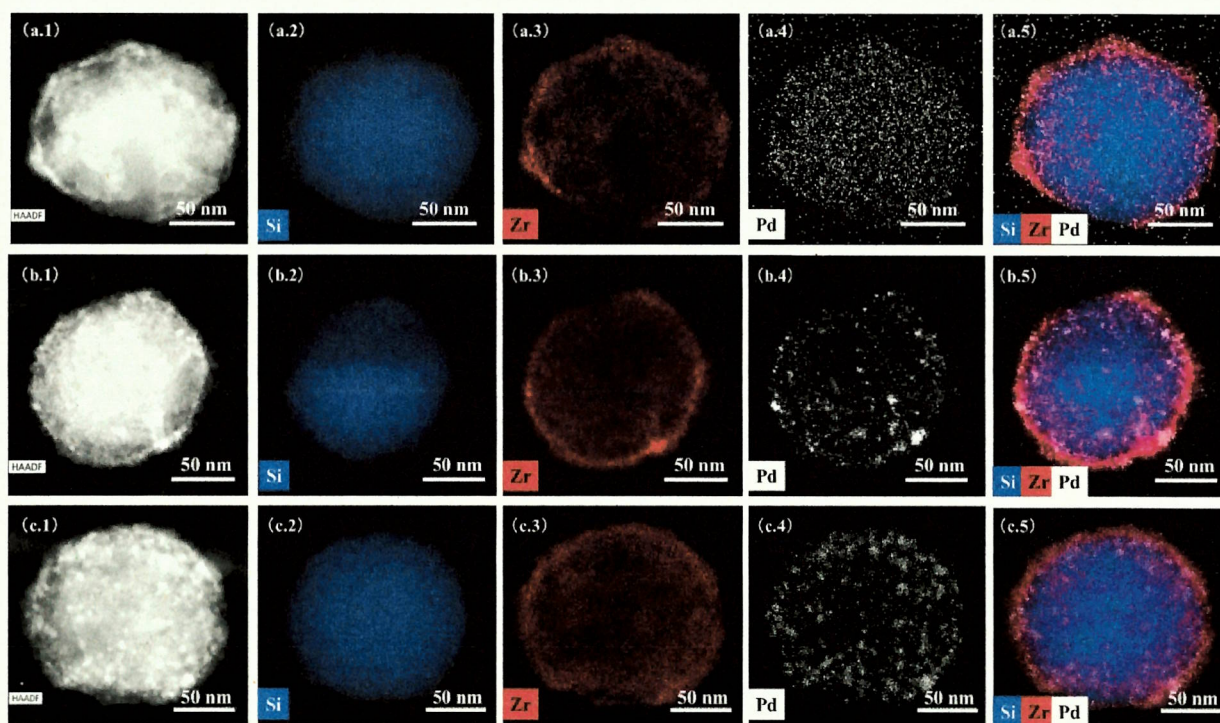


Fig. 2. HAADF-STEM images and EDS elemental maps of fresh (a.1-5) 1 wt.% Pd/SiO₂@Zr, (b.1-5) 2 wt.% Pd/SiO₂@Zr, and (c.1-5) 4 wt.% Pd/SiO₂@Zr catalysts.

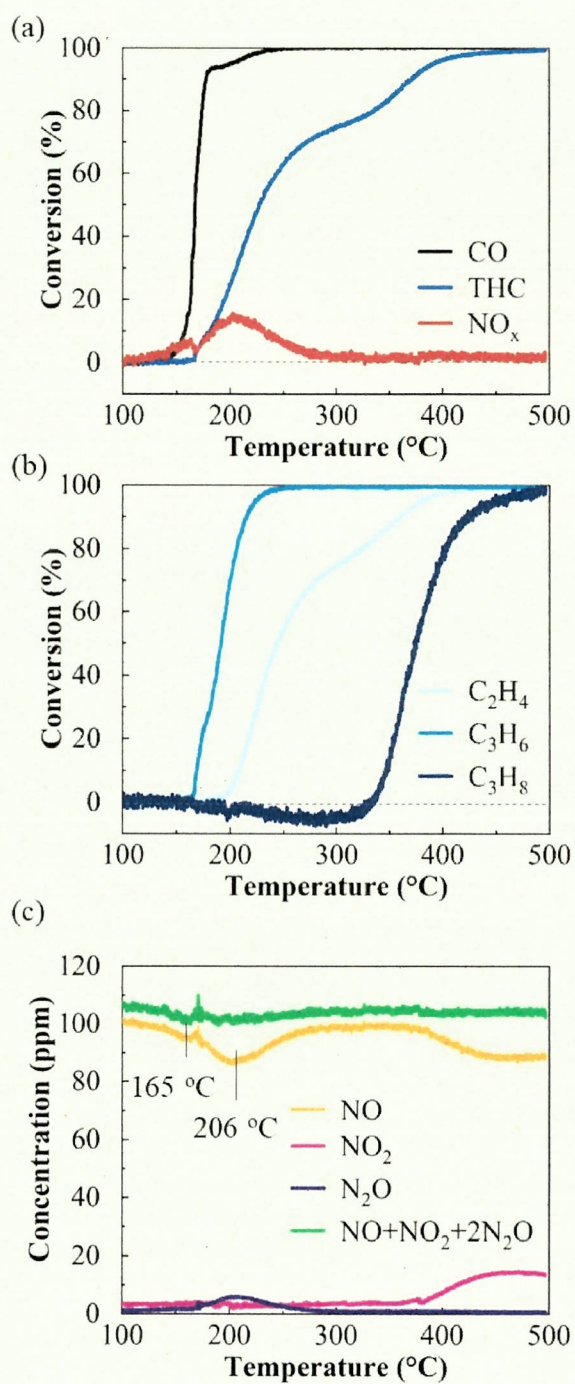


Fig. 3. (a) CO, THC, NO_x, (b) C₂H₄, C₃H₆, C₃H₈ conversions and (c) NO, NO₂, N₂O concentrations and their total concentration ($= [\text{NO}] + [\text{NO}_2] + 2[\text{N}_2\text{O}]$) as a function of temperature of degreened 1 wt.% Pd/SiO₂@Zr.

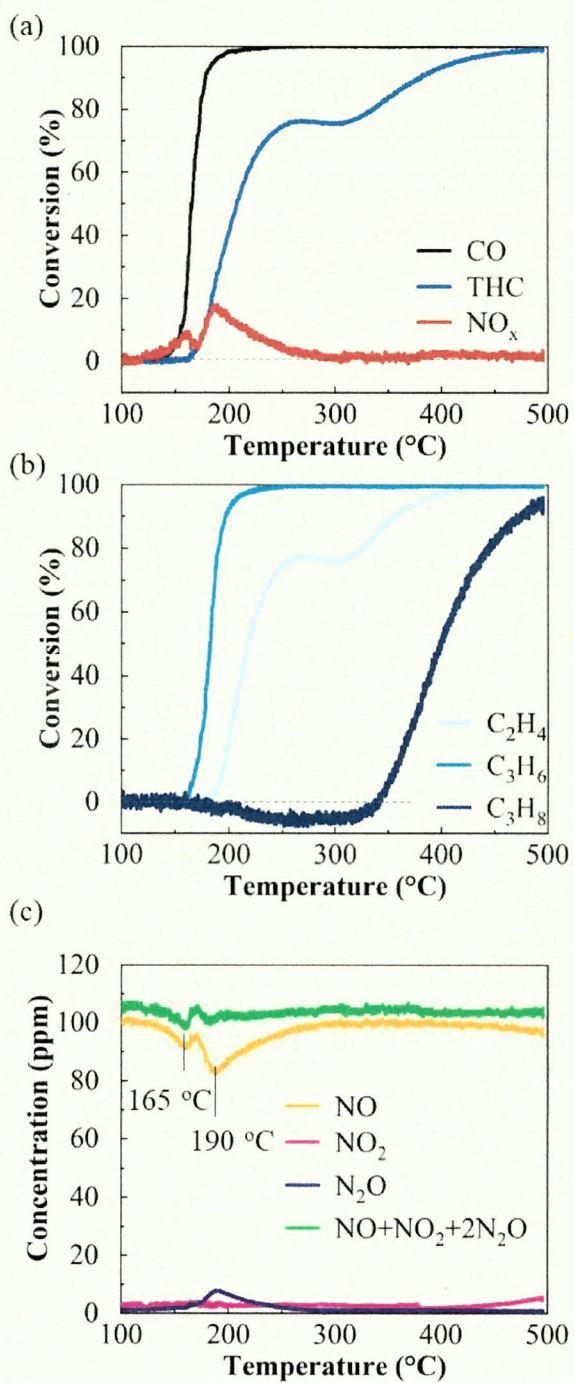


Fig. 4. (a) CO, THC, NO_x, (b) C₂H₄, C₃H₆, C₃H₈ conversions and (c) NO, NO₂, N₂O concentrations and their total concentration ($= [\text{NO}] + [\text{NO}_2] + 2[\text{N}_2\text{O}]$) as a function of temperature of hydrothermally aged 1 wt.% Pd/SiO₂@Zr.

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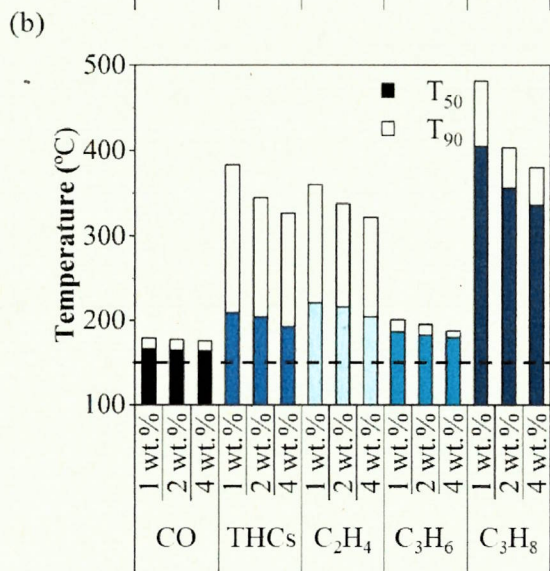
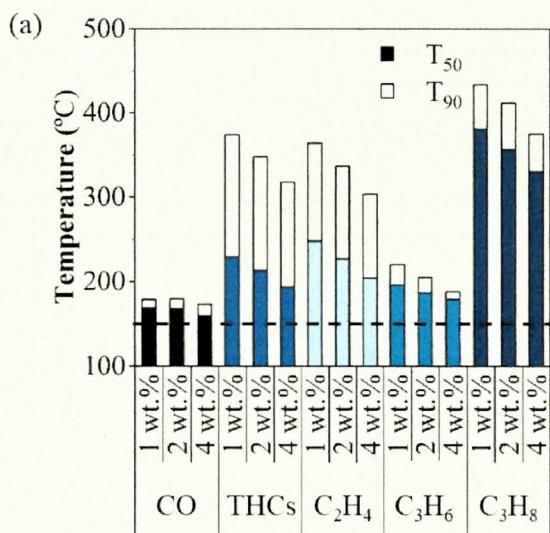


Fig. 5. Comparison of T_{50,90}'s of CO, THCs, C₂H₄, C₃H₆, C₃H₈ over (a) degreened and (b) hydrothermally aged 1, 2, 4 wt.% Pd/SiO₂@Zr catalysts. The horizontal dashed line denotes the 150 °C target temperature for achieving 90% conversion.

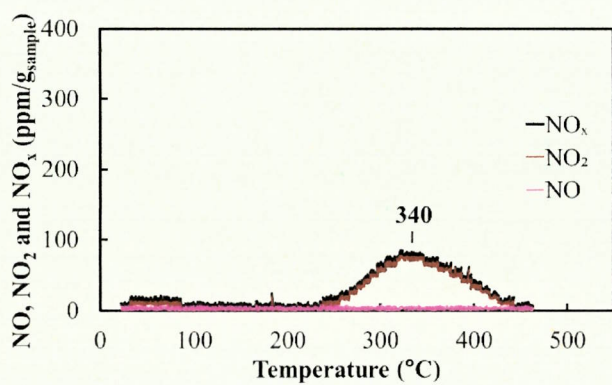


Fig. 6. NO_x-TPD profiles over fresh SiO₂@Zr.

Supplementary material

Hydrothermally Stable Pd/SiO₂@Zr Core@Shell Catalysts for Diesel

Oxidation Applications

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Reagents and materials

Zirconium(IV) butoxide solution ($\text{Zr}(\text{BuO})_4$) (80 wt.% in 1-butanol, Sigma-Aldrich), tetraethyl orthosilicate (TEOS) (98% purity, Strem), anhydrous ethyl alcohol (200 proof, Decon), ammonium hydroxide (NH_4OH , 28-30 wt.% solution of NH_3 in water, Sigma-Aldrich), nitric acid (65 wt.%, Fisher) and tetraamminepalladium nitrate ($\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$) (10% in H_2O , Sigma-Aldrich), zirconium silicate (98%, ACROS) were used as received. Brij30 (ACROS) was diluted with DI water to a 3.76 wt.% Brij30 solution prior to usage. Nitric acid was diluted with DI water to 0.1 M prior to usage. DI water purified to $18.2 \text{ M}\Omega\cdot\text{cm}$ (Milli-Q grade) was used for all reported synthesis.

Characterizations

HAADF-STEM images and EDS elemental maps of $\text{Pd}/\text{SiO}_2@\text{Zr}$ catalysts were obtained with a FEI Talos F200X STEM. The catalysts were first dispersed in isopropyl alcohol under ultrasonication for 15 minutes. One drop of the solution was added onto carbon-coated copper TEM grids followed by drying in air at ambient temperature.

The BET surface areas and BJH pore volumes of the studied samples were determined by N_2 physisorption with a Micromeritics Tri-Star II surface area and porosity analyzer. Before the measurement, all the samples were degassed at $150 \text{ }^\circ\text{C}$ for 2 h.

XRD was conducted in a Rigaku Ultima IV using a $\text{Cu-K}\alpha$ X-ray source (wavelength: 0.15406 nm) operating at 40 kV, 44 mA. XRD patterns were collected in a 2θ range of $5\text{-}85^\circ$, with a scan rate of $2^\circ/\text{min}$.

Fourier transform infrared (FT-IR) spectra of SiO_2 spheres and $\text{SiO}_2@\text{Zr}$ were collected between $400\text{-}4000 \text{ cm}^{-1}$ with a Bruker Vertex 70 FTIR spectrophotometer.

NO_x-TPD experiments were conducted following the procedure reported previously [1]. The catalysts (~500 mg) were first loaded in a U-shaped quartz reactor (I.D. = 15 mm) and pretreated at 500 °C /2 h with 100 sccm (100 mL/min, STP) 20% O₂/He. After cooling down to room temperature, the samples were exposed to the adsorption mixture (400 ppm NO_x and 8% O₂/He) for ~ 200 min. The samples were then purged with 8% O₂/He (230 sccm) to remove gas phase NO_x until negligible NO and NO₂ were detected at the reactor outlet, followed by heating up to 560 °C (3 °C /min) to perform the NO_x-TPD experiments. The NO and NO₂ concentrations were recorded by a chemiluminescence NO_x analyzer (42C-HT, Thermo Environmental Instruments). A correction for the weight loss due to dehydration of the samples was conducted for the NO_x-TPD profiles.

Table S1. Simulated exhaust for low temperature combustion of diesel (LTC-D) based on the low temperature oxidation protocol by U.S. Drive [2], balance Ar.

Components	Concentration
O ₂	12%
H ₂ O	6%
CO ₂	6%
H ₂	400 ppm
CO	2000 ppm
NO	100 ppm
Hydrocarbon - on C ₁ basis	
Total HCs	3000 ppm
C ₂ H ₄	1667 ppm
C ₃ H ₆	1000 ppm
C ₃ H ₈	333 ppm

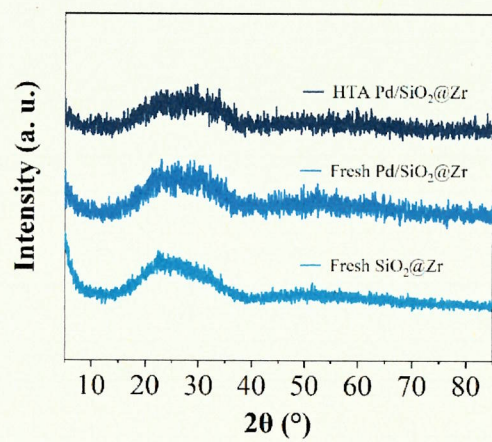


Fig. S1. XRD patterns of fresh SiO₂@Zr, fresh and HTA 1 wt.% Pd/SiO₂@Zr.

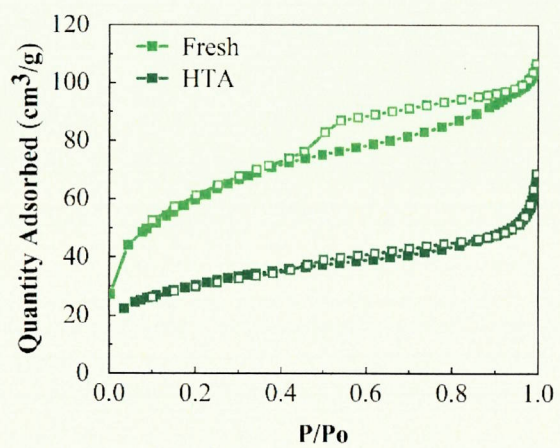


Fig. S2. N₂ adsorption (solid) – desorption (open) isotherms of fresh and HTA 1 wt.%

Pd/SiO₂@Zr.

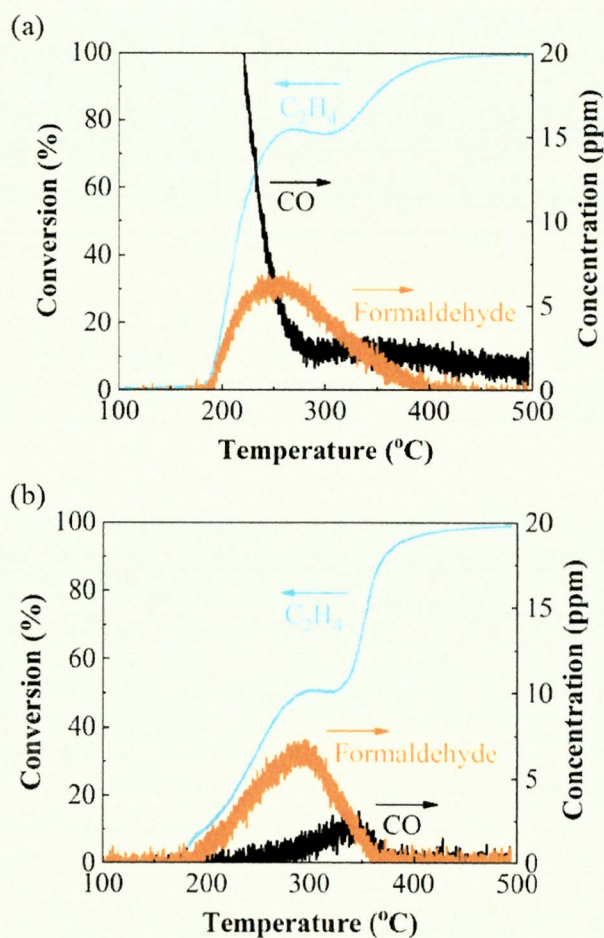


Fig. S3. C_2H_4 conversion (left y-axis) and CO, formaldehyde concentrations (right y-axis) over hydrothermally aged 1 wt.% Pd/SiO₂@Zr under reactor feed containing (a) 6% CO₂, 12% O₂, 6% H₂O, 400 ppm H₂, 2000 ppm CO, 100 ppm NO, 1667 ppm C₂H₄, 1000 ppm C₃H₆, 333 ppm C₃H₈ and (b) 6% CO₂, 12% O₂, 6% H₂O, 400 ppm H₂, 1667 ppm C₂H₄; HCs in C₁ basis. The slow light-off profile of C₂H₄ in Fig. S3b compared to Fig. S3a can be attributed to the decreased exothermic effect when C₃H₆, C₃H₈, and CO were removed from the reactor feed (data not shown).

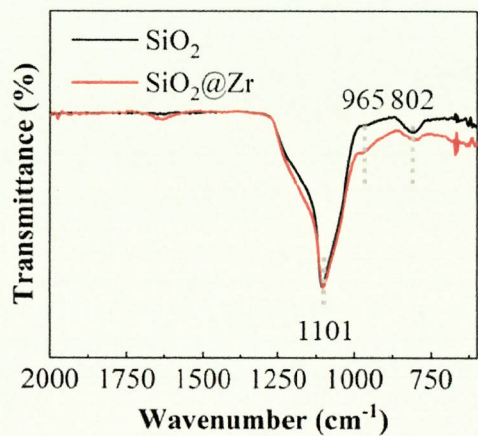


Fig. S4. FT-IR spectra of SiO₂ spheres and SiO₂@Zr support.

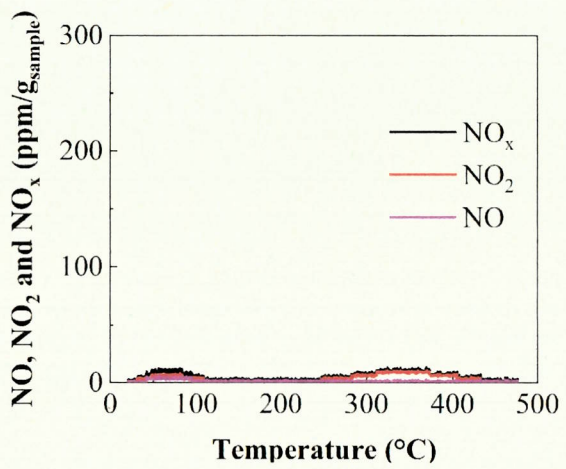


Fig. S5. NO_x-TPD profiles over fresh ZrSiO₄.

Video. S1. 3D tomography video of 1 wt.% Pd/SiO₂@Zr.

References:

- [1] H.Y. Law, J. Blanchard, X. Carrier, C. Thomas, NO_x-TPD as a Tool to Estimate the Accessible Zirconia Surface of ZrO₂-Containing Materials, *J. Phys. Chem. C* 114(21) (2010) 9731-9738.
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- [2] K.G. Rappé, C. DiMaggio, J.A. Pihl, J.R. Theis, S.H. Oh, G.B. Fisher, J. Parks, V.G. Easterling, M. Yang, M.L. Stewart, Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation: Low-Temperature Oxidation, Storage, Three-Way, and NH₃-SCR Catalyst Test Protocols, *Emiss. Control Sci. Technol.* 5(2) (2019) 183-214.
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