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Fabrication of ultrafine Pd nanoparticles on 3D ordered macroporous TiO₂ for enhanced catalytic activity during diesel soot combustion

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ABSTRACT

Nanocatalysts consisting of three-dimensionally ordered macroporous (3DOM) TiO₂-supported ultrafine Pd nanoparticles (Pd/3DOM-TiO₂-GBMR) were readily fabricated by gas bubbling-assisted membrane reduction (GBMR) method. These catalysts had a well-defined and highly ordered macroporous nanostructure with an average pore size of 280 nm. In addition, ultrafine hemispherical Pd nanoparticles (NPs) with a mean particle size of 1.1 nm were found to be well dispersed over the surface of the 3DOM-TiO₂ support and deposited on the inner walls of the material. The nanostructure of the 3DOM-TiO₂ support ensured efficient contact between soot particles and the catalyst. The large interface area between the ultrafine Pd NPs and the TiO₂ also increased the density of sites for O₂ activation as a result of the strong metal (Pd)-support (TiO₂) interaction (SMSI). A Pd/3DOM-TiO₂-GBMR catalyst with ultrafine Pd NPs (1.1 nm) exhibited higher catalytic activity during diesel soot combustion compared with that obtained from a specimen having relatively large Pd NPs (5.0 nm). The *T*₁₀, *T*₅₀ and *T*₉₀ values obtained from the former were 295, 370 and 415 °C. Both the activity and nanostructure of the Pd/3DOM-TiO₂-GBMR catalyst were stable over five replicate soot oxidation trials. These results suggest that nanocatalysts having a 3DOM structure together with ultrafine Pd NPs can decrease the amount of Pd required, and that this approach has potential practical applications in the catalytic combustion of diesel soot particles.

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The soot emitted from diesel engines contains particulate matter with sizes less than 2.5 μm (PM_{2.5}), which is known to have significant impacts on human health and the environment [1,2]. One efficient exhaust gas treatment system is the continuously regenerating particulate trap (CRT) technique, which is based on the use of highly active catalytic materials [3,4]. Over several decades of development, several materials exhibiting high catalytic activity for soot combustion have been identified, including noble metals, transition metal oxides, alkaline metal

oxides, perovskite-like oxides and ceria-based oxides [5–9]. However, it remains challenging to fabricate highly active catalytic systems for soot combustion, and developing high-performance catalysts requires an understanding of the properties that affect catalytic activity. Catalytic soot combustion is a typical heterogeneous process occurring over solid particles and takes place at triple-phase contact points between catalyst and soot particles (both of which are solids) and gaseous reactants [10,11]. The activity of catalysts during the deep

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oxidation associated with soot combustion is primarily determined by two key factors: the intrinsic capacity for O₂ activation and the degree of contact between soot particles and the catalyst [12–16]. Our previous work found that the nanostructure of three-dimensionally-ordered macroporous (3DOM) materials having large pore sizes (> 50 nm) enhanced the catalytic activity during diesel soot combustion as a result of more efficient contact between soot and catalyst [17–20]. It was also determined that depositing supported noble metal (Au or Pt) nanoparticles (NPs) on the surfaces of 3DOM oxides as active components further improved the catalytic activity during diesel soot combustion [21–26]. As an example, nanocatalysts composed of 3DOM oxides with supported Au@Pt core-shell nanoparticles exhibited high catalytic activity during soot combustion, although the practical applicability of these materials is limited due to their expense [27]. Supported Pd catalysts have recently received much attention in the field of automobile emission purification as a substitute for Pt-based materials because they exhibit unexpected catalysis of oxidation reactions [28]. However, there has been little research focused on the design and fabrication of systems incorporating Pd nanoparticles on the surfaces of 3DOM oxides as a means of improving catalytic activity. Therefore, the relationship between Pd nanostructure and catalytic activity during soot combustion remains unknown.

In the present work, a nanocatalyst consisting of ultrafine Pd NPs supported on the surface of 3DOM TiO₂ (Pd/3DOM-TiO₂-GBMR) was designed and synthesized by the gas bubbling-assisted membrane reduction (GBMR) method. This is a mature preparation technique and has been described previously in detail [21,22]. It was found that the nucleation and growth of the supported Pd nanocrystals could be efficiently controlled by generating a highly homogeneous dispersion of the reductant via the GBMR process. This, in turn, allowed control over the size of the Pd nanocrystals. The GBMR parameters consisted of a polyvinyl pyrrolidone-unit to Pd ratio of 100, 50 mL of a NaBH₄ solution (0.2 g L⁻¹), and NaBH₄ solution and hydrogen bubbling flow rates of 1 and 40 mL min⁻¹, respectively. The final products were obtained by filtration, drying and calcination at 500 °C for 2 h. The nominal Pd loading on the Pd/3DOM-TiO₂-GBMR catalyst was 2 wt%, and an actual value of 1.9 wt% was determined using inductively coupled plasma optical emission spectrometry (ICP-OES, OPTIMA 7300V, PerkinElmer, Inc. Beijing, CUPB), as shown in Table 1.

Table 1

The Pd contents and physical properties of 3DOM-TiO₂ and Pd/3DOM-TiO₂ catalysts.

Catalyst	Pd content ^a (wt%)	Pd particle size ^b (nm)	S _{BET} ^c (m ² g ⁻¹)
3DOM TiO ₂	—	—	59
Pd/3DOM-TiO ₂ -GBMR	1.9	1.1	61
Pd/3DOM-TiO ₂ -IMP	2.0	5.0	60

^a Determined by ICP-OES.

^b Determined by HRTEM.

^c Obtained by the BET method.

Fig. 1. SEM (a), TEM (b) and HRTEM (c) images and size distribution of Pd NPs in a Pd/3DOM-TiO₂ catalyst synthesized by the GBMR method; (d) HRTEM image of a Pd/3DOM-TiO₂ catalyst obtained using the impregnation method along with the associated particle size distribution. The insets in (a) and (b) show the enlarged 3DOM nanostructure of the TiO₂ support and the corresponding SAED pattern of the catalyst, respectively. The insets in (c) and (d) show enlarged images of the crystallinity of a single Pd nanoparticle.

Fig. 1 presents scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images of the Pd NPs on a Pd/3DOM-TiO₂ catalyst synthesized by the GBMR method, in addition to the Pd particle size distribution. For comparison purposes, an HRTEM image of a Pd/3DOM-TiO₂ catalyst with the same Pd loading but synthesized via an impregnation method (Pd/3DOM-TiO₂-IMP) is also shown, in Fig. 1(d). Fig. 1(a) demonstrates that the average diameter of the periodic voids in the 3DOM TiO₂ nanostructure was 280 nm, and that the voids in the long-range ordered structure were interconnected through open passages 109 nm in diameter (inset to Fig. 1(a)). These passages would be expected to allow soot particles to permeate into the internal pores in the 3DOM TiO₂ and so improve the contact efficiency between soot particles and catalyst. A 3DOM structure with overlapped pores can also be clearly observed in the TEM image in Fig. 1(b). Based on the selected area electron diffraction (SAED) pattern in the inset to Fig. 1(b), it is apparent that the pore walls of the Pd/3DOM-TiO₂-GBMR catalyst had a polycrystalline phase structure. The characteristic SAED rings are indexed to the (101), (004) and (200) lattice planes of the tetragonal phase structure of anatase 3DOM-TiO₂. SAED rings assignable to Pd nanoparticles were not detected, indicating that the supported Pd NPs were quite small.

Fig. 1(c) demonstrates the presence of highly disperse supported Pd NPs with uniform sizes. The size distribution of the Pd NPs on the 3DOM TiO₂ support was in the range of 0.4–1.8 nm, while the mean diameter was 1.1 nm based on a statistical analysis of more than 100 NPs. Lattice fringes generated by the

Pd NPs can be clearly seen in the HRTEM image provided as an inset to Fig. 1(c). The thickness of five layers of crystal planes in a single ultrafine hemispherical Pd NP was 1.2 nm, which is equal to a thickness of 0.24 nm for each indexed fcc (111) crystal plane. The contact interface between the TiO₂ and the Pd NPs also exhibits reconstruction, indicating a strong metal-support interaction (SMSI). This structure may therefore enhance the mobility of lattice oxygen in the bulk of the TiO₂ support and increase the production of oxygen vacancies on the surface of the Pd/3DOM-TiO₂ catalyst [29]. In the case of the Pd/3DOM-TiO₂-IMP catalyst shown in Fig. 1(d), the size distribution of the Pd NPs is relatively wide (from 1 to 8 nm), with a mean diameter of 5.0 nm based on an examination of 100 NPs. The contact interface between the TiO₂ and the Pd NPs is clearly defined, indicating that the intensity of the SMSI effect in this material was weaker relative to that of the Pd/3DOM-TiO₂-GBMR. Thus, a nanocatalyst composed of ultrafine Pd NPs supported on the surface of 3DOM TiO₂ (Pd/3DOM-TiO₂) having strong metal (Pd)-support (TiO₂) interactions should exhibit superior catalytic activity during soot combustion.

The phase structures of both the 3DOM TiO₂ and Pd/3DOM-TiO₂ catalysts were assessed using X-ray diffraction (XRD) and Raman spectroscopy with the results shown in Fig. 2. Fig. 2(a) demonstrates a series of diffraction peaks at 2θ values of 25.4°, 37.9°, 48.1°, 53.9°, 55.2°, 62.8° and 75.1° that can be indexed to the (101), (004), (200), (105), (211), (204) and (215) lattice planes of an anatase TiO₂ support with a tetragonal phase structure (JCPDS: 21-1272), respectively. A weak diffraction peak centered at 27.4° is also present and is attributed to the (110) lattice planes of a rutile TiO₂ support with a tetragonal phase structure (JCPDS: 65-0191). These data indicate that the support was primarily made of anatase TiO₂. Following the dispersion of the Pd NPs, there was no evidence of Pd diffraction peaks and no changes in the diffraction peaks generated by the 3DOM-TiO₂ support, which is attributed to the small size of the Pd NPs. The phase structures of the catalysts were further investigated by Raman spectroscopy and the results are presented in Fig. 2(b). The four Raman peaks centered at 145, 398, 517 and 639 cm⁻¹ can be attributed to the Ra-

man-active Eg, B1g, A1g and Eg symmetric modes of anatase TiO₂, respectively [30]. The peak centered at 145 cm⁻¹ is assigned to the bending vibration of the O–Ti–O bond, while the remaining three peaks are also related to Ti–O–Ti bending [31]. The less intense peak at 197 cm⁻¹ can be ascribed to the rutile phase of the TiO₂ support. These data demonstrate the coexistence of two crystal phases in the TiO₂ support, in accordance with the XRD results. Introducing the ultrafine Pd NPs on the inner walls of the TiO₂ does not change the Raman spectrum. The surface areas of the 3DOM TiO₂ and Pd/3DOM-TiO₂ catalysts are also summarized in Table 1, and are seen to be in the range of 60±1 m² g⁻¹. Based on the above XRD and Raman results, it is concluded that the TiO₂ was composed primarily of an anatase phase with some rutile phase, and that the ultrafine Pd NPs supported on the inner walls of the 3DOM TiO₂ had essentially no effect on the crystalline phase or crystallinity.

Due to the nature of the deep oxidation reactions that occur during soot combustion, the catalytic activity is strongly dependent on the redox properties of the catalyst [32]. Fig. 3(a) shows the H₂-temperature programmed reduction (TPR) profiles of 3DOM TiO₂ and Pd/3DOM-TiO₂ catalysts obtained using different synthetic methods. The 3DOM TiO₂ generated one main reduction peak centered at 591 °C, which can be assigned to the reduction of Ti⁴⁺ to Ti²⁺ (that is, bulk reduction). Another reduction peak in the range of 200–350 °C can be attributed to the reduction of surface absorbed oxygen on the TiO₂. After introduction of the Pd NPs, the reduction peaks shift to lower temperatures. In contrast, the Pd/3DOM-TiO₂-GBMR catalyst produced two clear reduction peaks at the relatively low temperatures of 262 and 457 °C. The former peak can be attributed to the reduction of chemisorbed oxygen species on the Pd NPs (that is, from Pd-O_x to Pd) and at the interface between the Pd NPs and the TiO₂ support (Ti-O_x-Pd to Pd). The latter peak is assigned to the reduction of bulk TiO₂ accompanied by a spill-over of hydrogen at the Pd-TiO₂ interface due to the strong metal(Pd)-support(TiO₂) interaction [33]. With increases in the Pd NP size, the reduction peaks generated by the Pd/3DOM-TiO₂-IMP are shifted to higher temperatures and the intensity of the peak at 262 °C is significantly decreased. These results indicate that the surface state of the Pd NPs on the

Fig. 2. XRD patterns (a) and Raman spectra (b) of the 3DOM TiO₂ (1) and Pd/3DOM-TiO₂-GBMR (2) catalysts, acquired using a 532 nm laser.

Fig. 3. H₂-TPR profiles (a) and Pd 3d XPS patterns (b) of 3DOM TiO₂ and Pd/3DOM-TiO₂ catalysts synthesized using different methods. (1) 3DOM TiO₂; (2) Pd/3DOM-TiO₂-GBMR; (3) Pd/3DOM-TiO₂-IMP.

3DOM TiO₂ is different from that on the Pd/3DOM-TiO₂-GBMR, and that the SMSI effect is decreased. The electronic states of the Pd NPs on the TiO₂ surface were examined by acquiring Pd 3d X-ray photoelectron spectroscopy (XPS) data for Pd/3DOM-TiO₂ catalysts synthesized using different methods, with the results shown in Fig. 3(b). The binding energy values of 334.3 and 339.6 eV, 335.6 and 340.9 eV, and 337.3 and 342.6 eV are assigned to the Pd 3d_{5/2} and Pd 3d_{3/2} spin-orbit couplings of Pd⁰, Pd²⁺ and Pd⁴⁺ species, respectively. It is therefore apparent that both metallic (Pd⁰) and ionic Pd (Pd²⁺ and Pd⁴⁺) species coexisted on the surface of the 3DOM TiO₂ support. The intensities of the peaks due to Pd²⁺ and Pd⁴⁺ are greater in the case of the Pd/3DOM-TiO₂-GBMR catalyst relative to the Pd/3DOM-TiO₂-IMP, indicating that the concentration of ionic Pd species was greater on the Pd/3DOM-TiO₂-GBMR. This is attributed to the smaller size of the Pd NPs on the Pd/3DOM-TiO₂-GBMR catalyst, which is beneficial to the adsorption and activation of O₂ and thus should improve the catalytic activity during soot combustion. Thus, it is evident that the Pd/3DOM-TiO₂-GBMR should promote H₂ oxidation as a result of its greater number of ionic Pd species, suggesting superior catalytic ability.

The catalytic activities of 3DOM TiO₂ and Pd/3DOM-TiO₂ catalysts during soot combustion in conjunction with loose contact between soot particles and the catalyst were evaluated using temperature-programmed oxidation (TPO), and the results are shown in Table 2 and Fig. 4. In these trials, Printex U

carbon (Degussa, Frankfurt, Germany) was used as a model for diesel soot particles. The catalytic activity was evaluated based on the resulting T_{10} , T_{50} and T_{90} values, defined as the temperatures at 10%, 50% and 90% soot conversion, respectively. The $S_{CO_2^m}$ value was also determined. This is defined as the selectivity for CO₂ formation (S_{CO_2}) at the maximum soot combustion rate. For comparison purposes, soot oxidation was also performed without a catalyst, and T_{10} , T_{50} and T_{90} values of 462, 585 and 643 °C were obtained, respectively. As shown in Fig. 4(a) and Table 2, both the 3DOM TiO₂ and Pd/3DOM-TiO₂ catalysts enhanced the soot combustion process. This effect is attributed to the improved contact efficiency between soot particles and the catalyst due to the open and interconnected macropore structure of the catalytic material. The addition of Pd NPs to the TiO₂ was also found to greatly increase the catalytic activity. The Pd/3DOM-TiO₂-GBMR specimen with smaller Pd NPs (1.1 nm) showed higher catalytic activity than the Pd/3DOM-TiO₂-IMP with larger Pd NPs (5.0 nm), giving T_{10} , T_{50} and T_{90} values of 295, 370 and 415 °C, respectively. These data indicate that the Pd NP size is a key factor in improving the catalytic activity, which may be related to the interface structure and the SMSI effect between the Pd NPs and the TiO₂ support. It is also noted that the Pd NPs increased the $S_{CO_2^m}$ values. As shown in Table 2, the $S_{CO_2^m}$ values of the Pd/3DOM-TiO₂ catalysts were greater than 96%, meaning that only a small quantity of CO would be included in the vehicle exhaust emission.

The stability of the 3DOM structure was examined, and Fig. 4(b) summarizes the catalytic activity of a Pd/3DOM-TiO₂-GBMR catalyst during five replicate soot-TPO tests. It is evident that T_{10} , T_{50} and T_{90} did not change significantly during the tests, meaning that the catalyst maintained its superior catalytic activity. Fig. 4(c) and (d) present TEM and HRTEM images of the Pd/3DOM-TiO₂-GBMR catalyst after five soot-TPO trials, and demonstrate that neither the Pd NP size nor the 3DOM TiO₂ nanostructure was modified. These results show that Pd/3DOM-TiO₂ catalysts exhibit a high degree of stability during soot combustion, as would be required in prac-

Table 2

The catalytic activities of 3DOM TiO₂ and Pd/3DOM-TiO₂ catalysts synthesized using different methods during soot combustion under loose contact conditions in the presence of O₂ and NO.

Catalyst	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	$S_{CO_2^m}$ (%)
Soot (without catalyst)	462	585	643	55.0
3DOM TiO ₂	347	470	518	84.4
Pd/3DOM-TiO ₂ -GBMR	295	370	415	97.6
Pd/3DOM-TiO ₂ -IMP	323	403	445	96.8

Reaction gas: 5% O₂ and 0.2% NO in Ar, 50 mL min⁻¹.

Data acquired at a soot/catalyst mass ratio of 1/10.

Fig. 4. (a) Soot conversion rates over 3DOM TiO₂ and Pd/3DOM-TiO₂ catalysts under loose contact conditions; (b) Catalytic and structural stability of Pd/3DOM-TiO₂-GBMR after five soot-TPO cycles; (c) TEM and (d) HRTEM images.

tical applications.

In summary, a nanocatalyst consisting of ultrafine Pd NPs supported on the inner walls of 3DOM TiO₂ was designed and synthesized using the GBMR method. A Pd/3DOM-TiO₂ catalyst with ultrafine Pd NPs, for which there was a high degree of contact between soot particles and the catalyst, exhibited superior redox properties at low temperatures based on the activation of O₂ by the Pd NPs. This material therefore showed improved catalytic performance and thermal stability during soot combustion. Catalysts having 3DOM structures and incorporating ultrafine active metals may have the potential for practical applications in the catalytic oxidation of solid particles. This work confirms that fundamental research regarding the SMSI and the reaction mechanism may be useful in the design and development of highly active catalysts for deep oxidation.

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Graphical Abstract

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Fabrication of ultrafine Pd nanoparticles on 3D ordered macroporous TiO₂ for enhanced catalytic activity during diesel soot combustionYuechang Wei *, Qiangqiang Wu, Jing Xiong, Jian Liu, Zhen Zhao *
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A nanocatalyst composed of three-dimensionally ordered macroporous TiO₂-supported ultrafine 1.1 nm Pd nanoparticles was readily fabricated by gas bubbling-assisted membrane reduction. This material exhibited high catalytic activity and good stability during diesel soot combustion.

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三维有序大孔二氧化钛表面超细钯纳米颗粒的构筑及其增强柴油炭烟催化燃烧性能

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摘要: 柴油机排放颗粒物(主要成分是炭烟)是城市大气PM_{2.5}中一次颗粒物的主要来源和二次颗粒物形成的重要组分, 严重危害大气环境和人类健康。利用颗粒物捕集器与催化剂相结合的连续过滤再生技术是满足柴油车国VI炭烟颗粒物排放标准的最有效技术, 目前该技术所面临的挑战是研发在排气温度的柴油炭烟颗粒物催化氧化催化剂。柴油炭烟催化燃烧反应的本质是典型的气(氧气)-固(炭烟颗粒)-固(催化剂)三相深度氧化反应, 因此我们研究组提出了高活性柴油炭烟燃烧催化剂设计应该遵循优化固-固接触与强化活化分子氧能力二者相结合的研究思路。

为满足此设计思路的要求, 本课题组前期采用孔径大于200 nm的三维有序大孔(3DOM)结构氧化物作为载体, 利用大孔效应来实现PM在催化剂内部的有效扩散, 从而提高催化剂与PM的接触效率。采用具有强活化分子氧能力的负载型贵金属(Au, Pt)纳米颗粒或贵金属-氧化物复合纳米颗粒作为活性位来提高催化剂对分子氧的活化能力, 进而设计了多个系列高活性催化剂, 并形成了担载贵金属纳米颗粒的可控制备方法与装置。然而, Au和Pt昂贵的价格限制了其广泛应用。价格相对便宜的Pd具有与Pt相似的催化性能, 是其良好替代品。但是, 目前关于3DOM氧化物表面负载型Pd纳米颗粒结构和尺寸与柴油炭烟催化燃烧性能之间的相关研究仍然较少。

基于此, 本文采用气泡辅助膜还原法制备了3DOM二氧化钛(TiO₂)担载超细Pd纳米颗粒催化剂。利用XRD, Raman, BET, SEM, TEM, ICP, XPS和H₂-TPR等技术手段对催化剂进行表征, 并以模拟柴油炭烟为研究对象, 利用程序升温氧化反应(TPO)对催化剂的活性进行评价, 深入探讨了催化剂的制备、结构及物化性质与炭烟催化燃烧反应性能之间的关系。

XRD和Raman结果表明, TiO_2 载体由锐钛矿(主)和金红石(次)两种物相组成. SEM照片显示, 所制催化剂为规整的有序大孔结构, 球形孔互相贯通, 孔径均一, 大孔腔平均尺寸为280 nm, 孔窗尺寸为109 nm, 这种三维有序大孔 TiO_2 的结构能够增强炭烟颗粒与催化剂之间的接触效率. TEM表征显示, 平均粒径为1.1 nm的超细半球型Pd纳米颗粒高度分散于 TiO_2 载体的内壁上, 两者间的优化界面面积有利于增加活化 O_2 的活性位密度, 这些活性位源于Pd与 TiO_2 间强相互作用. H_2 -TPR和XPS表征印证了上述观点, 具有1.1 nm超细Pd颗粒的Pd/3DOM- TiO_2 催化剂表现出强的低温氧化还原特性和丰富的表面吸附氧物种. 在TPO测试中, 相对于负载5.0 nm Pd颗粒的催化剂, 具有1.1 nm尺寸超细Pd颗粒的Pd/3DOM- TiO_2 催化剂展示了高的催化炭烟燃烧活性, T_{10} , T_{50} 和 T_{90} 分别为295, 370和415 °C, 且在5次TPO测试过程中表现出良好的催化和结构稳定性. 这种具有3DOM结构和超细Pd纳米颗粒的纳米催化剂能够有效降低Pd的使用量, 在催化炭烟燃烧的实际应用中大有潜力.

关键词: 有序大孔材料; 钯; 二氧化钛; 柴油炭烟燃烧; 超细纳米颗粒; 多相催化

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