Preparation and catalytic performance of Ag, Au, Pd or Pt nanoparticles supported on 3DOM CeO₂–Al₂O₃ for toluene oxidation

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Abstract:

Three-dimensionally ordered macro-/mesoporous 26.9 wt% CeO₂–Al₂O₃ (denoted as 3DOM 26.9CeO₂–Al₂O₃)-supported noble metal nanocatalysts ($x\text{M}/3\text{DOM } 26.9\text{CeO}_2\text{--Al}_2\text{O}_3$, $x = 0.27\text{--}0.81$ wt%; M = Au, Ag, Pd, and Pt) were prepared using the polymethyl methacrylate-templating and polyvinyl alcohol-protected reduction methods, respectively. It is shown that the $x\text{M}/3\text{DOM } 26.9\text{CeO}_2\text{--Al}_2\text{O}_3$ samples displayed a high-quality 3DOM architecture with a bimodal pore (macropore size = 180–200 nm and mesopore size = 4–6 nm) structure and a surface area of 102–108 m²/g, with the noble metal nanoparticles (3–4 nm in size) being highly dispersed on the 3DOM 26.9CeO₂–Al₂O₃ surface. The 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample performed the best ($T_{90\%} = 198$ °C at space velocity = 20,000 mL/(g h)) for toluene oxidation. The addition of moisture to the feedstock induced a positive effect on catalytic activity. The apparent activation energies obtained over the $x\text{M}/3\text{DOM } 26.9\text{CeO}_2\text{--Al}_2\text{O}_3$ samples were in the range of 46–100 kJ/mol, with the 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample possessing the lowest apparent activation energy. It is concluded that the good catalytic performance of 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ was associated with its higher adsorbed oxygen species concentration, better low-temperature reducibility, and stronger interaction between Pt and 3DOM 26.9CeO₂–Al₂O₃ as well as the unique bimodal porous structure.

Keywords: Three-dimensionally ordered macropore; ceria–alumina mixed oxide; supported noble metal catalyst; volatile organic compound removal; toluene oxidation.

1. Introduction

Volatile organic compounds (VOCs) belong to the main air pollutants that have harmful effects on the environment and human health. More and more countries have made increasingly stringent restrictions for the emission VOCs in the past years. Catalytic oxidation is an efficient, cost-effective, versatile, and environmentally benign technology to remove the VOCs at low concentrations. Development of high-performance catalytic materials, especially optimization of catalyst formulas, has been the focus of many studies. The noble metal-based materials, in spite of higher price than base transition-metal oxides, are the commonly used catalysts due to their high activity and good resistance to deactivation. Catalytic performance of a supported noble metal strongly depends upon the preparation method, precursor type, loading, dispersion, particle size of the noble metal, and nature of the support [1–3].

Porous alumina is a commonly used support. Niesz et al. [4] synthesized the ordered mesoporous alumina using the block copolymer as soft template. However, this procedure required a strict control of experimental conditions. Yuan et al. [5] prepared the mesoporous alumina via an evaporation-induced self-assembly route with triblock copolymer (Pluronic P123) as structuring agent. Relatively speaking, synthesis of macropores alumina has been less investigated. Titania, zirconia, and alumina with three-dimensional periodic arrays of macropores were firstly synthesized by Holland et al. [6]. In the same group, α -alumina with three-dimensionally ordered or randomly positioned macropores was also fabricated [7]. Ueda et al. [8] obtained three-dimensionally ordered macroporous (3DOM) alumina adopting an ethylene glycol (EG)-methanol mixed solution of aluminum nitrate. Working on the catalytic oxidation of methane or CO, Guan et al. observed that the inverse opal γ -Al₂O₃-supported Pd catalyst showed better activity than the

dense γ -Al₂O₃-supported counterpart [9], and the inverse opal γ -Al₂O₃-supported Pt–Rh catalysts showed higher catalytic activity (CO was completely oxidized below 150 °C at space velocity (SV) = 100,000 mL/(g h)) than the wash-coated Al₂O₃ layer-supported counterpart for the preferential oxidation of CO in the presence of excess hydrogen [10]. The interconnected macropores allow rapid mass transportation and provide easier access to the active sites, whereas mesopores provide a high surface area and increase the adsorption efficiency of reactant molecules [11–13]. Combination of macropores and mesopores in a material would be beneficial for the enhancement in catalytic performance. Synthesis of hierarchical macro-mesoporous metal oxides has become an exciting topic in catalysis [14]. For example, Idakiev et al. pointed out that the use of macro-mesoporous TiO₂ or ZrO₂ support gave rise to the catalysts with enhanced activity for the oxidation of benzene [15,16]. After synthesizing the hierarchical bimodal macro-mesoporous zirconia oxide via a simple route in the presence of CTMABr, Tidahy et al. [17] found that the highest catalytic activity was achieved over the 0.5 wt% Pd/macro-mesoporous ZrO₂ sample, a result due to the better Pd dispersion and a more amount of reducible PdO species. Recently, preparation and catalytic applications of hierarchically three-dimensionally ordered macro-mesoporous Al₂O₃ have attracted great interests [13,18–22]. For example, Bian et al. [19] used the soft/hard dual templates to make macro-mesoporous Al₂O₃, and observed that the 2 wt% Pt/macro-mesoporous Al₂O₃ catalyst showed considerably higher activity than the 2 wt% Pt/commercial Al₂O₃ in the range of 20–200 °C at SV = 60,000 mL/(g h) for CO oxidation. Huang et al. [20] reported that the hierarchically macro-mesoporous structured Co–Mo–Ni/ γ -Al₂O₃ catalyst exhibited much higher activity than the commercial Co–Mo–Ni/ γ -Al₂O₃ catalyst in the hydrodesulfurization of thiophene.

Ceria with the unique redox property and good releasing oxygen capacity can be used as a reducible support. Zhang and coworkers [23,24] prepared 3DOM CeO₂-supported Au catalysts, and observed that the 1 wt% Au/3DOM CeO₂ materials exhibited superior catalytic activity with 100 % formaldehyde conversion at ca. 75 °C and SV = 66,000 mL/(g h). Liu et al. synthesized 3DOM CeO₂ using a dual “hard-soft” templating strategy, and found that the hierarchical porous CeO₂-supported Ir catalysts exhibited better performance than the conventional macroporous or bulk CeO₂-supported counterpart in the preferential oxidation of CO [25]. CeO₂ as a support promoter exerts a great promoting effect in three-way catalysts, because it can improve the thermal stability of the support, promote the dispersion of noble metals, and favor the catalytic activity at the metal–support interfacial sites [26]. For example, Liu et al. [27] fabricated the Au/3DOM CeO₂–Co₃O₄ catalysts with well-defined macroporous skeletons and mesoporous walls via a precursor thermal decomposition-assisted colloidal crystal templating route, and observed that the porous catalysts showed superior activity and long-term stability in the preferential oxidation of CO in the presence of H₂-rich atmosphere, as compared to the Au-loaded CeO₂ or Co₃O₄ catalysts. Wei et al. [28] synthesized the 3DOM Ce_{1-x}Zr_xO₂-supported gold catalysts using the gas bubbling-assisted membrane reduction method, and found that the 1.3 wt% Au/3DOM CeO₂ catalyst exhibited the best catalytic performance ($T_{50\%} = 349$ °C and $T_{90\%} = 396$ °C at SV = 30,000 mL/(g h), respectively) for soot combustion, which is strongly related to the role of support including the structure and active oxygen supply pathway.

Previously, our group reported the synthesis of 3DOM Al₂O₃ using the triblock copolymer (Pluronic F127)-assisted polymethyl methacrylate (PMMA) microsphere-template strategy [22]. We realize that the synthesized bimodal porous

alumina can be used as a support. Considering the good redox property of CeO₂, we envision that the generation of CeO₂ and Al₂O₃ in a 3DOM structure would enhance the performance of the supported noble metal catalysts. To the best of our knowledge, however, there have been few reports on the preparation of CeO₂-doped 3DOM Al₂O₃-supported noble metal NPs and the comparative investigation on catalytic activity of the supported materials in toluene oxidation. For example, Haghighi and coworkers [29,30] adopted a wet impregnation method to fabricate the 1 wt% Pt/Al₂O₃-yCeO₂ (y = 10, 20, 30 wt%) nanocatalysts that were highly active (ca. 100 % of toluene or xylene and 78 % of benzene could be removed at 250 °C and SV = 8,400 mL/(g h)). Jin et al. [31] prepared 3DOM Al-Ce mixed oxide catalysts using the colloidal crystal templating method, and observed that the 3DOM-structured materials showed higher catalytic activity than the disordered macroporous counterpart for soot combustion. Herein, we report the preparation, characterization, and catalytic properties of xM/3DOM yCeO₂-Al₂O₃ (x = 0.27–0.81 wt%; y = 8.8–26.9 wt%; M = Au, Ag, Pd, Pt) for toluene oxidation. As seen from Figs. S1 and S2, the 3DOM Al₂O₃, 3DOM 8.8CeO₂-Al₂O₃, 3DOM 17.8CeO₂-Al₂O₃, and 3DOM 26.9CeO₂-Al₂O₃ samples possessed a high-quality 3DOM structure with a macropore diameter of 180–200 nm and Au NPs were highly dispersed on the surface of 3DOM CeO₂-Al₂O₃ in the 0.78Au/3DOM 8.8CeO₂-Al₂O₃ and 0.73Au/3DOM 17.8CeO₂-Al₂O₃ samples. Fig. S3 shows the catalytic activities of the 0.74Au/3DOM Al₂O₃ and xAu/3DOM yCeO₂-Al₂O₃ (x = 0.78, 0.73, and 0.75 wt%; y = 8.8, 17.8, and 26.9 wt%) samples for toluene oxidation. It is found that the 0.75Au/3DOM 26.9CeO₂-Al₂O₃ sample performed the best (Table S1). Therefore, we used the 3DOM 26.9CeO₂-Al₂O₃ as support to prepare the xM/3DOM 26.9CeO₂-Al₂O₃ (x = 0.27–0.81 wt%; M = Au, Ag, Pd, Pt) samples and investigate their catalytic behaviors

for toluene oxidation.

2. Experimental

2.1. Catalyst preparation

Well-packed monodispersive colloidal crystal template, PMMA microspheres with an average diameter of ca. 300 nm, was synthesized using the approach reported elsewhere [22]. The 3DOM $\gamma\text{CeO}_2\text{--Al}_2\text{O}_3$ (γ is the weight percentage of CeO_2 ; the theoretical CeO_2 weight percentage was 9, 18, and 27 wt%, respectively) supports were fabricated using the Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) as soft template and PMMA microspheres as hard template. The typical preparation procedures are as follows: 1.0 g of H_2O , 19.0 g of ethanol, and 2.0 g of F127 were mixed under stirring until a homogeneous solution was formed. Then, 20.0 mmol of the desired amounts of $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ was added to the above mixed solution and continuously stirred. After complete dissolution, 4.0 g of PMMA microspheres was added to the mixed solution for the thoroughly wetting of the colloidal crystal PMMA microspheres, and the excessive solution was filtered via a Buchner funnel connected to vacuum. After being dried at room temperature (RT) for 48 h, the obtained solid was calcined in an oven at a ramp of 1 $^\circ\text{C}/\text{min}$ from RT to 300 $^\circ\text{C}$ and kept at 300 $^\circ\text{C}$ for 3 h, and then at the same ramp from 300 to 600 $^\circ\text{C}$ and kept at 600 $^\circ\text{C}$ for 5 h, thus obtaining the 3DOM $\gamma\text{CeO}_2\text{--Al}_2\text{O}_3$ support.

The $x\text{M}/3\text{DOM } \gamma\text{CeO}_2\text{--Al}_2\text{O}_3$ (x is the weight percentage of M; the theoretical M weight percentage was 1.0 and 0.5 wt%, respectively; M = Ag, Au, Pd, and Pt) samples were prepared using the polyvinyl pyrrolidone (PVP)- or polyvinyl alcohol (PVA)-protected reduction method [32]. The typical preparation procedures are as follows: (i) The noble metal aqueous solution (0.01 mol/L) was in advance prepared with AgNO_3 , HAuCl_4 , PdCl_2 , and H_2PtCl_6 as noble metal source; (ii) a stoichiometric

amount of the noble metal aqueous solution was first diluted with deionized water to be 2.0×10^{-4} mol/L in concentration, and a desired amount of PVP (for supported Ag sample) or PVA (for supported Au, Pd, and Pt samples) was then added to the above aqueous solution (M/PVP (or PVA) mass ratio = 1.0 : 1.5) in an ice–water bath under vigorous stirring for 10 min; (iii) after rapidly injecting the 0.1 mol/L NaBH₄ aqueous solution (M/NaBH₄ molar ratio = 1.0 : 5.0) and continuously stirring for 20 min, a sol was obtained; (iv) a desired amount of the 3DOM $y\text{CeO}_2\text{--Al}_2\text{O}_3$ support was added to the sol (the theoretical Ag or Au loading was 1.0 wt%, whereas the theoretical Pd or Pt loading was 0.5 wt%), and the obtained suspension was subjected to sonication (60 kHz) for 30 s. A N₂ bubble-assisted stirring operation was adopted to agitate the suspension for 10 h until complete adsorption of colloidal noble metals occurred; and (v) the solid was filtered, washed with 2.0 L of deionized water, dried at 80 °C for 12 h, and calcined in air at a ramp of 1 °C/min from RT to 450 °C and maintained at this temperature for 4 h, thus obtaining the $x\text{M}/3\text{DOM } y\text{CeO}_2\text{--Al}_2\text{O}_3$ samples. The results of inductively coupled plasma atomic emission spectroscopic (ICP–AES) studies show that the real Ag, Au, Pd, and Pt loadings (x) were 0.81, 0.72–0.78, 0.29, and 0.27 wt%, respectively; whereas the real CeO₂ contents (y) were 8.8, 17.8, and 26.9 wt% in the $x\text{M}/3\text{DOM } y\text{CeO}_2\text{--Al}_2\text{O}_3$ samples (Table 1 and Table S1), respectively.

To better compare the catalytic activity, we prepared the bulk- or commercial Al₂O₃-supported noble metal samples. The bulk Al₂O₃ was prepared via the thermal decomposition of Al(NO₃)₃·9H₂O at 600 °C for 5 h. The commercial alumina (hydrophilic fumed alumina (Degussa AEROIDE Alu C), denoted as com-Al₂O₃) with a surface area of 110 m²/g was purchased from Degussa company. The 0.72Au/bulk Al₂O₃ and 0.71Au/com-Al₂O₃ samples were also prepared via the above mentioned PVA-protected reduction route.

All of the chemicals (A.R. in purity) were purchased from Beijing Sinopharm Chemical Reagents Company and used without further purification.

2.2. Catalyst characterization

Physicochemical properties of the samples were characterized using the ICP–AES, X-ray diffraction (XRD), N₂ adsorption–desorption (BET), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), X-ray photoelectron spectroscopy (XPS), and hydrogen temperature-programmed reduction (H₂-TPR). The detailed characterization procedures can be seen from [the Supplementary material](#).

2.3. Catalytic evaluation

Catalytic activities of the samples were evaluated in a continuous flow fixed-bed quartz microreactor (i.d. = 4 mm). To minimize the effect of hot spots, 50 mg of the sample (40–60 mesh) was diluted with 0.25 g of quartz sands (40–60 mesh). Prior to the test, the sample was treated in O₂ (20 mL/min) at 250 °C for 1 h. After being cooled to a given temperature, the reactant gas containing toluene was passed through the catalyst bed. The total flow rate of the reactant mixture (1000 ppm toluene + O₂ + N₂ (balance)) was 16.7 mL/min, giving a toluene/O₂ molar ratio of 1/400 and a space velocity (SV) of ca. 20,000 mL/(g h). The 1000-ppm toluene was generated by passing a N₂ flow through a bottle containing pure toluene chilled in an ice–water isothermal bath. In the case of water vapor introduction, 3.0, 5.0, and 7.0 vol% H₂O was introduced by passing a reactant mixture flow of 16.7 mL/min through a water saturator at 25, 33, and 40 °C, respectively. Reactants and products were analyzed online by a gas chromatograph (GC-2010, Shimadzu) equipped with a flame ionization detector (FID) and a TCD, using a stabilwax@-DA column (30 m in length) for VOCs separation and a Carboxen 1000 column (1/8 inch in diameter and 3 m in

length) for permanent gas separation. We use the mass spectrometer (Hiden HPR20) to detect the products, and found that CO₂ and H₂O were the only products in the oxidation of toluene. The balance of carbon throughout the investigation was estimated to be $99.5 \pm 1.5\%$.

3. Results and discussion

3.1. Crystal phase composition

Fig. S4 shows the XRD patterns of bulk, commercial, and 3DOM Al₂O₃ and 26.9CeO₂–Al₂O₃ supports. By referring to the standard XRD patterns of Al₂O₃, one can deduce that three broad diffraction peaks at $2\theta = 26.0^\circ$, 42.0° , and 66.0° assignable to amorphous Al₂O₃ in the bulk Al₂O₃ and 3DOM Al₂O₃ supports; eight diffraction peaks at $2\theta = 32.8^\circ$, 34.5° , 36.5° , 39.5° , 45.6° , 56.9° , 61.0° , and 67.0° were recorded in the com-Al₂O₃ support, ascribable to the δ -Al₂O₃ phase (JCPDS PDF# 16-0394); and the XRD peaks at $2\theta = 28.6^\circ$, 33.2° , 47.5° , 56.4° , 69.4° , and 76.7° were detected in the 26.9CeO₂–Al₂O₃ support, attributable to the cubic CeO₂ phase (JCPDS PDF# 65-2975). Fig. 1 shows the XRD patterns of the as-prepared samples. By comparing to the XRD patterns of the standard Ag, Au, Pd, Pt, and CeO₂ samples, the XRD peaks in the 2θ range of 10 – 80° of the samples could be well indexed. There was a cubic CeO₂ phase in the xM/3DOM 26.9CeO₂–Al₂O₃ samples. No significant Ag, Au, Pd, and Pt phases were detected, indicating that the noble metal NPs were highly dispersed on the surface of 3DOM 26.9CeO₂–Al₂O₃ and com-Al₂O₃. It should be noted that since the diffraction peaks due to the cubic Au phase (JCPDS PDF# 04-0784) at $2\theta = 38.1^\circ$, 44.5° and 64.5° were overlapped with the rather broad diffraction peaks of amorphous Al₂O₃ ($2\theta = 26.0^\circ$, 42.0° , and 66.0°) in the XRD patterns of the 0.74Au/3DOM Al₂O₃ and 0.72Au/bulk Al₂O₃ samples, it is

hard to identify the detection of XRD signals due to cubic Au phase.

3.2. Morphology, pore structure, and surface area

Fig. 2 shows the TEM images of the as-obtained samples. It can be clearly seen that 3DOM Al₂O₃ displayed a high-quality 3DOM architecture with a macropore diameter of 180–200 nm. The doping of CeO₂ did not destroy the macroporous structure in the 3DOM y CeO₂–Al₂O₃ samples. It is worth pointing out that ordered mesopores with a diameter of 4–6 nm were generated on the skeletons of macropores. Therefore, the x M/3DOM y CeO₂–Al₂O₃ samples possessed a hierarchically ordered macro-/mesoporous morphology. However, the 0.72Au/bulk Al₂O₃ sample displayed an irregular nonporous morphology (Fig. 2a and b), whereas the 0.71Au/com-Al₂O₃ sample showed a wormhole-like mesoporous structure (Fig. 2c and d). Furthermore, a number of noble metal NPs were uniformly dispersed on the surface of 3DOM 26.9CeO₂–Al₂O₃. The lattice spacings (d value) of CeO₂ in the 3DOM 26.9CeO₂–Al₂O₃ samples was estimated to be ca. 0.312 nm (Fig. 2i, k, m, and o), rather close to that of the (111) plane of standard CeO₂ (JCPDS PDF# 65-2975). The d values of Au, Ag, Pd, and Pt NPs in the samples were measured to be ca. 0.238, 0.236, 0.229, and 0.229 nm (Fig. 2b, g, i, k, m, and o), in good consistence with those of the (111) planes of standard Au (JCPDS PDF# 04-0784), Ag (JCPDS PDF# 04-0783), Pd (JCPDS PDF# 46-1043), and Pt (JCPDS PDF# 87-0644), respectively. The average Au, Ag, Pd, and Pt particle sizes in the 0.72Au/bulk Al₂O₃, 0.71Au/com-Al₂O₃, 0.74Au/3DOM Al₂O₃, and x M/3DOM 26.9CeO₂–Al₂O₃ samples were in the range of 3.3–4.1 nm (Table 1 and Fig. S5).

Fig. 3 shows the N₂ adsorption–desorption isotherms and pore-size distributions of the samples. Except for the 0.71Au/com-Al₂O₃ sample that displayed a type IV isotherm with a H1 hysteresis loop (Fig. 3A(a)), the other samples displayed a type II

isotherm with a H3 hysteresis loop in the relative pressure (p/p_0) range of 0.8–1.0, indicating the presence of macropores [33]. In addition, there was also a small type H2 hysteresis loop in the p/p_0 range of 0.2–0.8, demonstrating the formation of mesopores (Fig. 3A) [33]. That is to say, the samples possessed a bimodal (macro/meso-) porous structure, which was confirmed by their pore-size distributions (Fig. 3B). For the 0.71Au/com- Al_2O_3 sample, there was a broad pore-size distribution (Fig. 3B(a)). The BET surface areas (101.6–107.8 m^2/g) of the 3DOM 26.9CeO₂– Al_2O_3 -supported samples were much higher than that (11.6 m^2/g) of the bulk Al_2O_3 -supported sample, but a slightly lower than that (117.5 m^2/g) of the 0.71Au/com- Al_2O_3 sample (Table 1).

3.3. Surface composition, metal oxidation state, and adsorbed oxygen species

XPS technique was a useful technique to investigate the surface element composition, metal oxidation state, and adsorbed oxygen species of a solid sample. Figs. 4 and S6(A) show the Ce 3d, O 1s, Au 4f, Ag 3d, Pd 3d, and Pt 4f XPS spectra of the $x\text{M}/3\text{DOM } 26.9\text{CeO}_2\text{--Al}_2\text{O}_3$ and 26.9CeO₂– Al_2O_3 samples. It can be seen from Fig. 4A and S6(A) that the Ce 3d XPS spectrum of each of the samples could be deconvoluted to two sets of four components: one was at BE = 882.3 eV (V), 884.9 eV (V'), 889.9 eV (V''), and 898.5 eV (V'''), ascribable to the Ce 3d_{5/2}, whereas the other was at BE = 901.2 eV (U), 903.7 eV (U'), 907.9 eV (U''), and 917.3 eV (U'''), assignable to the Ce 3d_{3/2} [34]. The components at BE = 884.9 eV (V') and 903.7 eV (U') were due to the surface Ce³⁺ species, while the ones at other BEs were due to the surface Ce⁴⁺ species [34,35]. Table 2 summarizes the surface Ce⁴⁺/Ce³⁺ molar ratios of the samples. The surface Ce⁴⁺/Ce³⁺ molar ratios on the surface of the 26.9CeO₂– Al_2O_3 and $x\text{M}/3\text{DOM } 26.9\text{CeO}_2\text{--Al}_2\text{O}_3$ (M = Au, Ag, Pd, and Pt) samples were 3.90, 2.17, 3.37, 1.61, and 1.32, respectively. Loading noble metal gave rise to

an decrease in $\text{Ce}^{4+}/\text{Ce}^{3+}$ molar ratio. The 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample possessed the lowest surface $\text{Ce}^{4+}/\text{Ce}^{3+}$ molar ratio, indicating that the surface Ce^{3+} concentration of this sample was the highest.

As shown in Figs. 4B and S6(B), the asymmetrical O1s spectrum of each sample could be decomposed to two components: the one at BE = 529.9 or 530.3 eV was ascribable to the surface lattice oxygen (O_{latt}) species, whereas the other at BE = 531.8 eV was attributable to the surface adsorbed oxygen (O_{ads} , e.g., O_2^- , O_2^{2-} or O^-) species [36]. It is seen from Table 2 that the doping of CeO₂ or loading of noble metal NPs gave rise to an increase in $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ molar ratio of the sample, with the highest $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ molar ratio (4.03) being achieved on the surface of the 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample. The $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ molar ratio of the 26.9CeO₂–Al₂O₃ support was 0.62. It is also observed that the changing trend in $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ molar ratio was consistent with that in $\text{Ce}^{4+}/\text{Ce}^{3+}$ molar ratio on the surface of the $x\text{M}/3\text{DOM}$ 26.9CeO₂–Al₂O₃ samples. As well known, the rise in O_{ads} concentration would enhance activity of a catalyst for organic oxidation.

Fig. 4C(a–d) illustrates the Au 4f XPS spectra of the 0.72Au/bulk Al₂O₃, 0.71Au/com-Al₂O₃, 0.74Au/3DOM Al₂O₃, and 0.75Au/3DOM 26.9CeO₂–Al₂O₃ samples. The Au 4f XPS spectrum of each sample could be decomposed into four components: the ones at BE = 83.7 and 87.4 eV were assignable to the surface metallic gold (Au^0), and the ones at BE = 84.5 and 88.3 eV were ascribable to the surface oxidized gold ($\text{Au}^{\delta+}$) [37]. The surface $\text{Au}^{\delta+}/\text{Au}^0$ molar ratio (1.19) of the 0.75Au/3DOM 26.9CeO₂–Al₂O₃ sample was much higher than those (0.36–0.54) of the 0.72Au/bulk Al₂O₃, 0.71Au/com-Al₂O₃ and 0.74Au/3DOM Al₂O₃ samples (Table 2). As shown in the inset of Fig. 4C(d), the Ag 3d spectrum of 0.81Ag/3DOM 26.9CeO₂–Al₂O₃ could be decomposed into four components: the ones at BE = 367.8

and 373.7 eV were due to the surface Ag⁰ species, whereas the ones at BE = 368.8 and 374.5 eV were due to the surface Ag⁺ species [38]. For the 0.29Pd/3DOM 26.9CeO₂–Al₂O₃ sample, the two components at BE = 335.9 and 340.8 eV were assigned to the surface Pd⁰ species, whereas the two components at BE = 337.9 and 342.4 eV (inset of Fig. 4C(e)) were attributed to the surface Pd²⁺ species [39]. The Pt 4f spectrum of 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ is shown in the inset of Fig. 4C(f), in which the components at BE = 72.1 and 73.6 eV could be ascribed to the surface Pt⁰ and Pt^{δ+} species, respectively. The surface M^{δ+}/M⁰ (M = Au, Ag, Pd, Pt) molar ratios of the as-prepared samples are summarized in Table 2. The presence of surface M^{δ+} species indicates a strong interaction between M and CeO₂ NPs possibly via the reaction of M⁰ + Ce⁴⁺ → M^{δ+} + Ce³⁺, causing the rise in surface Ce³⁺ concentration of the sample.

3.4. Reducibility

The reducibility of a catalyst has an important influence on its catalytic activity. To evaluate the reducibility of the as-prepared samples, we carried out TPR experiments and their H₂-TPR profiles are illustrated in Fig. 5A. Since there was no H₂ consumption signals in the H₂-TPR profile (Fig. S7(a, b, and c)) of the bulk Al₂O₃, com-Al₂O₃, and 3DOM Al₂O₃ samples, the small reduction peaks centered at 329, 297, and 274 °C for the 0.72Au/bulk Al₂O₃ (Fig. 5A(a)), 0.71Au/com-Al₂O₃ (Fig. 5A(b)) and 0.74Au/3DOM Al₂O₃ (Fig. 5A(c)) samples could be assigned to the removal of chemically adsorbed oxygen species on highly dispersed Au NPs (i.e., from Au–O_x to Au) [28,29,31]. The reduction peaks centered at 370, 625, 685, and 924 °C (Fig. S7(d)) of the 3DOM 26.9CeO₂–Al₂O₃ sample were attributed to the reduction of the surface and bulk CeO₂ species. When noble metal NPs were loaded on the 3DOM 26.9CeO₂–Al₂O₃ surface, several reduction peaks appeared in the ranges of 151–321

and 425–852 °C (Fig. 5A(d–g)), in which the reduction peaks below 400 °C were assigned to the reduction of cationic Au, Ag, Pd or Pt species and the possible reduction of the surface CeO₂ to Ce₂O₃ species, whereas the ones above 400 °C were ascribed to the reduction of the bulk CeO₂ to Ce₂O₃ species [40]. Compared to the temperature (329, 297 or 274 °C) at the first reduction peak (Fig. 5A(a–c)) of the 0.72Au/bulk Al₂O₃, 0.71Au/com-Al₂O₃ or 0.74Au/3DOM Al₂O₃ sample, the temperature for the reduction of cationic Au (194 °C), Pd (188 °C) or Pt (151 °C) in the 0.75Au/3DOM 26.9CeO₂–Al₂O₃, 0.29Pd/3DOM 26.9CeO₂–Al₂O₃ or 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample (Fig. 5A(d, f, and g)) was shifted to a lower temperature. In addition, the temperature for the reduction of cationic Ag in the 0.81Ag/3DOM 26.9CeO₂–Al₂O₃ sample was 292 °C (Fig. 5A(e)). These results suggest that there was presence of a strong interaction between noble metal and support. Similar interactions of precious metals (e.g., Pt, Pd, Rh, Ru, and Ag) and CeO₂ support have been also observed by Acerbi et al. [41]. Such a strong interaction gave rise to the improvement in low-temperature reducibility of the CeO₂–Al₂O₃-supported noble metal samples, which would be beneficial for the enhancement in catalytic activity. Table 2 summarizes the quantitative analysis results of the H₂-TPR profiles of the samples. Obviously, the total H₂ consumption (0.107 mmol/g_{cat}) of 0.74Au/3DOM Al₂O₃ was much higher than that (0.052–0.067 mmol/g_{cat}) of 0.72Au/bulk Al₂O₃ and 0.71Au/com-Al₂O₃, indicating that the former possessed a more amount of adsorbed oxygen species on Au NPs. The 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample showed the highest total H₂ consumption (2.273 mmol/g_{cat}), demonstrating that this sample had more amounts of adsorbed oxygen and Ce³⁺ species and stronger interaction between Pt and support, which is exactly consistent with the result of XPS analysis. In order to better evaluate the low-temperature reducibility of the samples, we calculated the

initial (where less than 25 % oxygen for the first reduction peak in the sample was removed) H₂ consumption rate [42], as shown in Fig. 5B. Apparently, the initial H₂ consumption rate (i.e., low-temperature reducibility) increased in a sequence of 0.72Au/bulk Al₂O₃ < 0.71Au/com-Al₂O₃ < 0.81Ag/3DOM 26.9CeO₂-Al₂O₃ < 0.74Au/3DOM Al₂O₃ < 0.75Au/3DOM 26.9CeO₂-Al₂O₃ < 0.29Pd/3DOM 26.9CeO₂-Al₂O₃ < 0.27Pt/3DOM 26.9CeO₂-Al₂O₃. The changing trend in low-temperature reducibility was in good agreement with those in O_{ads} concentration and catalytic activity.

3.5. Catalytic performance

We performed the blank experiment (only quartz sand was loaded in the microreactor) below 400 °C under the conditions of toluene concentration = 1000 ppm, toluene/O₂ molar ratio = 1/400, and SV = 20,000 mL/(g h), and found that no significant conversion of toluene was detected, indicating that there were no obvious homogeneous reactions under the adopted reaction conditions. We use the $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ (the reaction temperatures for achieving toluene conversions of 10, 50, and 90 %, respectively) to evaluate the catalytic activity of a sample. Fig. S8 shows the catalytic activities of the supports. Apparently, no significant catalytic activities were detected over the three alumina supports, but the 26.9CeO₂-Al₂O₃ sample gave a $T_{50\%}$ of 362 °C and a $T_{90\%}$ of 397 °C at SV = 20,000 mL/(g h). Fig. 6 shows the catalytic activities of the supported noble metal samples, and their $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ values are listed in Table 3. The 0.27Pt/3DOM 26.9CeO₂-Al₂O₃ sample performed the best: $T_{10\%}$ = 140 °C, $T_{50\%}$ = 187 °C, and $T_{90\%}$ = 198 °C. The $T_{10\%}$, $T_{50\%}$, and $T_{90\%}$ were much lower than 295, 332, and 360 °C over 0.72Au/bulk Al₂O₃, 270, 305, and 330 °C over 0.71Au/com-Al₂O₃, 250, 290, and 317 °C over 0.74Au/DOM Al₂O₃, 200, 250, and 279 °C over 0.75Au/3DOM 26.9CeO₂-Al₂O₃, 263, 308, and 338 °C over

0.81Ag/3DOM 26.9CeO₂-Al₂O₃, and 168, 204, and 228 °C over 0.29Pd/3DOM 26.9CeO₂-Al₂O₃, respectively. It should be noted that the catalytic activity over 0.81Ag/3DOM 26.9CeO₂-Al₂O₃ was lower than that over 0.74Au/3DOM Al₂O₃, similar to that over 0.71Au/com-Al₂O₃, but much higher than that over 0.72Au/bulk Al₂O₃.

Table S2 summarizes the catalytic activities for toluene oxidation over various catalysts reported in the literature. By comparing the activities of these samples with that of our present sample, one can realize that the catalytic activity ($T_{90\%} = 198$ °C at 20,000 mL/(g h)) over 0.27Pt/3DOM 26.9CeO₂-Al₂O₃ was much better than that ($T_{90\%} = 300$ °C at 35,000 h⁻¹) over 1.5 wt% Au/7.5 wt% CeO₂/Al₂O₃ [43], that ($T_{90\%} = 215$ °C at 8,400 mL/(g h)) over 1 wt % Pt/Al₂O₃-30 wt% CeO₂ [29], that ($T_{90\%} = 247$ °C at 3,000 mL/(g h)) over NiO/SiO₂ [44], that ($T_{90\%} = 226$ °C at 20,000 mL/(g h)) over 4.6 wt % Au/macroporous LaMnO₃ [45], and that ($T_{90\%} = 260$ °C at 20,000 mL/(g h)) over 6.55 wt % Au/Fe₂O₃ nanodisc [46], similar to that ($T_{90\%} = 202$ °C at 20,000 mL/(g h)) over 7.63 wt % Au/3DOM LaCoO₃[47], but inferior to that ($T_{90\%} = 170$ °C at 20,000 mL/(g h)) over 6.4 wt% Au/3DOM La_{0.6}Sr_{0.4}MnO₃ [48], and that ($T_{90\%} = 138$ °C at 20,000 mL/(g h)) over 6.5 wt% Au/*meso*-Co₃O₄ [49].

Toluene consumption rates versus reaction temperature over the as-prepared samples are shown in Fig. S9. Toluene consumption rate increased monotonously with the rise in temperature. It is known that there are several kinds of active sites (e.g., noble metal, transition-metal oxide, and interface between noble metal and transition-metal oxide) in the reducible metal oxide-supported noble metal catalysts, causing it difficult to identify a single active site. Therefore, accurate calculation of turnover frequencies (TOFs) is hard. For comparison purposes, however, we calculated toluene oxidation rate (r): $r = xV_0/m_{\text{cat}}$ or n_M , where x is the conversion at a

certain temperature, V_0 is the initial toluene concentration per second, m_{cat} is the weight of catalyst, and n_M ($M = \text{Au, Ag, Pd, Pt}$) is the molar amount of M . Table 3 lists the toluene oxidation rates at 230 °C over the samples. It should be noted that the r at 240 °C over 0.72Au/bulk Al_2O_3 was only 0.087 mol/(mol_M s), much lower than that (16.136 mol/(mol_M s)) at 210 °C over 0.27Pt/3DOM 26.9CeO₂–Al₂O₃. The r at 230 °C was 0.142, 0.375, 1.396, 0.119, and 8.071 mol/(mol_M s) over the 0.71Au/com-Al₂O₃, 0.74Au/3DOM Al₂O₃, 0.75Au/3DOM 26.9CeO₂–Al₂O₃, 0.81Ag/3DOM 26.9CeO₂–Al₂O₃, and 0.29Pd/3DOM 26.9CeO₂–Al₂O₃ samples, respectively. Obviously, the 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample showed the highest toluene oxidation rate.

Fig. 7 shows the toluene consumption rate at 230 °C as a function of $O_{\text{ads}}/O_{\text{latt}}$ molar ratio of the samples. It is observed that a higher O_{ads} concentration was favorable for the enhancement in catalytic activity of the sample. The toluene consumption rate (0.053 μmol/(g_{cat} s)) at 230 °C over 0.75Au/3DOM 26.9CeO₂–Al₂O₃ was ca. 18 times higher than that (0.003 μmol/(g_{cat} s)) over 0.72Au/bulk Al₂O₃, ca. 10 times higher than that (0.005 μmol/(g_{cat} s)) over 0.71Au/com-Al₂O₃, and ca. 4 times higher than that (0.014 μmol/(g_{cat} s)) over 0.74Au/3DOM Al₂O₃. Furthermore, the toluene consumption rate (0.009 μmol/(g_{cat} s)) at 230 °C over 0.81Ag/3DOM 26.9CeO₂–Al₂O₃ was lower than that (0.014 μmol/(g_{cat} s)) over 0.74Au/3DOM Al₂O₃. Although the toluene consumption rate (0.221 μmol/(g_{cat} s)) at 230 °C over 0.29Pd/3DOM 26.9CeO₂–Al₂O₃ was similar to that (0.223 μmol/(g_{cat} s)) at 210 °C over 0.27Pt/3DOM 26.9CeO₂–Al₂O₃, the former was ca. 4 times higher than that (0.053 μmol/(g_{cat} s)) over 0.75Au/3DOM 26.9CeO₂–Al₂O₃. Hence, the 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample exhibited the highest toluene oxidation rate and $O_{\text{ads}}/O_{\text{latt}}$

molar ratio, a result due to the presence of a hierarchically ordered macro-/mesoporous structure and strong interaction between Pt NPs and support. The interaction between Au and support could facilitate the activation of O₂ molecules to the active O_{ads} species and then enhance catalytic activity of 0.27Pt/3DOM 26.9CeO₂–Al₂O₃. It is well known that the reducibility of a metal oxide is associated with the formation of oxygen vacancies. Kleitz et al. [50] found that a metal oxide could induce surface defects more readily if it was more reducible, which would give rise to a higher O_{ads} concentration. Based on the results of characterization and activity evaluation, we conclude that the good catalytic performance of 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ was associated with its high O_{ads} concentration, good low-temperature reducibility, and strong interaction between Pt NPs and 3DOM 26.9CeO₂–Al₂O₃.

To examine the effects of moisture on catalytic activity, on-stream toluene oxidation at 200 °C in the presence of 3.0, 5.0, and 7.0 vol% H₂O for 40, 10, and 10 h was conducted over the 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample, respectively, and the results are shown in Fig. 8A. It is seen that a small loss (ca. 3.0%) in activity was detected at first, but the activity was fast restored to that (97.4%) of the fresh sample, and then maintained a slightly higher activity (nearly 100%) even in the presence of 3.0, 5.0 or 7.0 vol% H₂O. The 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample after treatment in 7.0 vol% H₂O performed slightly better than the fresh sample (Fig. 8B). The results indicate that the 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample was catalytically durable under the adopted conditions. A similar phenomenon of the positive effect due to water vapor introduction was also observed by Centeno et al. who employed the CeO₂/Al₂O₃-supported gold catalysts for CO oxidation [51]. The enhancement of catalytic activity for toluene oxidation over 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ in the

presence of moisture could be ascribed to a more oxidation degree of ceria for the re-oxidation of reduced ceria by water [52]. The positive effect of moisture on catalytic activity might be due to the formation of $-\text{OH}$ groups (e.g., $\text{Pt(II)}-\text{O}(\text{OH})_x-$) [53–55] on the highly dispersed Pt nanoparticles in 0.27Pt/3DOM 26.9CeO₂–Al₂O₃.

3.6. Apparent activation energy

It has been generally believed that the oxidation of VOCs over transition-metal oxides obeys a first-order reaction toward VOC concentration and zero-order reaction toward oxygen concentration [56]. Therefore, it is reasonably assumed that the oxidation of toluene in the presence of excessive oxygen (toluene/O₂ molar ratio = 1/400) would follow a first-order reaction mechanism with respect to VOC concentration (c): $r = -kc = (-A\exp(-E_a/RT))c$, where r , k , A , and E_a are the reaction rate (mol/s), rate constant (s⁻¹), pre-exponential factor, and apparent activation energy (kJ/mol), respectively. Fig. 9 shows the Arrhenius plots for toluene oxidation over the as-prepared samples, and the calculated E_a values are summarized in Table 3. It can be seen that the E_a decreased in the sequence of 0.72Au/bulk Al₂O₃ > 0.81Ag/3DOM 26.9CeO₂–Al₂O₃ > 0.71Au/com-Al₂O₃ > 0.74Au/3DOM Al₂O₃ > 0.75Au/3DOM 26.9CeO₂–Al₂O₃ > 0.29Pd/3DOM 26.9CeO₂–Al₂O₃ > 0.27Pt/3DOM 26.9CeO₂–Al₂O₃. Clearly, the E_a value over the supported Pt sample was much lower than that of the supported Au, Ag or Pd sample. The E_a (46.4 kJ/mol) over the best-performing 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample was much lower than those (120–144 kJ/mol) over CuO/Al₂O₃ and MnO_x/Al₂O₃ [57] and those (54–76 kJ/mol) over Au/3DOM Mn₂O₃ [58], but close to those (44–48 kJ/mol) over Au/3DOM La_{0.6}Sr_{0.4}MnO₃ [59] and those (45–55 kJ/mol) over Au/*meso*-Co₃O₄ [49]. These results indicate that toluene oxidation could proceed more readily over the 0.27Pt/3DOM 26.9CeO₂–Al₂O₃ sample.

4. Conclusions

The $x\text{M}/3\text{DOM } y\text{CeO}_2\text{--Al}_2\text{O}_3$ ($\text{M} = \text{Au}, \text{Ag}, \text{Pd}, \text{and Pt}$) samples could be prepared using the PMMA-templating and PVA-protected reduction methods. The $x\text{M}/3\text{DOM } y\text{CeO}_2\text{--Al}_2\text{O}_3$ samples displayed a hierarchically 3DOM architecture (macropore diameter = 180–200 nm and mesopore diameter = 4–6 nm) and a surface area of 102–108 m^2/g . Noble metal NPs with a size of 3–4 nm were uniformly dispersed on the surface of 3DOM $26.9\text{CeO}_2\text{--Al}_2\text{O}_3$. Among the $x\text{M}/3\text{DOM } 26.9\text{CeO}_2\text{--Al}_2\text{O}_3$ samples, $0.27\text{Pt}/3\text{DOM } 26.9\text{CeO}_2\text{--Al}_2\text{O}_3$ possessed the highest O_{ads} concentration and the best low-temperature reducibility, thus resulting in the highest catalytic activity for toluene oxidation ($T_{90\%} = 198^\circ\text{C}$ at $\text{SV} = 20,000 \text{ mL}/(\text{g h})$). The introduction of water vapor to the feedstock induced a slight increase in activity. The apparent activation energies obtained over the $x\text{M}/3\text{DOM } 26.9\text{CeO}_2\text{--Al}_2\text{O}_3$ samples were in the range of 46–100 kJ/mol. Based on the activity data and characterization results, we conclude that the higher O_{ads} concentration, better low-temperature reducibility, and stronger interaction between Pt NPs and 3DOM $26.9\text{CeO}_2\text{--Al}_2\text{O}_3$ as well as the unique bimodal macro-/mesoporous structure were responsible for the good performance of $0.27\text{Pt}/3\text{DOM } 26.9\text{CeO}_2\text{--Al}_2\text{O}_3$.

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Captions of Tables and Figures

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Table 1. BET surface areas, pore volumes, average pore sizes, noble metal (M = Au, Ag, Pd, and Pt) particle sizes, and real M and CeO₂ contents of the samples.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)	M particle size ^a (nm)	Real M/CeO ₂ content ^b (wt%/wt%)
0.72Au/bulk Al ₂ O ₃	11.6	–	–	4.1	0.72/–
0.71Au/com-Al ₂ O ₃	117.5	0.474	16.1	3.7	0.71/–
0.74Au/3DOM Al ₂ O ₃	107.8	0.517	17.6	3.8	0.74/–
0.75Au/3DOM 26.9CeO ₂ –Al ₂ O ₃	102.2	0.560	18.0	3.3	0.75/26.9
0.81Ag/3DOM 26.9CeO ₂ –Al ₂ O ₃	101.9	0.516	21.6	3.6	0.81/26.9
0.29Pd/3DOM 26.9CeO ₂ –Al ₂ O ₃	103.0	0.581	21.0	3.4	0.29/26.9
0.27Pt/3DOM 26.9CeO ₂ –Al ₂ O ₃	101.6	0.564	19.5	3.7	0.27/26.9

^a Estimated according to the TEM images;

^b Determined by the ICP–AES technique.

Table 2. Surface element compositions and H₂ consumption of the samples.

Sample	Ce ⁴⁺ /Ce ³⁺ molar ratio	O _{ads} /O _{latt} molar ratio	M ^{δ+} /M ⁰ (M = Au, Ag, Pd or Pt) molar ratio	H ₂ consumption ^a (mmol/g _{cat})		
				< 400 °C	≥ 400 °C	total
0.72Au/bulk Al ₂ O ₃	—	0.45	0.36	0.052	—	0.052
0.71Au/com-Al ₂ O ₃	—	0.98	0.54	0.067	—	0.067
0.74Au/3DOM Al ₂ O ₃	—	1.08	0.50	0.107	—	0.107
0.75Au/3DOM 26.9CeO ₂ –Al ₂ O ₃	2.17	2.27	1.19	0.357	0.683	1.040
0.81Ag/3DOM 26.9CeO ₂ –Al ₂ O ₃	3.37	0.66	0.59	0.367	0.207	0.574
0.29Pd/3DOM 26.9CeO ₂ –Al ₂ O ₃	1.61	2.88	1.20	0.498	0.559	1.057
0.27Pt/3DOM 26.9CeO ₂ –Al ₂ O ₃	1.32	4.03	1.50	0.473	1.800	2.273

^a The data were estimated by quantitatively analyzing the H₂-TPR profiles.

Table 3. Catalytic activities, apparent activation energies (E_a), and toluene oxidation rates at 230 °C of the samples.

Sample	Activity and apparent activation energy				Toluene oxidation rate at 230 °C	
	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)	E_a (kJ/mol)	$\times 10^{-6}$ (mol/(g _{cat} s))	$\times 10^{-3}$ (mol/(mol _M s)) ^a
0.72Au/bulk Al ₂ O ₃	295	332	360	100.3	0.003 ^b	0.087 ^b
0.71Au/com-Al ₂ O ₃	270	305	330	91.4	0.005	0.142
0.74Au/3DOM Al ₂ O ₃	250	290	317	86.4	0.014	0.375
0.75Au/3DOM 26.9CeO ₂ -Al ₂ O ₃	200	250	279	70.8	0.053	1.396
0.81Ag/3DOM 26.9CeO ₂ -Al ₂ O ₃	263	308	338	93.2	0.009	0.119
0.29Pd/3DOM 26.9CeO ₂ -Al ₂ O ₃	168	204	228	53.7	0.221	8.071
0.27Pt/3DOM 26.9CeO ₂ -Al ₂ O ₃	140	187	198	46.4	0.223 ^c	16.136 ^c

^a M = Au, Ag, Pd or Pt;^b The datum was obtained according to toluene conversion = 1.4% at 240 °C;^c The datum was obtained according to toluene conversion = 98.4% at 210 °C.

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Graphical Abstract

Noble metal/3DOM 26.9CeO₂–Al₂O₃