



# Size effect of Pt nanoparticles on the catalytic oxidation of toluene over Pt/CeO<sub>2</sub> catalysts

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## ABSTRACT

The present work elucidated the size effect of Pt nanoparticles on the activity of Pt/CeO<sub>2</sub> catalysts toward catalytic oxidation of toluene. Size-controllable Pt nanoparticles, ranging from 1.3 to 2.5 nm, were successfully loaded on CeO<sub>2</sub> nanorod support by the adsorption method. The structure and chemical properties of Pt/CeO<sub>2</sub> catalysts are much dependent on Pt particle size. As size increases, the Pt dispersion declines while more Pt–O–Ce bonds, Ce<sup>3+</sup> and oxygen vacancies exist on ceria. The catalytic activity test of toluene oxidation shows that Pt/CeO<sub>2</sub>-1.8 sample exhibits the best catalytic performance due to the balance of both Pt dispersion and oxygen vacancy concentration of ceria. Three types of TOFs values based on Pt dispersion, oxygen vacancy concentration and both of them are calculated respectively, and the result demonstrates that the reaction rate is controlled by both of the exposed Pt atom and oxygen vacancies. In addition, the Pt/CeO<sub>2</sub>-1.8 catalyst could work properly for 120 h with various inlet toluene concentration and be completely negligible for 5 vol% water vapour at 155 °C.

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## 1. Introduction

Volatile organic compounds (VOCs) are considered as the significant air pollutants due to their contribution to major environmental problems such as ozone and photochemical smog [1]. Recent years, several technologies of VOCs control have been investigated, of which catalytic oxidation is generally recognized as one of the most promising method with the advantages of high destructive efficiency, lower operation cost and no organic by-product [2–4]. In order to make the reaction more economically competitive, it is necessary to develop higher performance catalytic materials which could operate at lower temperature. Various catalysts have been studied for this purpose, including supported noble metals (NMs) and transition-metal oxides [5–8].

Supported noble metals, especially Pt-based materials, have been generally regarded as the most desirable catalysts for VOCs combustion [9,10]. One interesting and promising factor that may control the activity is the Pt size, and much effort has focused on it in recent years [11–17]. For example, Song et al. synthesized a

series of Pt/SBA-15 catalysts with Pt particle size of 1.7–7.1 nm, and the apparent activation energy of ethane hydrogenolysis increased linearly up to a Pt particle size of ~4 nm and then remained constant [11]. Kon et al. investigated the oxidant-free dehydrogenation of alcohols over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with different Pt size, and the result showed that the sample with 1.4 nm exhibited the highest activity, suggesting the low-coordinated Pt sites and metal/support interface played important roles [14]. Chen et al. studied toluene oxidation over ZSM-5 supported Pt nanoparticles ranging from 1.3 to 2.3 nm, and found that Pt-1.9/ZSM-5 had the highest activity due to the relatively higher Pt dispersion and Pt<sup>0</sup> proportion [17]. These investigations suggest that different Pt size could lead to various Pt dispersion, chemical state and coordination number, then strongly influencing the catalytic activity.

While, for the system that Pt particle is loaded on “active support” such as CeO<sub>2</sub>, TiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>, the size effect of Pt particle on the reaction is much different. Unlike “inert support” mentioned above, Pt size could also affect surface properties of active support due to various strength of interaction between metal and support, influencing catalytic activity. Moreover, the reaction process and active sites would be much diverse and complex [18–21]. An et al. suggested that Pt size could adjust the redox properties and O<sub>2</sub>-activation abilities of Pt/Fe<sub>2</sub>O<sub>3</sub> catalysts, and the Pt-FeO<sub>x</sub> interface

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were the primary active sites for CO oxidation [19]. Li et al. proposed elementary steps of CO oxidation over Pt/TiO<sub>2</sub> catalysts involved chemisorption of CO on Pt atoms and chemisorption of O<sub>2</sub> on TiO<sub>2</sub> through the investigation of Pt size effect on CO oxidation [20]. Liu et al. prepared a series of Pt/CeO<sub>2</sub> catalysts with different Pt size and investigated the CO oxidation activity, and the results showed that the oxygen vacancies and Pt–O–Ce solid solution could accelerate the mobility of lattice oxygen and consequently affect the activity [21]. Though these researches give a good understanding for the size effect of Pt particle supported on active support, the dependence of Pt particle size distribution for VOCs oxidation is much less clear-cut as well as its active sites.

Herein, we employed a series of size-controllable Pt nanoparticles (mean size ranges from 1.3 to 2.5 nm) and then loaded them on CeO<sub>2</sub> with a shape of nanorod. The structure and chemical properties were characterized by X-ray diffraction (XRD), High resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), UV Raman, Temperature programmed reduction by hydrogen (H<sub>2</sub>-TPR) and OSC (Oxygen Storage Capacity) test. Through these techniques, size effect of Pt nanoparticle on the catalytic oxidation of toluene over Pt/CeO<sub>2</sub> catalysts has been investigated, affording a better understanding of the nature of their catalytically active sites.

## 2. Experimental section

### 2.1. Catalysts preparation

#### 2.1.1. Preparation of CeO<sub>2</sub> nanorods

All the materials used were of analytical purity. The CeO<sub>2</sub> support with a shape of nanorod was prepared by a hydrothermal method [22]. 5 mmol cerous acetate was dissolved in 20 ml deionized water, and then 55 ml NaOH solution (7 mol L<sup>-1</sup>) was added in it. This stock solution was stirred at room temperature for 30 min and then transferred into a 100 ml Teflon-lined stainless steel autoclave. Hydrothermal treatment was carried out at 130 °C for 5 h. After the reaction was completed, the obtained solid product was washed with deionized water and ethanol sever times and then dried at 70 °C for 12 h.

#### 2.1.2. Synthesis of Pt nanoparticles

A series of Pt nanoparticles with mean diameters from 1.3 to 2.5 nm were synthesized by a method of glycol reduction [17]. The general steps were as follows: a certain of chloroplatinic acid and 220 mg NaOH were dissolved in 50 ml glycol together with an appropriate amount of deionized water. After stirring at room temperature for 1 h, the obtained transparent yellow solution was transferred into a 100 ml three-necked flask. Then the mixed solution was heated to 90 °C quickly for 2 h with a N<sub>2</sub> flow passing through the reaction system, and a change in colour to dark-brown was observed without any precipitate which indicated the formation of Pt clusters. The particles were extracted from the solution by addition 0.3 mol L<sup>-1</sup> HCL solution, collected by centrifugation (8000 rpm, 5 min), and dissolved in ethanol containing 40 mg PVP. The Pt nanoparticles size was controlled by the added amount of deionized water and chloroplatinic acid.

#### 2.1.3. Synthesis of Pt/CeO<sub>2</sub>

An appropriate amount of Pt nanocrystals (to give a final loading content of 0.25 wt%) with various size dissolved in ethanol was added to a dispersion of ceria in 20 ml ethanol. After stirring for 12 h, the solid was recovered by centrifugation (8000 rpm, 5 min) and washed twice with ethanol. Finally, the powders were dried at 70 °C overnight and calcined at 300 °C for 3 h in 5% H<sub>2</sub>/N<sub>2</sub>. The

obtained catalysts were denoted as Pt/CeO<sub>2</sub>-x, where x stands for the Pt nanoparticles mean diameter in parent solution.

### 2.2. Catalysts characterization

TEM and HRTEM images were taken in a JEM-2100HR (JEOL, Japan). The mean size of the controllable Pt nanoparticles was determined from HRTEM images of the as-prepared Pt nanoparticles. The equation was as followed:

$$d \approx \frac{\sum_i n_i d_i}{\sum_i n_i} \quad (1)$$

Where n<sub>i</sub> is the particle number, d<sub>i</sub> is the particles diameter.

Moreover, it is assumed that the Pt nanoparticles showed a spherical or hemispherical shape, so the dispersion of the Pt nanoparticles could be estimated based on the following equation:

$$D_{Pt} = \frac{600M_{Pt}}{\rho d a_{Pt} N_A} \quad (2)$$

Where M<sub>Pt</sub> denotes the molar weight of Pt (195.08 g mol<sup>-1</sup>), ρ is the density of Pt (21.45 g cm<sup>-3</sup>), d is the average particle diameter observed from the TEM images, a<sub>Pt</sub> represents the surface area of Pt atom (8.06 × 10<sup>-20</sup> m<sup>2</sup> atom<sup>-1</sup>), and N<sub>A</sub> is the Avogadro constant (6.02 × 10<sup>23</sup> mol<sup>-1</sup>).

The crystalline structure of the samples was obtained by XRD (D8 ADVANCE diffractometer Bruker, Germany) with Cu Kα radiation (40 kV, 40 mA, scanning step = 0.02°). Their chemical composition was determined by inductively coupled plasma/optical emission spectroscopy (ICP-OES, Perkin-Elmer plasma 8000). The specific surfaces area (SSA) was measured used nitrogen adsorption and desorption isotherms at 77 K on an ASAP 2020 system in static measured mode, and the Brunauer-Emmett-Teller (BET) model was used to calculate the SSA.

XPS analysis was performed using a Thermo ESCALAB 250 with Al Kα (hv = 1486.8 eV) as the excitation source. The likely charging of catalysts was corrected by setting the binding energy of the adventitious carbon (C 1s) to 284.6 eV. H<sub>2</sub>-TPR was performed on a chemisorption analyzer (Micromeritics Chemisorb 2920II). 100 mg sample was first treated under a He flow containing 5 vol% O<sub>2</sub> (30 ml min<sup>-1</sup>) at 300 °C for 1 h, following by purging with Ar at the same temperature for 30 min and then cooling down to room temperature. After that, a flow of 10% H<sub>2</sub>/Ar (30 ml min<sup>-1</sup>) was switched into the tube and the samples were heated up to 800 °C at a ramp of 10 °C min<sup>-1</sup>.

UV Raman spectra were obtained in back-scattering configuration on a LabRAM HR Evolution Laser Raman Spectrometer (HYJ, France) with a CCD detector and a spectral resolution of 1 cm<sup>-1</sup>. The Kinmon He-Cd laser (325 nm) was employed as the excitation source. The laser power on the sample was maintained at 8 mW, the spectra collected with gratings of 2400 grooves mm<sup>-1</sup> and the hole was 80. The spectrum was recorded by two times 100 s subsequent laser exposer.

The concentration of surface oxygen vacancy was measured by oxygen pules injection method on the chemisorption analyzer. The experimental procedure follows previous research [23]. The consumption of oxygen by catalyst was accordingly calculated and defined as OSC<sub>catalyst</sub>, and the consumption of oxygen by Pt was calculated based on the following definitions, which was defined as OSC<sub>Pt</sub>:

$$OSC_{Pt} = 2 \frac{D_{Pt} X_{Pt}}{M_{Pt}} \quad (3)$$

Where X<sub>Pt</sub> is the weight fraction of Pt in the sample as determined by ICP-OES and the stoichiometric factor between oxygen and metal atom is set as 2:1. The value of surface oxygen vacancy

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