

## 分散度对负载型铂基催化剂 CO 氧化性能的影响

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**摘要:** 以氧化铈、氧化硅和氧化铝为载体, 采用浸渍法制备了一系列不同负载量的 Pt 基催化剂, 并利用透射电子显微镜、X 射线粉末衍射和 X 射线光电子能谱等技术对催化剂进行了表征。结果表明, 对于 Pt/CeO<sub>2</sub> 催化剂, 随着负载量减小, Pt 的分散度提高; 对于相同负载量的 Pt 基催化剂, 各催化剂上 Pt 分散情况为: Pt/SiO<sub>2</sub> < Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> < Pt/CeO<sub>2</sub>。CO 氧化反应结果表明, 0.25% Pt/CeO<sub>2</sub> 催化剂表现出更加优良的低温活性, 室温下其单位 Pt 原子上 CO<sub>2</sub> 的生成速率为  $2.2 \times 10^{-3} \text{ s}^{-1}$ 。

**关键词:** 铂; 氧化铈; 氧化硅; 氧化铝; 分散度; 一氧化碳; 氧化

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## Effect of Dispersion on Catalytic Performance of Supported Pt Catalysts for CO Oxidation

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**Abstract:** A series of ceria, silica, and  $\gamma$ -alumina-supported platinum catalysts were prepared by the incipient-wetness impregnation method. Transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were used to determine the dispersion of Pt. For the Pt/CeO<sub>2</sub> catalysts, XRD studies suggest that Pt was better dispersed as its concentration decreased. This observation correlated well with XPS analysis. For catalysts with the same Pt mass loading, TEM and XRD results suggest that Pt dispersion displays an increasing order as Pt/SiO<sub>2</sub> < Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> < Pt/CeO<sub>2</sub>. Catalytic activities for CO oxidation were investigated. Results showed that the 0.25 wt% Pt/CeO<sub>2</sub> exhibited a higher activity than other oxide supported catalysts with a turnover frequency of  $2.2 \times 10^{-3}$  CO<sub>2</sub> per total Pt per second at room temperature.

**Key words:** platinum; ceria; silica; alumina; dispersion; carbon monoxide; oxidation

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CO oxidation over platinum catalysts has attracted much study because of its importance in both practical applications and fundamental research, e.g., automotive applica-

tions, preferential oxidation of CO in fuel cells, and as a probe reaction [1-3]. However, the supported Pt catalysts are traditionally considered to be inert at low temperature

[4]. As the catalytic performance is affected strongly by the dispersion of the catalytically active metal on an oxide support, dispersion is becoming one of the most important factors in controlling catalytic performance [5,6]. However, literature results on the effect of Pt dispersion on turnover rates differ significantly. Meanwhile, the catalytic performance for supported Pt catalysts studied near room temperature has rarely been reported.

Owing to the support effect, the use of conventional hydrogen or CO chemisorption may not provide a reliable indication of Pt metal dispersion [7]. On the contrary, transmission electron microscopy (TEM) combined with X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) have been considered powerful tools to determine the dispersion of these systems [8,9]. Using these technologies, it has been reported that most of the Pt supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> with low loading could be dispersed as atoms, ions, or 2D clusters [10,11]. The Pt catalysts with different loadings were therefore prepared by the incipient-wetness impregnation method in this study. The dispersion of Pt was determined by TEM, XRD, and XPS. CO oxidation was used to investigate catalytic performance. A turnover frequency of  $2.2 \times 10^{-3} \text{ s}^{-1}$  was achieved at room temperature for the highly dispersed 0.25 wt% Pt/CeO<sub>2</sub> catalyst.

## 1 Experimental

### 1.1 Catalyst preparation

The Pt catalysts were synthesized by the incipient wetness impregnation method. A solution of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Alfa Aesar) was mixed with the supports with different mass ratio and maintained for 4 h before drying. After being dried at 90 °C for 4 h and overnight at 120 °C, the precursors were calcined at 260 °C for 1 h in a flow of air (30 ml/min, 0.1 MPa). Then the Pt/CeO<sub>2</sub> catalysts were reduced under hydrogen (30 ml/min, 0.1 MPa) at 700 °C for 3 h, and the Pt/SiO<sub>2</sub> and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were reduced at 650 °C for 3 h. The surface areas were 34, 298, and 172 m<sup>2</sup>/g for

the CeO<sub>2</sub>, SiO<sub>2</sub>, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (all Alfa Aesar), respectively.

### 1.2 Catalyst characterization

Particle sizes and Pt dispersion were determined by TEM, XRD, and XPS. TEM was carried in a Tecnai F30 microscopy at 300 kV. The Pt particles were measured and counted to obtain a particle size frequency distribution. XRD patterns of the catalysts were recorded on a Philips Panalytical X'Pert Pro diffractometer using Cu K $\alpha$  ( $\lambda = 0.15406 \text{ nm}$ ) radiation with the tube voltage of 40 V and current of 30 mA. XPS spectra were recorded using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe spectrometer using the Al K $\alpha$  source (1486.6 eV). The powder samples were made into 6 mm diameter pellets. The binding energies were corrected with respect to C 1s of 284.6 eV.

### 1.3 Catalytic test

CO oxidation was carried out under atmospheric pressure at a CO:O<sub>2</sub>:H<sub>2</sub> ratio of 1:1:98 and flow rate of 30 ml/min. Before in-situ pretreatment, the Pt/CeO<sub>2</sub> catalysts were diluted using CeO<sub>2</sub> to a total weight of 400 mg and placed in a fixed-bed reactor. The amounts of catalysts used was 400, 100, 50, 28.6, and 20 mg for the 0.25, 1.0, 2.0, 3.5, and 5.0 wt% samples (60–80 mesh), respectively. CO conversion was calculated from the change in concentration between the inlet and outlet gases, using a FL9510 GC instrument. The catalytic activity was indicated by the formation rate of CO<sub>2</sub> per Pt atom per second (turnover frequency).

## 2 Results and discussion

### 2.1 TEM studies

The TEM characterization of the 2 wt% supported Pt catalysts is shown in Fig. 1. Results showed that the Pt metal particles were uniformly dispersive over SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with an average size of 3.9 and 1.5 nm, respec-

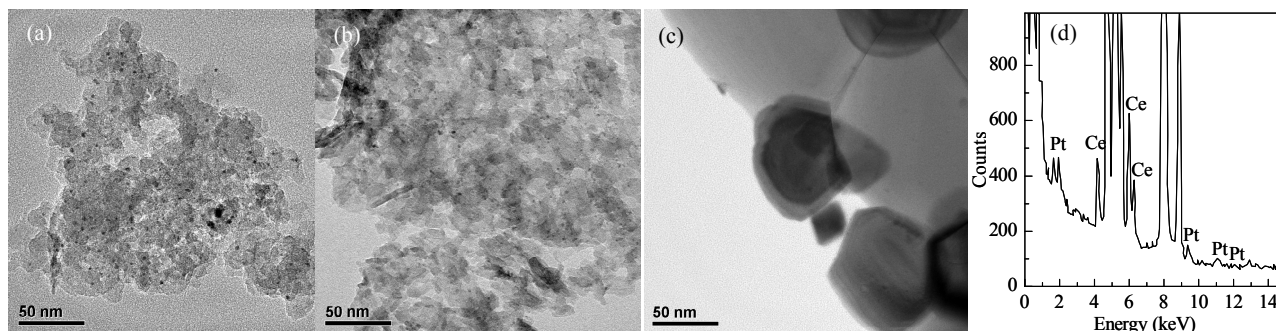


Fig. 1. TEM micrographs of 2 wt% Pt/SiO<sub>2</sub> (a), Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (b), and Pt/CeO<sub>2</sub> (c) catalysts and EDX profile of Pt/CeO<sub>2</sub> (d).

tively. For the Pt/CeO<sub>2</sub> catalysts, no obvious Pt clusters were observed, while energy dispersive X-ray spectroscopy (EDX) confirmed the presence of Pt species. The results demonstrated that Pt was highly dispersed over CeO<sub>2</sub>. Hence, for catalysts with the same Pt mass loading, the Pt dispersion displayed an increasing order as Pt/SiO<sub>2</sub> < Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> < Pt/CeO<sub>2</sub>.

## 2.2 XRD studies

The XRD patterns for the 0.25 wt% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 0.25 wt% Pt/SiO<sub>2</sub>, and 0.25–2 wt% Pt/CeO<sub>2</sub> catalysts are shown in Fig. 2. From Fig. 2(a), compared with the fresh 0.25 wt% Pt/SiO<sub>2</sub>, weak peaks at  $2\theta$  of 39.9°, 46.4°, and 67.6° were observed for the catalyst calcined in air at 650 °C for 6 h. These can be assigned to Pt(111), (200), and (220), respectively. The size of the Pt clusters increased owing to sintering when the 0.25 wt% Pt/SiO<sub>2</sub> was calcined at high temperature. This suggested that the 0.25 wt% loading was higher than the XRD detection limit. Therefore, no observable Pt diffraction peak indicated that the Pt was well-dispersed on these catalysts. For the Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples (Fig. 2(b)), as the mass ratio of Pt increased, the new diffraction peak appeared at  $2\theta = 39.9^\circ$ , which was assigned to Pt(111). The appearance of this peak suggests the formation of Pt nanoparticles. Comparing with the 2 wt% catalysts, diffraction peaks of Pt existed for Pt/SiO<sub>2</sub> and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> while none existed for Pt/CeO<sub>2</sub>, indicating that Pt was better dispersed over CeO<sub>2</sub> than others. In this sense, the dispersion of Pt over CeO<sub>2</sub> would be higher than on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. In fact, only the Pt loading increased up to 3.5 wt%. Peaks of Pt can be seen in the Pt/CeO<sub>2</sub> catalysts, and the peaks were sharper at 5.0 wt% (Fig. 2(c)).

## 2.3 XPS studies

XPS spectra of the Pt 4f core level region in Pt/CeO<sub>2</sub>

catalysts with various Pt loading are shown in Fig. 3(a). XPS of these catalysts could be identified as two components. It was reported that the 4f<sub>7/2</sub> and 4f<sub>5/2</sub> peaks are observed at 71.1 and 74.4 eV, respectively. Accordingly, the first peak of Pt 4f<sub>7/2</sub> at 71.1 eV can be assigned to Pt<sup>0</sup>, and the peak at 72.1 eV can be assigned to Pt <sup>$\delta$ +</sup> [12]. The amount of Pt<sup>0</sup> and Pt <sup>$\delta$ +</sup> was taken into account as shown in Fig. 4(a).

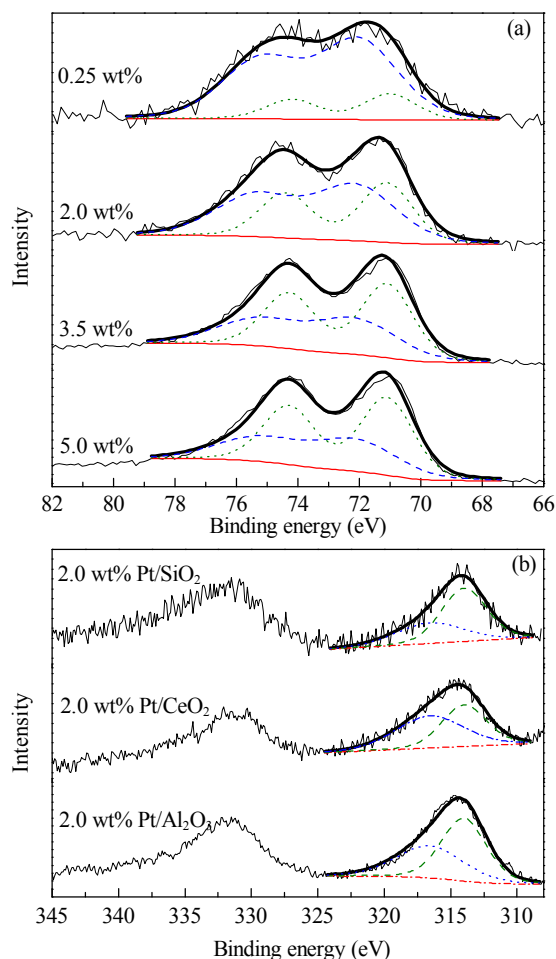


Fig. 3. XPS profiles of core level spectra of Pt 4f (a) and Pt 4d (b).

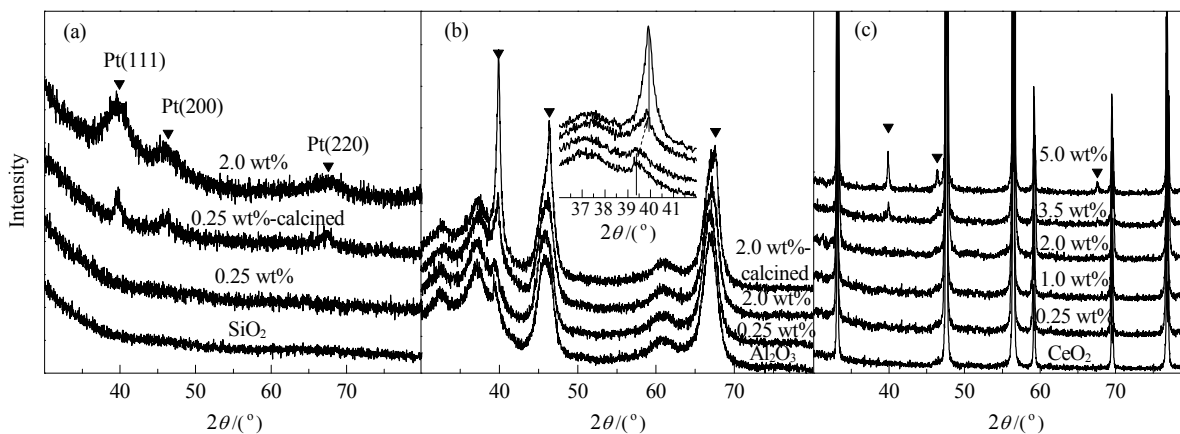


Fig. 2. XRD patterns of Pt/SiO<sub>2</sub> (a), Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (b), and Pt/CeO<sub>2</sub> (c) catalysts.

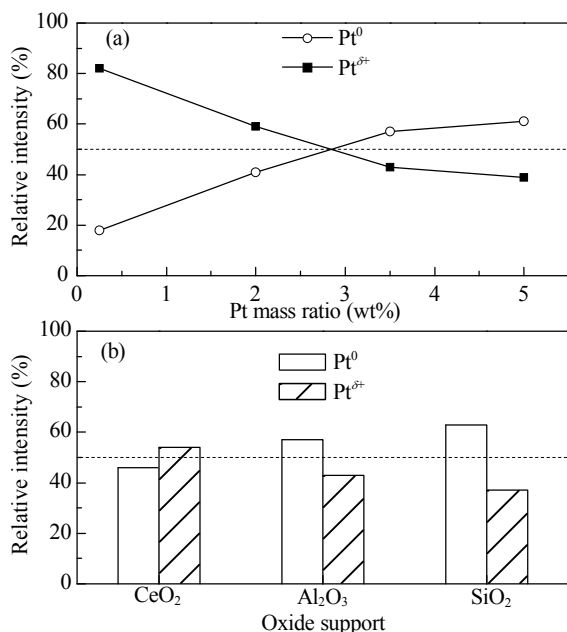


Fig. 4. Relative intensities of different Pt species for various Pt/CeO<sub>2</sub> catalysts (a) and different supports (b).

There were significant changes in the related amount of Pt<sup>0</sup> and Pt<sup>δ+</sup> as the Pt loading increased. The higher percentage Pt<sup>δ+</sup> obtained at lower Pt loading may occur because the smaller Pt particles are more easily oxidized, and the Pt interface is located on the oxide surface bond with surface oxygen [13,14]. Hence, the Pt was better dispersed over lower loading Pt/CeO<sub>2</sub> catalysts. Since the peak of Pt 4f overlapped with that of Al 2p, the valence of Pt loaded on various supports can only be obtained from the very broad Pt 4d peak (Fig 3(b)). The 4d<sub>5/2</sub> peak observed at 314.1 eV could be assigned to Pt<sup>0</sup>, and the peak at 316.6 eV could be Pt<sup>δ+</sup> [15,16]. The relative intensity of Pt<sup>δ+</sup> over these catalysts displayed an increasing trend as Pt/SiO<sub>2</sub> < Pt/γ-Al<sub>2</sub>O<sub>3</sub> < Pt/CeO<sub>2</sub>, indicating that Pt was better dispersed over CeO<sub>2</sub> than others. Overall, the XPS results showed a good correlation with the XRD results.

#### 2.4 Kinetic measurements

The CO oxidation activity over various Pt catalysts is shown in Figs. 5 and 6. The CO oxidation was carried out at a broad temperature range of 30–200 °C with the same weight hourly space velocities of 1800 L/(g<sub>Pt</sub>·h). The Pt/CeO<sub>2</sub> catalysts (Fig. 5) show a better low-temperature catalytic activity as the Pt loading decreased. For different supports, as shown in Fig. 6, catalytic activities displayed an increasing order as Pt/SiO<sub>2</sub> < Pt/γ-Al<sub>2</sub>O<sub>3</sub> < Pt/CeO<sub>2</sub>. As in the above discussion, TEM, XRD, and XPS results suggested that the catalysts with lower Pt loading dispersed

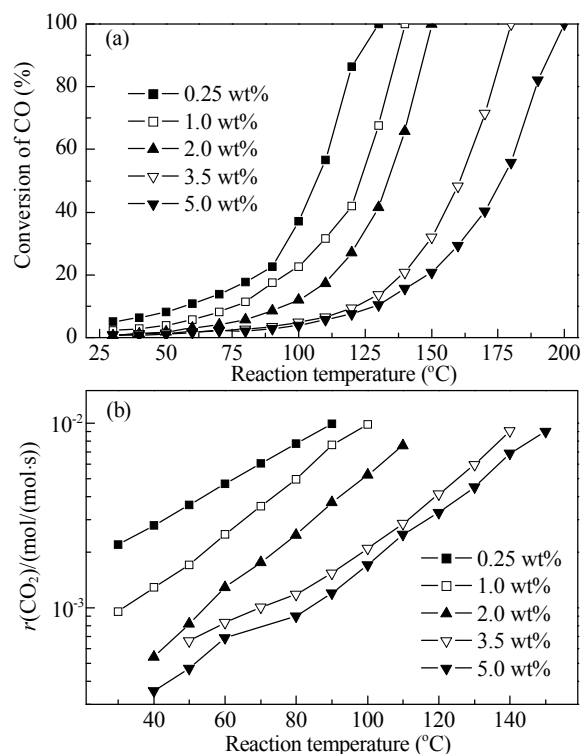


Fig. 5. CO conversion rate (a) and CO<sub>2</sub> production rate (b) of various Pt/CeO<sub>2</sub> catalysts for CO oxidation at different temperatures. The reaction was carried out under atmospheric pressure at a CO:O<sub>2</sub>:H<sub>2</sub> ratio of 1:1:98 and flow rate of 30 ml/min. The amounts of catalysts used were 400, 100, 50, 28.6, and 20 mg for the 0.25, 1.0, 2.0, 3.5, and 5.0 wt% Pt/CeO<sub>2</sub> catalysts (60–80 mesh), respectively.

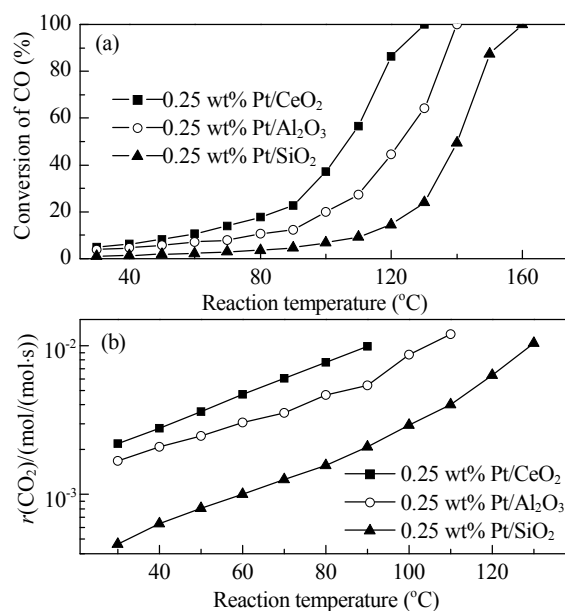


Fig. 6. CO conversion rate (a) and CO<sub>2</sub> production rate (b) for Pt catalysts supported on various supports for CO oxidation at different temperatures. The reaction was carried out under atmospheric pressure at a CO:O<sub>2</sub>:H<sub>2</sub> ratio of 1:1:98 and flow rate of 30 ml/min. The amount of catalyst was 400 mg.

better, and those on CeO<sub>2</sub> Pt dispersed better. The results demonstrated that the highly dispersed Pt species had an important effect on the room-temperature CO catalytic oxidation activity. The Pt catalysts supported on SiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub> were considered to be 'inactive' in low-temperature CO oxidation owing to the CO self-poisoning effect [17]. In this study, the highly dispersed 0.25 wt% Pt catalysts showed a good catalytic activity for low-temperature CO oxidation. The reaction rates at room temperature calculated from the total amount of Pt loaded on the support were  $2.2 \times 10^{-3}$ ,  $1.7 \times 10^{-3}$ , and  $0.5 \times 10^{-3} \text{ s}^{-1}$  for Pt/CeO<sub>2</sub>, Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Pt/SiO<sub>2</sub>, respectively. It is thought that such activity differences originate mainly from the different dispersions of Pt on CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>, although the oxygen vacancies may affect the catalytic activities for CO oxidation, as reported by Liu et al. [18] and Martinez-Arias et al. [19]. The ability of the CeO<sub>2</sub> activity to support itself near room temperature is negligible as compared with the current Pt/support catalysts, including the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supported catalysts. The low temperature activity was probably attributed to the highly dispersive Pt species on the oxide surfaces.

### 3 Conclusions

TEM, XRD, and XPS characterization showed that Pt was better dispersed (i) as the Pt loading decreased, and (ii) on CeO<sub>2</sub> than on SiO<sub>2</sub>. The lower Pt-loading catalysts exhibited better catalytic activities for CO oxidation near room temperature. The low temperature activity can be attributed to the highly dispersive Pt species on the oxide surfaces.

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